

VCT 2020

Virtual Conference on Thermoelectrics

An online event to highlight the work
of early-career researchers
in the thermoelectrics community

July 21-23, 2020

Book of Abstracts



International Thermoelectric Society

Organizers

A team of faculty members, postdocs, and graduate students
have contributed to organizing the
Virtual Conference on Thermoelectrics 2020

Primary Organizers



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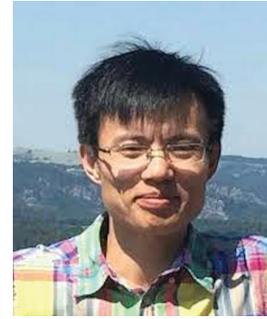
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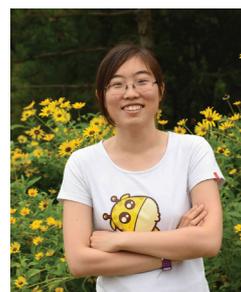
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Foreword

In light of the cancellation of the International Conference on Thermoelectrics (ICT), we are organizing the first [Virtual Conference on Thermoelectrics](#) (VCT) on July 21-23, 2020. In organizing VCT 2020, our vision was to provide early-career researchers in the thermoelectrics community with an online platform to highlight and share their work. In this spirit, the call for oral contributions was restricted to students and postdocs. Oral presentations were selected based on nominations from principal investigators and senior researchers. Poster contributions are open to all registered participants and held over Twitter. VCT 2020 is a free event, with no registration fee.

Given the initial positive reception of VCT 2020, we organized three regional chapters– Asia, Europe, and the US. In response to the call for abstracts, we received in excess of 300 nominations for oral presentations. In addition, we also received about 100 abstracts for poster presentations. The oral presentations are scheduled across 12 time zones to accommodate the global scale of this event. Registered participants can attend talks in all regional chapters.

VCT 2020 is endorsed by the [International Thermoelectrics Society](#) (ITS). We are happy to announce that [ACS Applied Energy Materials](#) has partnered with us for VCT 2020. Finally, the organization of VCT 2020 is made possible by a dedicated team of faculty members, senior researchers, postdocs, and graduate students from across the world.

Best wishes,

VCT 2020 Organizers

Conference website: conferences.mines.edu/vct2020

Index

- Program-at-a-glance 3

- Asia abstracts 5
 - Oral abstracts 6
 - Poster abstracts 150

- Europe abstracts 175
 - Oral abstracts 176
 - Poster abstracts 267

- US abstracts 313
 - Oral abstracts 314
 - Poster abstracts 380

Program-at-a-Glance

US Program	EU Program	Asia Program			
		IN, TH	CN, SG	JP, KR, AUS	
Los Angeles	Brussels	New Delhi	Beijing	Tokyo	
UTC-7	UTC+2	UTC+5.5	UTC+8	UTC+9	
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19:00	4:00	7:30	10:00	11:00	
20:00	5:00	8:30	11:00	12:00	
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7:00	16:00	19:30	22:00	23:00	
8:00	17:00	20:30	23:00	0:00	Day 2: July 22
9:00	18:00	21:30	0:00	1:00	
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Asia Program

Anisotropic thermoelectric transport in textured bismuth-antimony chalcogenide nanomaterials synthesized by facile bottom-up physical process

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High anisotropy in electrical conductivity values has resulted in a good average figure of merit (zT) in textured bismuth-antimony chalcogenide nanomaterials, which have been synthesized by a facile bottom-up physical synthesis process and consolidated by direct current hot pressing (DCHP). This zT value is limited by conversely high anisotropy in Seebeck coefficient and in thermal conductivity along the ab -plane. Our facile bottom-up physical synthesis process requires a controlled melting of ingredient metals at just above their melting point-rocking and air quenching. This energy-efficient process does not require any milling and produces single phase nanomaterial in ubiquitous plate-like morphology, which easily results in high texturing. This texturing has been studied by XRD analysis and SEM images and correlated with texture factor by thermoelectric measurements. HRTEM image has shown high grain boundary density within the plates. Sample temperature and laser power-dependent Raman spectroscopy have revealed that $E_g(2)$ mode is dominant phonon transfer modes along the textured ab -plane direction. This study shows that scattering of $E_g(2)$ mode phonon should be able to further enhance zT in such textured samples. Also, a study of anisotropy in power output density and thereby, engineered power factor under practical temperature gradients showed that the effect of anisotropy is much higher than, what can be inferred from the conventional power factor anisotropy.

Carrier engineering in layered *p*-type thermoelectric CuSbSe₂ chalcostibite

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Recently, thermoelectric (TE) technology, converts waste-heat into usable electricity, has been regarded to help overcoming the energy crisis due to depletion of fossil fuels and to boost up the conventional gasoline based secondary technology. However, low heat-to-electricity conversion efficiency (η_{TE}) limits large-scale production of TE devices, where arrays of *p*- and *n*-type materials are arranged electrically in series and thermally in parallel. As the η_{TE} of TE devices related linearly with the dimensionless figure of merit, $zT = S^2\sigma T / (\kappa_{ele} + \kappa_{lat})$, where σ , S , T , κ_{ele} and κ_{lat} are the electrical conductivity, the Seebeck coefficient, the absolute temperature and the electronic and lattice thermal conductivity, respectively, improving the zT increases η_{TE} , that is challenging as TE parameters are interdependent on each other. For decades, state-of-art materials: Bi₂Te₃, PbTe, (GeTe)_{100-x}(AgSbTe₂)_x, and SiGe, have exhibited maximum zT in the range of 1-2, that yields a theoretical efficiency of 10-20%, but it constitutes toxic and expensive elements. Here, we have synthesized a *p*-type layered CuSb_{1-x}Pb_xSe₂ chalcostibite by vacuum sealing method and doping Pb²⁺ at Sb sites to enhance electrical conductivity, without disturbing its inherently ultra-low κ . Further, Material characterizations and thermoelectric properties of Pb doped CuSbSe₂ will be discussed.

Charge carrier optimization and enhanced thermoelectric properties of doped SnTe

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In spite of being an analogue to PbTe, pure SnTe has limited applicability for thermoelectric research due to very high hole concentration arising from intrinsic Sn vacancies. Careful addition of extra Sn and extrinsic isovalent doping at Sn sites are a well understood approach for enhancing the thermoelectric performance of SnTe. We will present our results of thermoelectric performance of transition metal, Mn and rare earth element Yb doped SnTe. The *p*-type thermopower enhances by four times in Mn-doped self-compensated SnTe whereas similar enhancement can be realized with a lower concentration of Yb doped SnTe [1,2,3,4]. The observed power factor enhancement for $\text{Sn}_{0.93}\text{Mn}_{0.1}\text{Te}$ from $\text{Sn}_{1.03}\text{Te}$ has been explained based on generated magnetic moments, magnetic entropy, presence of anomalous Hall effect and high effective thermal mass while the enhancement in thermopower of Yb doped samples has been explained with electronic band modification supported by first-principle calculations [1,3,4]. The poor thermal conductivity is understood based on point defect scattering and appearance of impurity driven soft phonon mode [1,3,4].

References

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Density functional study of electronic structure and thermoelectric transport in tin selenide-copper selenide alloy

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Density function theory and semi classical Boltzmann transport theory have been employed to study the electronic structure and thermoelectric (TE) transport in SnSe-Cu₂Se alloy. Detailed study shows that SnSe is *p*-type with band gap of 0.66 eV, and the alloy is *n*-type with band gap of 0.064 eV. In both systems, two fold band degeneracy have been observed. The calculation of electron localization function shows the existence of selenium lone pair (LP) in both cases due to unhybridized Se 4s electrons, however, the LP is more delocalized in the alloy than SnSe. Chemical potential map confirms the existence of SnSe₂ as a secondary phase is more favourable than Cu₂Se because of having lower formation energy. TE and electrical transport coefficients have been calculated as a function of carrier concentration and temperature to predict the range of optimized TE operation. Transport properties are anisotropic in case of SnSe due to anisotropy in effective mass, however, the alloy shows more isotropic transport due to its isotropic effective mass. Bipolar transport due to minority carriers is present in SnSe, while it is absent in the alloy. The behavior of Seebeck coefficient in both cases is described by Mott's theory and DOS modification near Fermi energy. In SnSe, acoustic phonon scattering is the main scattering mechanism, whereas ionized impurity scattering and inter carrier scattering are dominant in the alloy. Alloy scattering with $U = 2$ eV also contribute significantly.

Enhancement of thermoelectric performance of transition metal doped Bi_2Te_3 by retaining topological insulating phase

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Thermoelectric (TE) materials can effectively harvest electricity from waste heat for power generation. Bi_2Te_3 is a potential TE material with high TE performance and 3D Topological Insulator (TI) [1]. TI is highly emerging area in the field of material science with fascinating physics and high potential application [2]. In this work, we focus on Cobalt [Co, Transition Metal (TM)] doped Bi_2Te_3 samples i.e., $\text{Bi}_{2-x}\text{Co}_x\text{Te}_3$ ($x = 0$ and 0.1). No additional, XRD peak and Raman active mode due to Co doping, which reveals that the samples are single phase in nature. Further, XPS analysis confirms the presence of Co in doped sample. The thermal variation of resistivity, r and thermopower, S measurement have been carried out and enhancement of power factor ($PF = S^2/r$) is observed with Co doping. The result depicts the betterment in TE properties with TM doping. From the magnetic susceptibility (χ) vs. Field (H) curve, we observe a large cusp near zero-field region, which confirms the presence of TI phase in both the samples [3]. Large positive magnetoresistance (MR) $\sim 80\%$ is observed for pristine Bi_2Te_3 . A cusp like MR at low magnetic field regime indicates weak anti-localization (WAL) behavior, which further supports the existence of surface state of the TIs [4]. Thus Co doping helps in enhancing the TE performance by retaining the TI behavior in Bi_2Te_3 .

References

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Enhancing the thermoelectric properties of sputted Sb_2Te_3 thick films via post-annealing treatment

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Sb_2Te_3 films of more than 10 μm in thickness were deposited on flexible polyimide substrates by heat treatment-assisted DC magnetron sputtering. The post-annealing parameters including the temperature (150–350 °C) and time (15–60 min) were varied to investigate the microstructure, chemical composition, porosity and thermoelectric properties of the thick films. X-ray diffraction showed that both the as-deposited and post-annealed films were polycrystalline with significant preferential growth along the (015) plane. The films showed slightly off-stoichiometric compositions after post-annealing treatment. Increasing the annealing temperature and annealing time led to an increase in crystalline size and a decrease in porosity of the thick films. This was related to grain growth, agglomeration and surface improvement. The electrical transport and thermoelectric properties including carrier concentration, carrier mobility, electrical conductivity and Seebeck coefficient were investigated using Hall effect measurements and a ZEM-3 apparatus. A maximum power factor of 1.7 $\text{mW}/\text{K}^2\text{m}$ was obtained following annealing at 350 °C for 30 min.

Improvement of thermoelectric performance in Te incorporated Sb_2Te_3 hetero-structure

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Sb_2Te_3 is well known for its potential thermoelectric (TE) applications around room temperature. A promising approach to increase the figure of merit $ZT=S^2T/\rho\kappa$ (with ρ the electrical resistivity, S the Seebeck Coefficient, κ the thermal conductivity, and T the absolute temperature) is to introduce scattering centres which can scatter phonons more effectively than electron [1].

$\text{Sb}_2\text{Te}_3/\text{Te}$ hetero-structures were synthesized by dispersing different mole percentage of Te with Sb_2Te_3 through solid state reaction method. Te, an elemental semiconductor, is chosen as a second phase following its high TE performance [2]. Presence of second phase, i.e, Te is confirmed by X-ray diffraction. $\rho(T)$ is found to increase with incorporation of Te. Temperature dependent thermopower $[S(T)]$ reveals that S also increases upto certain concentration of Te, but decreases with further Te addition. $\kappa(T)$ as well as Lattice thermal conductivity $\kappa_L(T)$ decreases with Te incorporation indicating that defects of different dimensionalities produced by Te effectively scatter phonons of different frequency spectrum. As a result, ZT increases in $\text{Sb}_2\text{Te}_3/\text{Te}$ heterostructure as compared to its pristine counterpart. Attempts have been made to highlight the scattering mechanism governing the $\rho(T)$, $S(T)$ data and establish its correlation with thermoelectric performance.

References

- [1] A. Soni et al., Nano Letters 12, 4305 (2012).
- [2] S. Lin et al., Nature Communications 7, 10287 (2016).

Interface engineering of PANi incorporated ultrathin layered MoS₂ nanosheets for promising thermoelectric performance

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In this work, ultrathin layered molybdenum disulphide (MoS₂) nanosheets/PAni nanocomposites are prepared by hydrothermal route. The effect of varying PANi wt% in the nanocomposites and its role on thermoelectric properties are investigated. The successful incorporation of PANi between the MoS₂ layers confirmed by high resolution transmission electron microscope (HRTEM). The conductivity is raised up highly due to insertion of PANi in layered van der Waal's gap of MoS₂ where the effective interface facilitates charge for fast transport and the variable range hopping mechanism is identified. The significantly enhanced potential difference of MoS₂/ PANi nanocomposites by low-kinetic carrier scattering with increasing PANi content is well clarified by the increased Seebeck value. The reduction in thermal conductivity is observed of about 0.248 Wm⁻¹K⁻¹ for 2.5 wt% addition of PANi, the involvement of interface phonon scattering is also efficient. Most importantly, the stability of the sample is improved for MoS₂/ PANi nanocomposites than pristine MoS₂. Our work paved a new approach to improve TE performance by preparing TE MoS₂ material through simple chemical route.

Investigation of copper-based chalcogenides for thermoelectric applications

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The conversion of heat energy into electrical energy using advanced thermoelectric (TE) materials is the best available solution to the severe environmental damage and energy scarcity issues faced by humanity in the recent times. The performance of the thermoelectric materials mainly depends on the various properties of materials, including the Seebeck coefficient, electrical conductivity, thermal conductivity, and thermal stability. The superionicity and Cu disorder at the high temperature can dramatically affect the electronic structure of Cu_2X (S, Se, Te) and in turn result in temperature-dependent carrier-transport properties. Since most of the waste energy generated from industries is in the range between low to mid scale temperatures (673K to 1073K), copper based chalcogenide materials are mostly used for this purpose due to the fact that they're highly efficient in this temperature range. Effective strategies are incorporated for enhancing the thermoelectric performance of Cu-based nanostructures. Copper sulfide (Cu_2S) nanoparticles have been synthesized using a facile hydrothermal method with cubic crystal structure which was analyzed using X-ray diffraction. The as-synthesized sample was characterized with morphological and elemental analyses. The pure Cu_2S sample showed a low thermal conductivity of $0.7 \text{ Wm}^{-1}\text{K}^{-1}$ at the temperature of 723 K. Further thermoelectric properties of pure and efficient composite nanostructures are to be studied.

Investigation of thermoelectric properties of perovskite structured lanthanum cobalt oxide (LaCoO₃)

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Over the last two decades, the demand for an alternative energy technology is increased to reduce our dependency on non-renewable energy sources, has opened various avenues of research leading to a desirable solution. One such solution for non-renewable energy sources is thermoelectric technology, which converts waste heat energy to electrical energy based on Seebeck effect. The main focus in thermoelectrics research has been driven by the pursuit of higher thermoelectric efficiency defined by dimensionless figure of merit $zT = S^2\sigma T / (\kappa_l + \kappa_e)$, where T is the absolute temperature, S is the Seebeck coefficient, σ is the electrical conductivity and κ_e is the electronic thermal conductivity and κ_l lattice thermal conductivity of the material. Recently, oxide perovskite materials have attracted much attention for thermoelectric applications, because of their elemental abundance, low toxicity, eco-friendliness, high stability even at elevated temperatures and the electrical and thermal properties can be easily tailored by appropriate doping. In this work, LaCoO₃ materials were prepared by solid state reaction. The X-Ray diffraction analysis confirm the formation of perovskite structured LaCoO₃. The morphological analysis were carried out by field emission scanning electron microscopy. Further, the samples are subjected to cold press and the thermoelectric characterization will be carried out.

Investigation on influence of indium incorporation on thermal conductivity of polycrystalline SnSe

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Tin selenide has attracted more interest as thermoelectric material due to the anharmonic nature and they have achieved a record high ZT of 2.6 for single crystalline SnSe. The polycrystalline SnSe has better mechanical properties compared with single crystalline materials. But poor electrical properties due to inhomogeneous phase segregation limit the use of SnSe as a thermoelectric material. In this work indium incorporated tin selenide has been prepared by vacuum melting followed by ball milling. XRD and HRTEM confirmed the pure phase formation along with the high crystalline nature of the samples. Presence of indium has been confirmed using X-ray photoelectron spectroscopy. Indium leads to the formation of nano inclusions, which has observed using electron probe micro analyser technique. These nano inclusions enhanced the phonon scattering and reduced the thermal conductivity. Thus, SnSe incorporated with 10 wt% indium gives a minimum thermal conductivity of around 0.48 W/mK at 615 K.

Metal chalcogenides as thermoelectric material ---- A review

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Demand of energy in our life is rising day by day. Thermoelectric materials can convert waste heat into electricity and produces almost no pollution in environment so this class of materials have attracted tremendous research interests over the past few decades. The efficiency of a thermoelectric material to convert waste heat into electricity is determined by a dimensionless quantity called Figure of Merit (ZT). Higher the value of ZT better the material is as thermoelectric. So the aim is to find out materials which have ZT value greater than unity and can commercially be used in devices like thermoelectric generators or thermoelectric coolers to convert heat into electricity or vice versa. In this review it will be discussed how to increase the thermoelectric efficiency of a material and the progress of metal chalcogenides as thermoelectric materials over past few years. Metal chalcogenides are good thermoelectric materials. $PbTe$ and Bi_2Te_3 are two traditional thermoelectric materials. But the toxicity of Pb reduces its demand in practical uses. So lead free metal chalcogenides are now attracting research interests. For mid-temperature thermoelectric power generation IV–VI metal chalcogenides are good. Performance of germanium chalcogenides, Tin chalcogenides, copper based chalcogenides and their alloys, ternary derivatives of Cu_2X and their other derivatives as thermoelectric materials and their uses in different thermoelectric modules will be briefly discussed here.

Modulation of charge carriers and thermoelectric performance of inherently *p*-Type Bi_2Te_3 by Ge doping

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Stoichiometric Bi_2Te_3 is inherently a *p*-type semiconductor, but hole-dominated transport is seldom realized experimentally due to dominant electron donor Te vacancies and TeBi anti site defects. In the present study, we report on the effect of Ge incorporation on the structural aspects as well as electronic and thermal transport properties of Bi_2Te_3 . Carrier density (N_p) of Bi_2Te_3 increases by an order with Ge content, suggesting formation of acceptor states, which consequently improves the electrical conductivity (σ). The *p*-type thermopower (α) enhances providing a significant gain in the power factor ($\alpha^2\sigma$) from $0.32 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$ to $2.52 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$ for Bi_2Te_3 to $\text{Bi}_{1.95}\text{Ge}_{0.05}\text{Te}_3$, respectively. Here, Ge being tetravalent contributes an extra hole to the Bi_2Te_3 which leads to an optimized 'n' for improved thermoelectric properties. Thus, room temperature thermoelectric figure of merit $ZT \sim 0.95$ have been realized for $\text{Bi}_{1.95}\text{Ge}_{0.05}\text{Te}_3$. Additionally, the applicability of prepared Ge doped Bi_2Te_3 materials for segmented thermoelectric devices has been discussed.

Optimizing the thermoelectric properties of *n*- and *p*-type Ag_2Te

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The recent discovery of phonon-liquid electron-crystal concept has led to an intensive research in some superionic compounds, $\text{Ag}_2\text{X}/\text{Cu}_2\text{X}$ where X can be S, Se or Te. In their high-temperature superionic phase they show liquid-like behavior. Here we focus on Ag_2Te which becomes superionic above a temperature of about $T_{\text{SI}} = 425\text{K}$. In previous reports on Ag_2Te a puzzling behavior has been observed: in some reports the thermopower (S) shows a sharp transition from negative to positive at T_{SI} , in others it is shown to remain negative but with a small jump at T_{SI} . Hereafter, we shall refer to these samples as *p*-type and *n*-type Ag_2Te respectively.

In this talk, with a brief introduction to the TE properties of this class of compounds, I will discuss the sample dependence of the sign of S above and below T_{SI} . We have confirmed the presence of two different behaviors of S in a series of $\text{Ag}_{2+\delta}\text{Te}$ samples.

We also observed very low-thermal conductivity ($< 1 \text{ Wm}^{-1}\text{K}^{-1}$) in our samples which can be attributed to their layered texture. Depending on the stoichiometry, we observed a wide range of electrical conductivity (σ) varying from almost 100 to 2000 Scm^{-1} at room temperature (RT). On the other hand, the S near RT was found to not to vary so dramatically indicating a decoupling of σ and S , which in turn suggested factors other than the carrier concentration may play role in optimizing the TE properties of Ag_2Te . We found the best maximum zT value of 0.78 at 390 K for *n*- type Ag_2Te .

Phonon-plasmon coupling in thermoelectric Cu_{2-x}Te using raman spectroscopy

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Superionic Cu_{2-x}Te (CT) compounds are emerging as promising *p*-type thermoelectric (TE) materials due to their layered structure and possibility of ultra-low thermal conductivity owing to presence of Phonon-Liquid-Electron-Crystal mechanism [1]. CT exhibits complex crystal structure and polymorphic phases which undergoes several structural phase transitions [2]. The vibrational properties of Cu_{2-x}Te compound, which plays an important role in achieving ultra-low thermal conductivity, are not well understood due to complex crystal structure, phase transition and Cu-vacancy mediated doping [3]. We have investigated the vibrational properties of $\text{Cu}_{1.25}\text{Te}$, $\text{Cu}_{1.6}\text{Te}$, and Cu_2Te using Raman studies in the temperature range of 300-773 K. The study revealed complex structural and compositional transitions which categorised the CT compounds into Cu deficit and Cu rich classes. Cu rich Cu_2Te demonstrates structural transition from trigonal to orthorhombic and cubic phase above ~ 553 K [4]. The intensity of several Raman modes showed strong dependence on charge carriers and strong plasmon-phonon coupling. Cu_2Te depicted lowest thermal conductivity compared to other CT compounds as estimated through Raman spectroscopy.

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Realization of high thermoelectric figure of merit in solution synthesized 2D SnSe nanoplates via Ge alloying

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Recently single crystals of layered SnSe have created a paramount importance in thermoelectrics owing to their ultralow lattice thermal conductivity and high thermoelectric figure of merit (zT). However, nanocrystalline or polycrystalline SnSe offers a wide range of thermoelectric applications for the ease of its synthesis and machinability. Here, we demonstrate high zT of ~ 2.1 at 873 K in two-dimensional nanoplates of Ge-doped SnSe synthesized by a simple hydrothermal route followed by spark plasma sintering (SPS). Anisotropic measurements also show a high zT of ~ 1.75 at 873 K parallel to the SPS pressing direction. Ge doping (3 mol %) in SnSe nanoplates significantly enhances the *p*-type carrier concentration, which results in high electrical conductivity and power factor of $\sim 5.10 \mu\text{W}/\text{cmK}^2$ at 873 K. High lattice anharmonicity, nanoscale grain boundaries, and Ge precipitates in the SnSe matrix synergistically give rise to the ultralow lattice thermal conductivity of $\sim 0.18 \text{ W/mK}$ at 873 K.

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Simple model for thermoelectric properties of bulk and monolayer compound

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Finding a highly efficient and environmental friendly thermoelectric material has become a challenge in this high energy demanding world. For fast and high through-put prediction of thermoelectric material, an accurate predictive transport model is very important. We have used a simple model based on relaxation time approximation to calculate the electronic and thermal properties [1]. This model is used to calculate the thermoelectric properties of various bulk and monolayer compound based on chalcogenides. More than 90% agreement is observed between theoretically predicted and experimental values.

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Simultaneous optimization of power factor and thermal conductivity via te and se double substitution in $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ tetrahedrite

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The present study reports the influence of Te and Se double substitution on the structural, electronic, elastic and thermoelectric properties of $\text{Cu}_{12}\text{Sb}_{3.9}\text{Te}_{0.1}\text{S}_{13-x}\text{Se}_x$ ($x = 0, 0.1, 0.5, 0.75$ and 1) tetrahedrite. X-ray diffraction (XRD) and electron probe microanalysis (EPMA) results reveal successful substitution of Te and Se at the Sb 8c and S(1) 24g Wyckoff sites respectively. Differential scanning calorimetry (DSC) plots reveal an enhanced thermal stability of the double substituted samples upto ~ 680 - 700 K. The Raman spectra of the samples reveal a red-shift of the Sb-S bending/stretching modes with increasing x , due to a weakening of the Sb-S bond and a local chemical disorder induced by Se. Resonant ultrasound spectroscopy (RUS) measurements of the $x = 1$ sample reveal a mean sound velocity of 1933 m/s and a Debye temperature of 213 K, indicating a significant lowering of the phonon group velocities due to double substitution. Density functional theory (DFT) results show that Te^{+4} at the Sb^{+3} site lifts the EF towards the bandgap indicating effective compensation of holes. Whereas, isovalent Se^{-2} at the $\text{S}(1)^{-2}$ site introduces light hole bands with an increase in the density of states (DOS) near EF, thereby optimizing the power factor. Combined with an anomalously low lattice thermal conductivity, a maximum zT of ~ 0.84 was achieved in the double substituted $\text{Cu}_{12}\text{Sb}_{3.9}\text{Te}_{0.1}\text{S}_{12.5}\text{Se}_{0.5}$ sample.

*equal contribution

Spin-orbit coupling effect on thermopower and power factor of CoSbS

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The global energy crisis demands the search for new materials for efficient thermoelectric (TE) energy conversion. Thermoelectricity is needed not only at room temperature and above but it also has importance below room temperature for TE/Peltier cooling. So far Peltier Cooling is the biggest commercial application in TE technology with more than 90% market share among the devices. Chalcogenides of cobalt (Co) have been identified as promising materials for TE applications due to their high electrical conductivity and high Seebeck coefficient [1]. A recent experimental report by Du et. al. [2] showed colossal values of thermopower for CoSbS at 40K and also showed that the values decrease with the application of magnetic field. We investigated the thermoelectric power factor of CoSbS by using Boltzmann transport equations and density functional theory (DFT) including the spin-orbit coupling (SOC) terms in the calculation [3]. The reduction of thermopower with magnetic field is explained by the effect of SOC and it is shown that by tuning atomistic magnetic moment, the power factor can be further optimized. We show that a huge increase ($\sim 10^7$ times) in power factor is possible by increasing SOC interaction.

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Stabilizing the thermoelectric properties of Cu₂Se by W incorporation

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Thermoelectric power generation is gaining much attention for conversion of waste heat into electricity. In recent years the superionic conductors such as Cu₂Se and Cu₂S have been widely explored due to their potential in Thermoelectric applications. These superionic conductors exhibit high figure-of-merit (ZT) with low thermal conductivity (κ) by phonon scattering through the liquid-like ionic motion while the static Se or S sublattice provides a pathway for facile electrical conduction. The ionic movement under temperature gradient leads to chemical instability in these materials, hence there is a need to stabilize these materials for thermoelectric application. In the present work it is demonstrated that the incorporation of W in Cu₂Se matrix results in peak ZT of 2.1 ($ZT_{avg} = 0.93$) at 878 K. After the first thermal cycle, the peak ZT of the composite decreases to stable value of 1.5 ($ZT_{avg} = 0.97$). The enhanced stability of the nanocomposite along with the high ZT_{avg} is attributed to the covering of Cu₂Se grain boundaries with W that inhibits Cu⁺ migration, reduces Se loss, and improves charge carrier mobility.

Strong chemical bond hierarchy leading to exceptionally high thermoelectric figure of merit in oxychalcogenide AgBiTeO

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The chemical bond hierarchy (CBH) in typical cage structures are considered as the key parameter for realising high thermoelectric performance. Using first principles calculations and lattice dynamics, we demonstrate CBH hosted unique rattling motion in a non-caged system AgBiTeO, causing ultra low lattice thermal conductivity (κ_l) of 0.9 W/m K at 300K [1]. CBH in this compound leads to a distinct structural bonding, wherein Ag and Te atoms are loosely bonded to the rigid framework of the lattice, forming distorted four-centered Ag-Te tetrahedra. These loosely bound clusters exhibit large amplitude atomic vibrational motions with a very shallow potential energy surface, leading to rattling motion. The rattling induced thermal damping is further confirmed by the presence of several avoided-crossing points of low lying optical phonon mode with longitudinal acoustic ones. Additionally, unique in-plane collective vibrations of Ag-Te tetrahedra provide localised flat phonon dispersion that lower the group velocity, hence, significantly reduce the κ_l . Most importantly, this phenomenon prevents carrier-phonon scattering, resulting into a high electrical conductivity in AgBiTeO. Combination of ultralow lattice thermal conductivity and exceptional electronic transport properties give an unprecedented range of ZT from 1.00 to 1.99 in a large temperature range of 700-1200 K, for *n*-type charge carriers.

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Study of thermoelectric properties of multilayers of $\text{Bi}_2\text{Te}_3/\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$

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Technological advancement needs development of modes and methods for harvesting of waste heat. Telluride compounds are very good thermoelectric materials. They have shown excellent thermoelectric properties in the temperature range 50°C - 200°C. Recent reports indicate that their multilayer designs will have better thermoelectric properties. In this work preparation and characterisation of alternate multilayer thin films of Bismuth telluride (Bi_2Te_3) and Selenium doped Bismuth telluride ($\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$) have been reported. These layers having single layer thickness of about 30 - 40 nm were fabricated using electron beam assisted thermal evaporation on glass and Si substrates. The electrical properties of these films, i.e. Hall measurements, carrier concentration, carrier mobility, conductivity have been studied at room temperature. Thermoelectric behavior has been analyzed on the basis of Seebeck coefficient which show results in coherence to earlier reported values. X-Ray diffraction (XRD) was done using BL-14 at INDUS-II, RRCAT, Indore, India alongwith atomic force microscopy (AFM) and Scanning Electron microscopy (SEM) and Tunnelling Electron Microscopy (TEM) techniques to inquire the crystallographic structure and surface morphology of specimen. Results show that good quality multilayer films have been grown.

Thermoelectric properties of nano-structured *p*-type FeSe₂ for mid-temperature power generation

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Thermoelectric (TE) materials are known to convert untapped waste-heat, generated from various heat engines and power plants, into usable electricity so as to power the small-scale electronics devices. The performance of conversion ability of TE materials can be determined by figure of merit, $zT = S^2\sigma T / \kappa_{total}$ where σ , S , κ_{total} and T stand for electrical conductivity, Seebeck co-efficient and total thermal conductivity and absolute temperature, respectively [1]. Alloys of Bi₂Te₃, PbTe and SiGe are of champion TE materials as it exhibits high zT at elevated temperature; however those are very expensive and toxic in nature which in fact limits their large-scale production [2].

Here, we have successfully synthesized the rGO decorated low-cost FeSe₂ nano-composites by hydrothermal method. The XRD studies show the highly crystalline and single phase of FeSe₂ that could be indexed with orthorhombic pyrite structure. The bandgap of FeSe₂ ($E_g = 0.78$ eV) was calculated using Kubelka-Munk relation, which reduces to $E_g = 0.71$ eV for the composition of 5 wt.% rGO+FeSe₂. Further, vibrational modes of FeSe₂ with the presence of D and G bands of rGO were identified by means of Raman spectra. Interestingly, agglomerated FeSe₂ nano-particles with rGO decorated nanostructured FeSe₂ were clearly seen in FE-SEM and TEM studies. An influence of rGO on temperature-dependent thermoelectric properties of nanostructured FeSe₂ is studied and the experimental results will be presented.

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Topological quantum materials for thermoelectric energy conversion

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Topological quantum materials, TQM characterized by their nontrivial electronic surface states, have created a sensation in designing new thermoelectric (TE) materials. Underlying reason for TQM being a source of potential candidates for TE is ascribed to the fact that both TQM and TE materials demand similar material features such as the presence of heavy constituent elements, narrow band gap and strong spin-orbit coupling [1]. In our recent work, we have studied TE properties with detailed understanding of structure property correlation of few intriguing TQM with layered hetero-structure from $(\text{Bi}_2)_m(\text{Bi}_2\text{X}_3)_n$ ($x = \text{Se/Te}$; m, n - integer) homologous family. We have reported realization of ultralow lattice thermal conductivity, κ_{lat} of $\sim 0.5 - 0.9$ W/mK and high *n*-type TE performance in BiSe ($m = 1, n = 2$), a weak topological insulator from $(\text{Bi}_2)_m(\text{Bi}_2\text{X}_3)_n$ homologous family, driven by localized vibrations of Bi bi-layers in BiSe [2]. Recently, we have demonstrated simultaneous occurrence of intrinsically low κ_{lat} of $\sim 0.5-0.8$ W/mK and high carrier mobility, μ of $\sim 500 - 707$ cm^2/Vs in *n*-type BiTe, facilitated by its unique dual topological quantum phases [3]. These present results pave way to look for unconventional TQM for efficient TE materials.

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Tuning electrical and thermal transport via thermal stress field in Bi_2Te_3 thermoelectric fibers

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Bismuth telluride (Bi_2Te_3) has attracted much attention in the field of thermoelectrics since it is one kind of commercial room-temperature thermoelectric material. Herein Bi_2Te_3 thermoelectric fibers with glass cladding are fabricated utilizing an optical fiber template method. The effects of thermal stress field on the microstructure and the electrical/thermal transport properties of Bi_2Te_3 thermoelectric fibers are investigated. The Bi_2Te_3 cores in the fibers are highly crystalline and possess a nanosheet structure with preferential orientation, internal thermal stress, and element-diffusion surface as evidenced by X-ray diffraction, Raman, and TEM studies. The tensile stress can be applied to enhance electrical transport of the fibers and the element-diffusion surface can deduce their thermal transport as well. Then a paper cup generator covered with 20 pieces of optimized fibers provides a μW -level output power. It is inferred that thermal stress tuning can be an effective tool for the material optimization of thermoelectric performance.

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Achieving High Average zT Value in Sb_2Te_3 Based Segmented Thermoelectric Materials

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A tiny amount of Mn is doped $In_{0.15}Sb_{1.85}Te_3$ sample to tailor its carrier concentration, thus boosting the power factor and suppressing the bipolar effect. Furthermore, large amounts of nano-twins are constructed to effectively scatter the phonons and reduce the lattice thermal conductivity. As a result, the zT value of $Mn_{0.02}In_{0.15}Sb_{1.83}Te_3$ is enhanced up to 1.0 at 673 K, making this material a robust candidate for medium temperature (500~673 K) thermoelectric applications. Then, combining with the low-temperature thermoelectric material $Mn_{0.0075}Bi_{0.5}Sb_{1.4925}Te_3$ previously reported by our group and using Nickel as barrier layers, a high average zT value of 1.08 during a broad temperature range from 303 to 673 K, together with an Ohmic contact interface bonding, is achieved in the p-type segmented leg fabricated via simple one-step sintering. Finally, the maximum theoretical conversion efficiency with a temperature difference of 370 K reaches ~12.7%.

Evolution of the Intrinsic Point Defects in Bismuth Telluride Based Thermoelectric Materials

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In polycrystalline bismuth-telluride-based thermoelectric materials, mechanical deformation induced donor-like effect can introduce a high concentration of electrons to change thermoelectric properties through the evolution of intrinsic point defects. However, the evolution law of these point defects during sample preparation remains elusive. Herein, we systematically investigate the evolution of intrinsic point defects in n-type Bi₂Te₃-based materials from the perspective of thermodynamics and kinetics, in combination with positron annihilation measurement. It is found that not only the mechanical deformation, but also the sintering temperature is vital to the donor-like effect. The mechanical deformation can promote the formation of cation vacancies and facilitate the donor-like effect, and the sintering process can provide excess energy for Bi antisite atoms to surmount the diffusion potential barrier. This work provides us a better understanding on the evolution law of intrinsic point defects in Bi₂Te₃-based alloys and guides us to control the carrier concentration by manipulating intrinsic point defects.

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Enhancing the thermoelectric performance of *n*-type $\text{Bi}_2\text{Te}_{2.5}\text{Se}_{0.5}$ by $\text{BaFe}_{12}\text{O}_{19}$ magnetic nanoparticles

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How to lower the carrier concentration is the key to improve the thermoelectric properties of *n*-type Bi_2Te_3 -based materials. Herein, $\text{BaFe}_{12}\text{O}_{19}$ magnetic nanoparticles were prepared and used to regulate the carrier concentration of *n*-type $\text{Bi}_2\text{Te}_{2.5}\text{Se}_{0.5}$ materials. Structure characterization study performed on the $\text{BaFe}_{12}\text{O}_{19}/\text{Bi}_2\text{Te}_{2.5}\text{Se}_{0.5}$ magnetic nanocomposites revealed that the embedded $\text{BaFe}_{12}\text{O}_{19}$ magnetic nanoparticles are distributed on the grain boundaries of $\text{Bi}_2\text{Te}_{2.5}\text{Se}_{0.5}$ matrix with good chemical stability. Due to the retained strong ferromagnetism, the magnetic nanoparticles act not only as scattering centers for carriers and phonons, but also as a magnetic trap to lower the carrier concentration of the $\text{Bi}_2\text{Te}_{2.5}\text{Se}_{0.5}$ matrix by trapping free electrons. The reduction of carrier concentration has a positive effect on the Seebeck coefficient enhancement and thermal conductivity reduction. Consequently, a large thermoelectric figure of merit ZT of 1.0 is achieved at 490 K for the magnetic nanocomposites added with 0.30 wt% $\text{BaFe}_{12}\text{O}_{19}$, showing about a 20% enhancement as compared to that of the matrix. This work demonstrates that ferromagnetic nanoparticles can be used to regulate the carrier concentration and improve the thermoelectric performance of *n*-type $\text{Bi}_2\text{Te}_{2.5}\text{Se}_{0.5}$ materials.

Point defects evolution induced thickness-dependent electronic transport of MBE-grown Bi_2Te_3 thin films

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The manipulation of intrinsic point defects is capable of effectively optimizing the electronic transport properties of Bi_2Te_3 thin films. The interactions among various film growth parameters such as substrate temperature (T_{sub}), film thickness and composition play a crucial role in controlling the type and amount of the intrinsic point defects, which can be modulated for improving electronic transport properties of Bi_2Te_3 films. Here, n-type Bi_2Te_3 films with different thickness have been epitaxially grown by molecular beam epitaxy (MBE) at different T_{sub} . Considering the electronic transport properties and the upward band bending, two up-to-date insights about the underexplored intrinsic point defects in Bi_2Te_3 thin films are discovered in this study. (i) The negatively charged defects $V_{\text{Te}}^{\cdot\cdot}$, which is known as the initial major point defects, would gradually transform into the p-type defect Bi'_{Te} during the growth process, due to the *in-situ* annealing effect originating from continuously heated substrate. (ii) The density of defects $V_{\text{Te}}^{\cdot\cdot}$ decreases from the film surface to bulk, while the density of defects Bi'_{Te} increases accordingly, leading to a graded distribution of $V_{\text{Te}}^{\cdot\cdot}$ and Bi'_{Te} along the film thickness direction. As a result, the electron density of Bi_2Te_3 films reduces monotonically with increasing thickness. In addition, elevating T_{sub} leads to a more significant *in-situ* annealing effect and intrinsic excitation, giving rise to deteriorated electrical properties. Finally, at room temperature, a maximum PF of $1.6 \text{ mWm}^{-1}\text{K}^{-2}$ and the highest electron density of $2.03 \times 10^{20} \text{ cm}^{-3}$ are obtained in the thinnest Bi_2Te_3 thin film (16 nm) grown at $T_{\text{sub}} = 245 \text{ }^\circ\text{C}$. This work provides a comprehensive understanding about the formation and evolution of intrinsic point defects in Bi_2Te_3 films, and gives instructive suggestions for further optimizing carrier concentration and electronic transport properties by rational engineering of point defects.

Enhanced Electrical Transport Properties via Defect Control for Screen-Printed Bi_2Te_3 Films over a Wide Temperature Range

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The application of screen-printed thin-film thermoelectric (TE) devices is still in its infancy, mainly due to low TE performance of screen-printed films, especially the poor electrical transport properties. Herein, we design and prepare a high-performance screen-printed Bi_2Te_3 film through introducing excessive Te-based nanosolder (Te-NS) to simultaneously realize the conduction channel construction and defect control. On one hand, the promoted carrier migration makes the electrical conductivity dramatically rise about 7 times, with a maximum power factor of $4.65 \mu\text{W cm}^{-1} \text{K}^{-2}$. Meanwhile, the defect formation mechanism in screen-printed Bi_2Te_3 film after the introduction of Te-NS is also in-depth studied, and the bipolar conduction is reduced by more generation of Te_{Bi}^\bullet , and/or more suppression of Bi_{Te}' , resulting in postponed temperature of maximum Seebeck coefficient. Hence, the large engineering power factor is achieved with excellent temperature linearity, indicating a possibility of screen-printed film application in a large temperature region. Then, a TE device with single leg has been fabricated to further demonstrate the generation validity. The open-circuit voltage of 11.34 mV and the maximum output power of 27.1 μW at temperature gradient of 105 K have been achieved over a wide temperature range from 303 to 478 K. This study provides a theoretical and practical basis for the performance improvement of screen-printed TE films and devices.

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Effect of GdCo₂ magnetic nanoparticles on the interfacial composition and thermoelectric properties of p-type BiSbTe alloys

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Magnetolectric interaction has been recently proposed as an adoptable strategy to improve the electrical and thermal properties of some thermoelectric materials. However, the feasibility of adopting this strategy on the most important room-temperature thermoelectric materials, Bi₂Te₃-based alloys, is still not fully addressed. Herein, enhanced thermoelectric performance on Bi₂Te₃-based alloys is reported by embedding GdCo₂ magnetic nanoparticles in the p-type Bi_{0.37}Sb_{1.63}Te₃ matrix. It was found that the embedded GdCo₂ magnetic nanoparticles have chemical reaction with Bi_{0.37}Sb_{1.63}Te₃ matrix, which led to the formation of other nanoprecipitations and the intercalation of Co atoms inside the Van der Waals gap of Bi_{0.37}Sb_{1.63}Te₃ matrix. Effected by chemical composition variation of the composites, the electrical conductivity was reduced and the Seebeck coefficient was improved, which led to high power factor. Owing to the enhanced phonon scattering from additional point defects and nanoscale interfaces, the lattice thermal conductivity was largely reduced. Consequently, a peak *ZT* value of ~1.3 was achieved at 350 K when the addition content of GdCo₂ was 0.35 wt%. The addition of GdCo₂ nanoparticles also improved the mechanical property of the matrix. This work provides a route to optimize the thermoelectric and mechanical properties of p-type Bi₂Te₃ alloy by adding an appropriate amount of GdCo₂ magnetic nanoparticles.

Zintl phases SrAgSb and BaAgSb for waste heat recovery

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Zintl-phase thermoelectric materials have caught great attention due to their intrinsic electron-crystal and phonon-glass structures. In this work, ZrBeSi-type Zintl-phase compounds (SrAgSb and BaAgSb) were prepared, and their thermoelectric properties were investigated. The carrier concentration of Sr_xAgSb was subsequently optimized by Sr self-doping. The increased Sr content suppresses the intrinsic hole concentration, and leads to decreased total thermal conductivity. The peak ZT of $\text{Sr}_{1.01}\text{AgSb}$ reaches ~ 0.6 at 773 K. The intrinsic excitation leads to decreased ZT of BaAgSb at high temperature. The introduction of Ba vacancy is beneficial to suppress intrinsic excitation by increasing the carrier concentration, and leads to a ZT value of ~ 0.56 at 773 K for $\text{Ba}_{0.98}\text{AgSb}$. Furthermore, Eu alloying at the Ba site can both improve the electrical properties and lower the lattice thermal conductivity of BaAgSb. Finally, a ZT of ~ 0.73 at 773 K is achieved for $\text{Ba}_{0.78}\text{Eu}_{0.2}\text{AgSb}$. As a result, ZrBeSi-type Zintl-phase SrAgSb and BaAgSb thermoelectric materials provide a new family for exploring higher ZT .

Crystal structures and thermoelectric properties of Sb-based LiGaGe-related compounds

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Despite their diverse physical properties, it seems a pity that most TiNiSi-type intermetallic compounds bear poor thermoelectric properties. Interesting phase transitions and enhanced thermoelectric properties have been discovered in the TiNiSi-related system, for which inclusion of rare-earth metals on the Ca site or the transition metal Ag site both resulted in phase transitions from the orthorhombic structure to the hexagonal structure. Specifically, Zn atoms could be incorporated in the transition metal Ag site of CaAgSb, which leads to extensive disorder between the Ag and Zn atoms, the transition from TiNiSi-type CaAgSb into the LiGaGe-type $\text{CaZn}_{1-x}\text{Ag}_{1-y}\text{Sb}$ and a broad high zT plateau ($zT \sim 1.0$) from 800 to 1100 K. In this work, $\text{Ca}(\text{Mn}_{0.36(1)}/\text{Ag}_{0.29(1)})\text{Sb}$ and $\text{Yb}(\text{Mn}_{0.43(1)}/\text{Ag}_{0.14(3)})\text{Sb}$ single crystals, with considerably high defect level at the transition metal site, were synthesized and proved to adopt LiGaGe-type structure as well. Polycrystalline materials $\text{AMn}_{(1-x)/2}\text{Ag}_x\text{Sb}$ ($A = \text{Yb, Ca}; 0 < x < 1$) were synthesized and thermoelectric properties were characterized. Seebeck coefficient of both $\text{YbMn}_{0.45}\text{Ag}_{0.1}\text{Sb}$ and $\text{CaMn}_{0.4}\text{Ag}_{0.2}\text{Sb}$ approaches the maximum value of $\sim 200 \mu\text{V}/\text{K}$, which is attributed to the enhanced m^* compared to that of $\text{CaZn}_{1-x}\text{Ag}_{1-y}\text{Sb}$ series. Bearing a highly disordered and complex structure, it is not surprising that $\text{AMn}_{(1-x)/2}\text{Ag}_x\text{Sb}$ samples feature very low thermal conductivity generally with values of $0.5 \sim 1.2 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. These works further enrich LiGaGe-related compounds and prove their great flexibility and potential. Such a system is advantageous for the design of thermoelectric materials.

A Dual Role by Incorporation of Magnesium in YbZn_2Sb_2 Zintl Phase for Enhanced Thermoelectric Performance

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1-2-2-type Zintl phase compounds have promising thermoelectric properties because of their complex crystal structures and multiple valence-band structures. In this work, series of single phase $(\text{Yb}_{0.9}\text{Mg}_{0.1})\text{Mg}_x\text{Zn}_{2-x}\text{Sb}_2$ ($x = 0, 0.2, 0.4, 0.6, 0.8, \text{ and } 1$) compounds were prepared by alloying YbZn_2Sb_2 with 10 atm. % MgZn_2Sb_2 and different content of YbMg_2Sb_2 . The incorporation of Mg at the Yb site, as well as at the Zn site, not only leads to an effectively orbital alignment confirmed by the dramatically enhanced density of states effective mass and Seebeck coefficients, but also intensively increases the point defect scattering, contributing to a low lattice thermal conductivity $\sim 0.54 \text{ W m}^{-1} \text{ K}^{-1}$ at 773 K. Combined with the optimization of the carrier concentration by Ag doping at the Zn site, a highest ZT value ~ 1.5 at 773 K was achieved in $(\text{Yb}_{0.9}\text{Mg}_{0.1})\text{Mg}_{0.8}\text{Zn}_{1.2}\text{Ag}_{0.002}\text{Sb}_2$, which is higher than that of all the reported 1-2-2-type Zintl phase compounds.

Study on relationship of the structural evolution and the thermoelectric properties by doping of $\text{Ca}_9\text{Zn}_{4+x}\text{Sb}_9$ based Zintl

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Zintl phase have become a promising thermoelectric material due to its feature of Phonon Glass Electron Crystal. As a class of Zintl compounds, $\text{Ca}_9\text{Zn}_{4+x}\text{Sb}_9$ based Zintl thermoelectric materials have been widely studied due to their complex crystal structures and excellent performance. Previous studies show that thermoelectric performance can be significantly enhanced with inducing the lattice thermal conductivity by doping Eu in $\text{Ca}_9\text{Zn}_{4+x}\text{Sb}_9$. With the Eu content increasing, an interesting phase transition has been discovered during the crystal structure from the orthorhombic (*Pbam*) to the hexagonal (*P6₃/mmc*). In order to make clear the structure transition, we use the spherical aberration-corrected electron microscopy to characterize the crystal structure at the atomic level. It is found that there is an interphase which plays a key role for the structure transition from the orthorhombic to hexagonal. Then, we determined the crystal structure of this interphase.

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Pressure-induced enhancement of electrical transport properties of Mg_3Sb_2

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We performed density-functional calculations to study the effects of hydrostatic pressure on the electronic structure of Mg_3Sb_2 and find the enhancement of the power factors of both n-type and p-type Mg_3Sb_2 under pressure. There is a non-monotonic change of the DOS effective mass near the conduction band edge with increasing pressure. High multi-valley conduction states ($N_v = 8$) are formed at 5GPa, resulting in a significantly increased Seebeck coefficients of n-type Mg_3Sb_2 . In addition, pressure suppresses the electron phonon interaction near the valence band edge, which leads to a larger electrical conductivity of p-type Mg_3Sb_2 at 5GPa.

Enhanced thermoelectric performance of Ga-doped ZnO epitaxial thin films via defect engineering and sandwich structure design

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With good chemical and thermal stabilities, zinc oxide (ZnO) is a promising thermoelectric material that can be operated over a wide temperature range, particularly for high temperatures. For two dimensional (2D) thin films, modifying the thermal and electrical transport properties could be simplified due to the loss of one dimension. Herein, highly c-axis-orientated Ga-doped ZnO (GZO) thin films have been epitaxially deposited on sapphire substrate in our work. The GZO thin films were grown at 673 K, the optimal deposition temperature for GZO thin films investigated in our previous work, and then annealed at 723 K under vacuum to increase carrier concentration. Compared with GZO thin films as-deposited, the electrical conductivity of GZO thin films as annealed has been increased largely, while the Seebeck coefficient decreased. To maintain the high electrical conductivity without degrading the Seebeck coefficient, sandwich-like structure GZO-ZnO-GZO thin films with different thickness of ZnO layer were adopted to improve the electrical properties, as quantum well structure can modify the electronic structure to increase density of states (DOS). Finally, an improved power factor value of $433 \mu\text{W m}^{-1} \text{K}^{-2}$ at 623 K has been achieved, demonstrating that defect engineering combined with sandwich structure design could be a promising strategy for enhancing the thermoelectric properties of ZnO-based epitaxial films and other materials.

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First-principles investigation of the electronic structures and Seebeck coefficients of PbTe/SrTe interfaces

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By introducing a suitable barrier, the carrier filtering effect can yield a high Seebeck coefficient via filtering out low energy electrons (or holes). Although this mechanism has been proposed and applied widely in experiments, it is still unclear how to improve the charge Seebeck coefficient. To understand carrier filtering effect in the PbTe/SrTe interface, the first-principles method and semiclassical Boltzmann theory are carried out to investigate the electronic structures and Seebeck coefficients of PbTe/SrTe (110) and (100) interfaces. Additionally, the values of the Seebeck coefficient of the p-type PbTe/SrTe (110) are larger than those of the n-type one. The electronic properties of the PbTe/SrTe (100) interface are similar to those of the PbTe/SrTe (110) interface. This work provides theoretical guidance for the experiments, and also paves the way to further investigate spin transport properties of heterostructures.

Electronic transport descriptors for the rapid screening of thermoelectric materials

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In this work, we combine data-driven screening of potential candidates from the Materials Project Database and automate first principles calculations of the charge transport properties. By virtue of calculating both phonon- and impurity-scattering, we observe that the carrier scattering rate is dominated by optical phonons thus rendering mainstream predictors inaccurate. From the calculated data, we observe that in addition to low effective masses, high dielectric constant is an important factor towards high carrier mobility. Further, a quadratic correlation between dielectric constant and mobility was established and validated with literature data. Leveraging upon these results, we derive two easy-to-compute electronic transport descriptors for the screening of materials with potentially high mobility and power factor.

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High-throughput prediction of the carrier relaxation time via data-driven descriptor

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It has been demonstrated that many good thermoelectric materials such as tetradymite compounds also belong to a new class of quantum materials named topological insulators. In both cases, a fundamental question is the appropriate treatment of the carrier relaxation time, which is usually a rough task since complex scattering mechanisms are involved. Earlier attempts using the simple deformation potential theory or considering complete electron-phonon coupling are however restricted to small systems. By adopting a recently developed data analytics approach named SISSO (Sure Independence Screening and Sparsifying Operator), we propose an efficient and physically interpretable descriptor to evaluate the relaxation time, using tetradymites as prototypical examples. Without any input from first-principles calculations, the descriptor contains only several elemental properties of the constituent atoms, and could be utilized to quickly and reliably predict the carrier relaxation time of a substantial number of tetradymites with arbitrary stoichiometry.

First-principles database for two-dimensional materials

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Two-dimensional materials (2DMs) have been flourished for decades. Their novel physical and chemical characteristics provide access to unexplored areas in both fundamental researches and engineering applications. Especially, 2DMs offer a new platform for thermoelectrics. The quantum confinement effect for layered materials makes it having high electrical conductivity which coexists with high Seebeck coefficient. Many 2DMs have been systematically studied as thermoelectric materials, such as graphene, phosphorene, transition metal dichalcogenides and so on, though it is still only the tip of the iceberg. In this research, we report a newly established database for 2DMs, called MIP-2D, mainly for thermoelectric applications. 2,914 2DMs structural entries are taken from C2DB, JARVIS, materials-cloud, and other sources. After filtered out the duplicate entries, 2,217 entries are obtained. All the entries have been theoretically studied via a first-principles high-throughput workflow, from structure relaxations to electrical transport properties. It is notable that all the electrical transport properties are obtained through the more accurate constant electron-phonon coupling approximation. Furthermore, the elastic properties are also calculated in MIP-2D, which offer rough estimations on the lattice thermal conductivities for 2DMs. Based on MIP-2D, novel 2DMs with potentially excellent thermoelectric performance can be proposed.

The prediction of ABO_3 perovskites' thermoelectric properties through high-throughput screening

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Thermoelectric (TE) materials have attracted great considerable attention in electricity generation and cooling owing to the famous Seebeck and Peltier effects. To evaluating the properties of TE materials, we usually use the dimensionless figure-of-merit ZT which plays a completely essential role in thermoelectric area. Meanwhile with the help of high-throughput (HT) screening according to first-principle calculation could save us time discovering more proper potential materials. The ABO_3 perovskite materials are considered to be promising for future thermoelectric applications because of the advantages of long service life, zero radiation, no harmful gaseous components, and silent operation. In this work, we choose 313 structures from Materials Informatics Platform (MIP), the space group of these structures is $Pm\bar{3}m$. We screened out 46 well-calculated results and selected different deformation potentials to calculate electrical transport properties at the temperature 700K according to the classification of energy bands. Combine the maximum power factor (PF) and the thermal conductivity obtained by the slack model to calculate the maximum ZT and we found that 9 of the materials have better thermoelectric properties than others.

Vibrational Entropy Stabilizes Distorted Half-Heusler Structures

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First-principles methods have been extensively used for prediction of half-Heusler (HH) phases for a wide range of functional properties. However, in some cases, suggested stable HHs are observed to be distorted phases ($P6_3mc$ or $Pnma$) in experiments. We examine the impact of vibrational entropy on the thermodynamics of HH and competing low-symmetry phases by performing phonon calculations. We find that, in general, the lower symmetry phases have larger vibrational entropies, favoring their stability at higher temperatures. The high vibrational entropy of the distorted phase possibly comes from the weak bonding associated with larger atom motion, which leads to a large phonon density of states at low frequency. Our work explains the discrepancy between first-principles predictions and experimental phase stability and emphasizes the important effect of including vibrational entropy on the phase stability.

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Surprisingly good thermoelectric performance of black phosphorus/blue phosphorus van der Waals heterostructure

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Thermoelectric properties of black phosphorus/blue phosphorus van der Waals heterostructure are investigated by using first-principles calculations and Boltzmann transport theory for both electrons and phonons. It is found that the heterostructure is both energetically and kinetically stable even at higher temperature. Compared with those of the constituent black and blue phosphorus monolayers, the thermoelectric performance of heterostructure is significantly enhanced due to sharply decreased thermal conductivity caused by the presence of van der Waals interactions, as well as obvious reduced band gap and multi-valley structure resulted from type-II band alignment. As a consequence, the room temperature ZT value can reach 1.6, which is much higher than those of the components. Furthermore, we obtain ZT over 2.0 in a wide temperature range from 400 to 800 K, and a maximum ZT of ~ 3.2 can be realized at 700 K, which is surprisingly good for systems consisting of light elements only.

A promising thermoelectric 3D halides perovskite from 2D electronic structures and ultralow thermal conductivity

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Electronic band structure engineering plays a crucial role in improving the thermoelectric performance. Here, we report a Pb-free 3D halide perovskite which is a promising thermoelectric material due to its intrinsic 2D electric transport properties and ultralow lattice thermal conductivity. Using first-principles calculation based on density functional theory and Boltzmann transport equations, we find that the 3D halide perovskite shows high Seebeck coefficients due the flat electronic bands, as well as the ultralow lattice thermal conductivity resulting from the low group velocity and large scattering rate between optical modes and acoustic modes. Our work suggests that the halides perovskites with 2D electronic properties could be promising thermoelectric materials.

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Active learning for the power factor predictions in diamond-like thermoelectric materials

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The Materials Genome Initiative requires the crossing of material calculations, machine learning, and experiments to accelerate the material development process. In recent years, data-based methods have been applied into the thermoelectric field, mostly on the transport properties. In this work, we combined data-driven machine learning and first-principles calculation into an active learning loop, to predict the power factors (PFs) of diamond-like pnictides and chalcogenides. Our active learning loop contains two procedures, 1) Based on a high-throughput calculated database, machine learning methods are employed to select new candidates; 2) Computational verification on these candidates about their transport properties. The newly calculated data will be added into the database, in order to improve the machine learning models. Different strategies of selecting candidates have been tested, finally the extrapolation accuracy of the Gradient Boosting Regression model in QBC strategy is the highest (the Pearson R = 0.95). The PFs the diamond-like pnictides and chalcogenides of the whole search space are then predicted, and those entries with high PFs are screened. Based on the prediction of that machine learning models, binary pnictides, vacancy and small atom-containing chalcogenides are predicted to have large PFs. The bonding analysis reveals that the alterations of anionic bonding networks are beneficial to the PFs in these compounds.

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Role of lone pair electrons in n-type thermoelectric properties of tin oxides

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Oxide materials have shown promising thermoelectric applications due to their availability, tenability, and thermal stability. Among oxide materials, the layered tin oxides (SnO) attract raising attention in the electronic and optoelectronic field owing to their lone pair electrons. We have investigated the thermoelectric properties of layered SnO structures through first-principle calculations. SnO exhibits superior n-type thermoelectric properties and the metallicity of SnO becomes stronger with the number of layers increasing. The lone pair electrons around Sn atoms are the key factor to n-type properties and they will get bonded and anti-bonded in the case of interlayer interaction. Monolayer SnO exhibits the best thermoelectric performances and the average n-type ZT value of monolayer SnO can achieve 0.85 at 500~700K. Our results demonstrate that layered SnO will be the potential n-type two-dimensional oxide thermoelectric material.

Spatial phonon-dislocation scattering process in PbTe: a molecular dynamic study

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Recently, phonon-dislocation scattering has been a very hot topic. Excellent theoretical and experimental works have shown that the phonon scattering comes from the dislocation strain field and dislocation core. However, the range and intensity of phonon-dislocation scattering is still missing. In this study, we use a non-equilibrium molecular dynamics simulation method to study the lattice thermal conductivity in PbTe with edge dislocations. The thermal conductivity is greatly suppressed by 43.6% under a dislocation density of $3.342 \times 10^{15} \text{ m}^{-2}$. The strain field analysis of dislocation shows a local strain scattering region and nonlocal shear strain scattering region. Then, the 1 D McKelvey-Shockley flux method is further developed with defects which enable us to separate the phonon scattering from the two regions of dislocation. The scattering rate of phonon-dislocation is much larger in the local strain scattering region than in the nonlocal shear strain scattering region, but the dislocation nonlocal shear strain region accounts for a larger volume. The two regions scatter different frequency phonons and both of them are vital to influence the lattice thermal conductivity. It is the first time we show a spatial phonon dislocation scattering progress. Our result will advance the knowledge of phonon-dislocation scattering study.

Interfacial thermal transport in MoS₂-MoSe₂, MoS₂-WS₂ and MoS₂-WSe₂ heterobilayers

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Transition metal dichalcogenide (TMDC) heterobilayers have inspired massive interest because of their unique performances for applications in nanoelectronic and energy conversion devices. The interfacial thermal transport in heterobilayers arises as a crucial issue. In this work, the interfacial thermal transport properties in MoS₂-MoSe₂, MoS₂-WS₂, and MoS₂-WSe₂ heterobilayers are systematically investigated by using molecular dynamics (MD) simulations. A transient pump-probe method is applied, which is an MD technique inspired by the experimental method. Effects of system size, temperature, interlayer coupling strength, strains, and vacancy defects are explored. It is found that the interfacial thermal resistance (ITR) of MoS₂-WS₂ heterobilayer achieves the lowest among the three heterobilayers. The ITR decreases monotonically with increasing temperature and coupling strength, which can be attributed to the enhanced Umklapp scattering and energy transmission probability. Tensile and compressive strains have no significant effect on interfacial thermal transport. When the sulfur vacancy concentration in the MoS₂ layer increases from 0.0 to 5.0%, the ITRs of the MoS₂-MoSe₂, MoS₂-WS₂, and MoS₂-WSe₂ heterobilayers decrease by 28%, 36%, and 38%, respectively. The reductions of ITR mainly originate from the interlayer thermal coupling enhancement. The analyses of spectral energy density (SED) and phonon density of states (PDOS) are performed to further reveal the interfacial thermal transport mechanism in heterobilayers. These findings are critical to the understanding of the interfacial thermal transport in TMDC heterobilayers, which are useful for the thermal management in the two-dimensional heterobilayer-based nanoelectronics. This work was supported by the National Natural Science Foundation of China under Grant No. 51825604 and 51721004, and the 111 Project under Grant No. B16038.

High thermoelectric performance of half-Heusler compound BiBaK with intrinsically low lattice thermal conductivity

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Half-Heusler compounds usually exhibit relatively higher lattice thermal conductivity that is undesirable for thermoelectric applications. Here we demonstrate by first-principles calculations and Boltzmann transport theory that the BiBaK system is an exception, which has rather low thermal conductivity as evidenced by very small phonon group velocity and relaxation time. Detailed analysis indicates that the heavy Bi and Ba atoms form a cage-like structure, inside which the light K atom rattles with larger atomic displacement parameters. In combination with its good electronic transport properties, the BiBaK shows a maximum n-type ZT value of 1.9 at 900 K, which outperforms most half-Heusler thermoelectric materials.

Localized dimers drive strong anharmonicity and low lattice thermal conductivity in ZnSe₂

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We calculate the lattice thermal conductivities of the pyrite-type ZnSe₂ at pressures of 0 and 10 GPa by using the linearized phonon Boltzmann transport equation. We obtain a very low value (0.69 W/mK at room temperature at 0 GPa), comparable to the best thermoelectric materials. The vibrational spectrums are characterized by the isolated high-frequency optical phonon modes due to the stretching of Se-Se dimers and the low-frequency optical phonon modes with a strong anharmonicity due to the rattling mode of Zn atoms, especially the rotations of Zn atoms around these dimers. Interestingly, two transverse acoustic phonon modes with similar frequencies and wave vectors have very different degrees of anharmonicity. We show that the transverse acoustic branch with strong anharmonicity is contributed by the atomic vibrations perpendicular to Se-Se dimers. Obviously, the existence of localized Se-Se dimers leads to the strong anharmonicity and low lattice thermal conductivity of ZnSe₂. Furthermore, to determine the thermoelectric performance of ZnSe₂, we also investigate its electrical transport properties. Our results show that both p-type and n-type ZnSe₂ can possess promising electrical transport properties contributed by the complex energy isosurfaces of both valence and conduction bands. The low thermal conductivities and promising electrical transport properties lead to a large thermoelectric figure of merit of ZnSe₂ for both p-type and n-type doping at different pressures. Our study reveals the effect of the localized nonmetallic dimers on the anharmonicity and lattice thermal conductivity in pyrite-type compound, which can be used to guide researchers to seek promising thermoelectric materials containing nonmetallic dimers.

Fabrication of thermoelectric conversion devices using porous Si with enhanced heat transfer capabilities

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Thermoelectric (TE) materials convert thermal energy to electric energy and vice versa. To obtain a large power, it is necessary to enhance heat transfer between the TE material and the heat source fluid. We conduct a fundamental investigation to develop novel high-efficiency TE conversion devices using porous TE materials with enhanced heat transfer into/from the TE materials, which enables efficient energy recovery from heat sources such as industrial heated water discharge or exhaust gas.

Si was picked as the TE material, and Ag was chosen as the electrode metal. Si and Ag were bonded using a diffusion bonding technique. Si and Ag pieces (7mm×7mm) was performed in a carbon die at high temperature (830°C) under a pressure of 10 or 20 MPa. The cross-sectional surface was observed with a scanning electron microscope. Tensile tests and electrical resistance measurements were carried out on the bonded samples fabricated under various conditions.

It was found that bonding strength increases as the bonding time increases until 90 min for both the bonding pressures, while, after 90 min, the variation in bonding strength is not significant. The resistivity increased by up to 5% compared to that of Si only. It is evident from these results that Ag is a good candidate for an electrode material for porous Si because it is bonded to Si well and there is no insulating layer formed such as an intermediate compound. Details will be discussed on the day.

Nanostructured thermoelectric materials fabricated from chemically synthesized I-III-IV-VI quaternary compound nanocrystals

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Thermoelectric (TE) materials based on earth-abundant and nontoxic elements consistently gained momentum for use in waste heat utilization technology. In this study, we synthesized $\text{Cu}_3\text{Zn}_{1-x}\text{Al}_x\text{SnS}_{5-y}$ nanocrystals for fabrication of nanobulk materials and systematically investigated TE properties. At $x = 1$, the $\text{Cu}_3\text{AlSnS}_5$ (CATS) nanobulk material possesses exceptionally low lattice thermal conductivity (κ_{lat}) and highest power-factor (PF) among fabricated pellets. However, ZT value was quite low owing to the high carrier thermal conductivity (κ_{car}) due to very high electrical conductivity (σ). To reduce κ_{car} , we synthesized $\text{Cu}_3\text{Al}_{1-x}\text{Ga}_x\text{SnS}_5$ nanocrystals and fabricated nanobulk materials for investigating TE properties. The ZT value of $\text{Cu}_3\text{Al}_{1-x}\text{Ga}_x\text{SnS}_5$ nanobulk at $x = 0.5$ ($ZT = 0.26$ at 665 K) was found to be more than twice that of pristine CATS nanobulk at 665 K, primarily because of the significant reduction in κ_{car} . Correlation among various transport parameters, crystal structure, and TE performance of the $\text{Cu}_3\text{Al}_{1-x}\text{Ga}_x\text{SnS}_5$ nanobulks ($0.25 \leq x \leq 1$) revealed that a larger fraction of the zinc blende (ZB) phase leads to a higher PF . In summary, the $\text{Cu}_3\text{Al}_{0.5}\text{Ga}_{0.5}\text{SnS}_5$ nanobulk exhibited the highest ZT value in the range of $0 \leq x \leq 1$ because of its significantly reduced κ_{car} value as compared to the CATS nanobulk. The reduced κ_{car} value is owing to the Ga substitution and the highest ZB phase fraction, resulting in the highest PF among $\text{Cu}_3\text{Al}_{1-x}\text{Ga}_x\text{SnS}_5$ nanobulks ($0.25 \leq x \leq 1$).

Enhancing thermoelectric performance of Mg₂Sn single crystals via point defect engineering and Sb-doping

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Mg₂Sn is a potential thermoelectric (TE) material with environmental compatibility and earth-abundant resources. In a previous work, we succeeded in significantly reducing the lattice thermal conductivity, κ_{lat} , of Mg₂Sn single-crystal ingots by the introduction of Mg vacancies (VMg). One remaining problem is the low electrical conductivity, σ ; therefore, we carried out Sb-doping on the Mg₂Sn single-crystal ingots while maintaining the VMg fraction.

Single-crystal X-ray diffraction measurements reveal that VMg defects exist in prepared Mg₂Sn_{1-x}Sb_x single-crystal ingots. With increasing x , the carrier concentration, n , significantly increases, indicating that the Sb atoms act as a donor. Comparing with the TE properties of the ingots with those of Mg₂Sn_{1-x}Sb_x polycrystals, the $x = 0.01, 0.02$ ingots show the slightly lower absolute Seebeck coefficient, $|S|$, by $\sim 15\%$, reflecting the higher n by $\sim 10\%$. The σ values of the $x = 0.01$ and 0.02 ingots are over 40% higher than those of polycrystals. This is mainly due to the higher carrier mobility, μ , by $\sim 30\%$. On the other hand, the κ_{lat} values of the $x = 0.01$ and 0.02 ingots are lower than those of polycrystals, reflecting the VMg and Sb atoms act as the scattering centres of phonons. Consequently, a maximum power factor, PF_{max} , of 5.1 mW/K²m and a maximum figure-of-merit, zT_{max} , of 0.72 are achieved for the $x = 0.01$ ingot, which are the highest values among the Mg₂Sn-based materials.

Enhancement of thermoelectric properties of hybrid-halide perovskites thin films using anti-solvent

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The conversion efficiency of thermoelectric material is quantified by figure of merit ZT ($=\sigma S^2 T/\kappa$: σ is electrical conductivity, S is Seebeck coefficient and κ is thermal conductivity). $\text{CH}_3\text{NH}_3\text{SnI}_3$ (MASnI_3) single crystals have intrinsic high value of Seebeck coefficient due to charge-carrier mobility and ultra-low thermal conductivity due to the rotational motion of cations in the lattice even though it has only focused for optical energy conversion. However, optimization of electrical conductivity is still challenging which can lead to a landmark for thermoelectric application of this material. In this study, we optimize the growth parameters of MASnI_3 thin films by spin coating technique.

Thin films are fabricated by spin coating technique using a yellow solution of MASnI_3 . The yellow solution is prepared by MAI , SnI_2 precursors. During the fabrication process, we optimized growth parameters such as baking time and the presence of anti-solvent. MASnI_3 thin films have shown p -type semiconducting behavior. MASnI_3 thin films were thoroughly characterized using several state of the art techniques including XRD and SEM. Temperature dependent Seebeck coefficient, electrical resistivity and thermal conductivity measurements were performed. MASnI_3 thin films baked at 100°C for 5 min with anti-solvent shows the best result with Seebeck coefficient about $65 \mu\text{V/K}$ and electrical conductivity of about 2 S/cm near room temperature.

Reactive consolidation of Al-Fe-Si powder activated via ball-milling

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Well known TE materials such as Bi_2Te_3 and PbTe exhibit high TE performances, whereas those compounds contain rare and toxic elements. Thus, developments of TE materials composing of abundant and environmentally friendly elements are desired for widespread use including independent power supplies for IoT sensors. Recently, it has been shown that $\tau_1\text{-Al}_2\text{Fe}_3\text{Si}_3$ intermetallic compound has excellent TE properties around room temperature [1]. However, it is not easy to obtain samples with high phase-purity of τ_1 phase via a usual melting technique due to the peritectic reaction. It is necessary to obtain pure phase material for optimizing its TE properties. In this work, we suggest a powder metallurgy route for fabricating of this material. We prepare nano-Si particles by ball milling Si powder first, mix it with Al/Si powders very well next, and then consolidate the activated mixture of powder by hot-pressing. The grinding and mixing processes make uniform dispersion of Al/Si particles in the powder, resulting in increased interface between starting materials and decreased diffusion distance. That could enable reactive consolidation at a relatively low temperature leading to high purity of the product. In the presentation, we will also discuss the TE properties of the τ_1 phase.

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Double half-Heusler: a new phase half-Heusler materials for thermoelectric power generation

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Multifunctional $X_2Y'Y''Z_2$ phase double half-Heuslers are a new addition of the multifunctional thermoelectric group materials, however, they are quite challenging to synthesize owing to their complex quaternary structure of $X_2Y'Y''Z_2$ phase. We have synthesized a pure single-phase of powder and bulk samples of $Ti_2FeNiSb_2$ double half-Heusler alloy as a representative, which thought to be formed by the merging of $TiNiSb$ and $TiCoSb$ ternary half-Heuslers. Characterizations are done by XRD, SEM and TEP measurements. Intrinsic lattice thermal conductivity originated from the crystal structure seems to be significantly low for $Ti_2FeNiSb_2$ ($\kappa_L \sim 3.5 \text{ Wm}^{-1}\text{K}^{-1}$) corresponding to the ternary $TiNiSb$ ($\kappa_L \sim 10 \text{ Wm}^{-1}\text{K}^{-1}$), and $TiCoSb$ ($\kappa_L \sim 20 \text{ Wm}^{-1}\text{K}^{-1}$) half-Heusler alloy. Several dopants have been utilized to find out the peak performance and Co doping at Fe site is found to be more favorable. The power factor enhanced from $\sim 0.6 \text{ mWm}^{-1}\text{K}^{-2}$ to $1.2 \text{ mWm}^{-1}\text{K}^{-2}$ which reproduce a corresponding ZT improvement from ~ 0.22 to ~ 0.57 for $Ti_2FeNiSb_2$ and $Ti_2Fe_{0.85}Co_{0.075}NiSb_2$ alloys, respectively.

Enhanced thermoelectric performance in *n*-type half-Heusler VFeSb compounds with cobalt-substitution

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Recently, half-Heusler VFeSb compound has drawn much attention due to its high power factor PF of 4.4 mW/K²m at 400 K, which can be a promising material for thermoelectric (TE) energy conversion. In our previous work, we revealed that a VFeSb compound has a deficient half-Heusler structure with vacancies in V 4a and Fe 4c site and interstitial Fe in 4d site, which is a major reason for *n*-type nature of transport. To achieve an optimal PF value, we selected cobalt to partially substitute Fe-site to tune carrier concentration. In this study, we investigate the effects of Co-substitution for Fe-site on the TE properties of the VFeSb compound.

Polycrystalline samples with nominal composition of V(Fe_{1-x}Co_x)Sb ($x = 0, 0.005, 0.01, 0.02, 0.05, 0.10,$ and 0.20) were successfully synthesized using arc-melting, annealing and spark plasma sintering. The crystal structures were refined by using Rietveld analysis of their XRD data, and the TE properties were measured (300 K ~ 800 K). All samples were single-phase and identified to have the deficient half-Heusler structure. Negative Seebeck coefficient was obtained in measured temperature range, which shows an *n*-type conduction in all samples. The carrier concentration increased by a slight Co substituting, leading to a high PF about 5.7 mW/K²m at 310 K by V(Fe_{0.99}Co_{0.01})Sb compound, which is the highest PF value reported in *n*-type VFeSb-based compounds.

Thermoelectric properties of I-doped Mo_3Sb_7

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Mo_3Sb_7 shows a *p*-type metallic character with poor thermoelectric properties. However, this material has a few bands crossing at the Fermi level and the thermoelectric properties can be improved by adding electrons to the structure, resulting in a progressive transition from a metallic-like to a semiconducting state. Häusserman et al. [1] demonstrated band structure calculations and revealed that the Fermi level can be moved into the band gap by adding two more electrons. Several attempts to add electrons have been performed by substituting Te (valence electrons = 6) for Sb (valence electrons = 5), leading to an enhancement in the zT . However, unfortunately, the solubility limit in the $\text{Mo}_3\text{Sb}_{7-x}\text{Te}_x$ system ($x \sim 1.6$) is lower than the theoretical value required to achieve semiconducting properties ($x = 2.0$). On the other hand, the substitution of I (valence electrons = 7) for Sb, i.e. $\text{Mo}_3\text{Sb}_{7-x}\text{I}_x$, which requires a smaller content ($x = 1.0$), has never been studied. In this study, we confirmed that I can be substituted for the Sb-sites and the thermoelectric properties of Mo_3Sb_7 were improved. It was revealed that the solubility limit for I in $\text{Mo}_3\text{Sb}_{7-x}\text{I}_x$ was $x = 1.25$. The maximum zT of 0.18 at 900 K was obtained for $x = 1.0$. This work was supported in part by the New Energy and Industrial Technology Development Organization (NEDO).

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Preliminary study of thin films of the filled skutterudite $\text{Sm}_y(\text{Fe}_x\text{Ni}_{1-x})_4\text{Sb}_{12}$

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Our team was lately involved in the characterization of dense skutterudites belonging to the $\text{Sm}_y(\text{Fe}_x\text{Ni}_{1-x})_4\text{Sb}_{12}$ system, finding a complex dependence from stoichiometry and applied pressure.

Respect to the bulks, thin films have several advantages such as low dimensionality, rapid fabrication and possibility to be used in miniaturized devices. Regarding skutterudites, only few research papers on binary CoSb_3 and IrSb_3 thin films have been published in the early 2000s, then films of filled skutterudites doped with Fe at the Co site were studied in the most recent years.

In this work, we present our preliminary results on thin films of skutterudites $\text{Sm}_y(\text{Fe}_x\text{Ni}_{1-x})_4\text{Sb}_{12}$. Films were prepared by pulsed laser deposition (PLD) on fused silica substrates focusing on dense pellets prepared by SPS a laser beam (YAG, $\lambda = 266$ nm) under the following conditions: frequency = 10 Hz, $d_{\text{sub-target}} = 35$ mm, $T_{\text{dep}} = 20\sim 300$ °C, $t_{\text{dep}} = 20\sim 60$ min, in $P_{\text{Ar}} = 20\sim 1000$ mTorr or high vacuum ($P = 10^{-4}$ Pa).

Under SEM the surface of the films appeared granular, and the size of grains decreases with decrease of P_{Ar} . The XRD showed that the films are amorphous and may require post-annealing.

The transport and thermoelectric properties of as-deposited samples were measured between 300 K ~ 500 K using a home-made apparatus. The best sample so far ($T_{\text{dep}} = 20$ °C and $t_{\text{dep}} = 60$ min, in high vacuum), with a thickness of 264 nm shows $\rho = 0.85$ mOhm/cm, $S = -24$ $\mu\text{V/K}$ and power factor $\sigma S^2 = 70$ $\mu\text{W/mK}^2$ at 500K.

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3D printing of compositionally segmented BiSbTe legs for high performance power generation

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Segmented TEGs comprising multiple TE elements are operated over a large thermal gradient without loss of ZT s, exhibiting higher efficiencies compared with conventional single element-TEGs. However, despite excellent theoretical efficiencies, the development of segmented TEGs suffers from critical challenges of a discrepancy of material compatibility and limited design flexibility of module by conventional processes. Herein, we report multi-material 3D printing of composition-segmented BiSbTe-based TEGs by sequential deposition method of all-inorganic viscoelastic TE inks containing $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ particles, tailored with Sb_2Te_4 -chalcogenidometallate binders. By composition engineering of $(\text{Bi,Sb})_2\text{Te}_3$ particles, the peak ZT s of 3D-printed materials are controllably shifted from room temperature to 250 °C. Furthermore, we design and fabricate the optimum TEG comprising 3D-printed, composition-segmented tri-block, which serves the extension of peak ZT s and full compatibility in the entire temperature range. Our approach offers a promising strategy to optimize segmented TEGs.

Branching of electrical and thermal conductivities in La- and Nb-substituted SrTiO₃

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Heat in crystals is transported by propagations of both quantized lattice vibrations (phonon) and/or conduction electrons. Phonon propagation needs to be suppressed while keeping the electron mobility to realize high ZT thermoelectric materials. Substitutional ion-doping such as La³⁺ in the Sr²⁺ site or Nb⁵⁺ in the Ti⁴⁺ site is a known way to increase the electrical conductivity (σ) of SrTiO₃. However, the effect of the ion-substitution on the thermal conductivity (κ) has not been clarified thus far. Here we demonstrate that both the σ and κ of Nb-substituted SrTiO₃ (NSTO) increase dramatically when the substituent exceeded ~50% (branching point) whereas those of La-substituted SrTiO₃ (LSTO) decrease. There are two differences between NSTO and LSTO. (1) Polaron: The polaron was maintained in the LSTO at overall La-concentration while disappeared in the NSTO when the Nb-concentration exceeds the branching point. (2) Symmetry: The lattice symmetry of the LSTO changes from cubic to orthorhombic, while that of the NSTO is maintained stable cubic. The present results would be helpful in designing SrTiO₃-based high ZT thermoelectric materials.

Cu-incorporation by melt-spinning in *n*-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ alloys

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In this study, we investigated the enhanced thermoelectric performance of *n*-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ polycrystalline alloys prepared using melt spinning (MS) and spark plasma sintering (SPS) processes by Cu addition, especially at the low (< 373 K) and medium (373 K – 673 K) temperature range. The electrical conductivity was greatly improved by the incorporation of Cu, and it was found that the main reason is the simultaneous increase of electron concentration and mobility along with the simultaneous decrease in hole concentration based on the theoretical analysis of a single parabolic band model. While, the Seebeck coefficient was rather moderately decreased, suggesting the favorable band modification in the presence of incorporated Cu atoms. Additionally, reduction of total thermal conductivity was observed even with the small increase of bipolar thermal conductivity by the Cu incorporation. Consequently, the zT (the dimensionless thermoelectric figure of merit) value higher than 0.90 was achieved at the wide range of temperature range of 350 – 450 K for the MS-SPSed $\text{Cu}_{0.008}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, compared to the maximum zT of 0.70 at 300 K for the MS-SPSed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample. The maximum efficiency of thermoelectric power generation could be enhanced in value about 4.2% at $\Delta T = 180$ K.

Enhancement of thermoelectric performance of Bi_2Te_3 based alloys through energy filtering effect

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Bi_2Te_3 based alloys are well known as high performance thermoelectric materials. However, for practical use in power generation, further improvement in the dimensionless figure of merit zT is needed. We have focused on energy filtering effect to improve the Seebeck coefficient S of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ (BTS_x). The energy filtering effect is usually utilized to enhance S in composites by blocking lower energy carriers which contribute negatively to S . According to the calculation results, the composites which is composed of nano-sized Au and Bi_2Te_3 based matrix can be expected to enhance S by the energy filtering effect [1]. However, there are few reports on demonstration of the energy filtering effect in $\text{Bi}_2\text{Te}_3/\text{Au}$ composites experimentally [2]. Here, we synthesized nano-sized Au embedded Bi_2Te_3 composites bulk in a simple procedure and succeeded in improving S compared with the control sample. The electrical transport properties including carrier concentration/mobility and electrical resistivity as well as S were measured at room temperature. We found a clear increase in the S of $\text{BTS}_{0.2}/\text{Au}$ composites compared with the Pisarenko plot for the control sample.

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Improving the thermoelectric properties of non-toxic and flexible Ag₂S material by electronic structure modification

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Development of thermoelectric (TE) generators is currently a major focus as devices capable of supplying input power to many sensors [1]. Improvement of ZT of TE materials used in such devices is very important. Besides, these materials are flexible [2]. Recently, Ag₂S is found to good flexible properties [3]. However, due to large electrical resistivity, ZT remains very low. To improve ZT , the substitutions at the sulfur site are studied [4,5]. So not appropriate to make flexible devices which directly used with body heat. To overcome this issue, modification in electronic structure is of crucial importance. Therefore, we carried the DFT calculations on Ag_{2-x}TM_xS (TM = transition metal) and successfully achieved both p and n -type TE property.

With transition metals substitutions at Ag site, we observed formation of impurity peak in DOS near VB and CB edge, which provides the better TE property of p -type and n -type materials, respectively. We synthesized Ag_{2-x}TM_xS materials, and investigated in 300-450 K. Polycrystalline samples were prepared and analyses of structural and TE properties were done by using XRD, SEM-EDX, LFA, and homemade setup [4].

With substitutions of transitional metals, we observed better p and n -type TE materials with flexibility.

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Power generation from colusite-based thermoelectric module

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Colusites $\text{Cu}_{26}\text{A}_2\text{E}_6\text{S}_{32}$ (A = V, Nb, Ta, Cr, Mo, W and E = Ge, Sn) have become promising high-performance *p*-type thermoelectric materials. Their complex crystal structure and degenerate semiconducting behavior lead to low thermal conductivity and high-power factor, respectively, which result in high thermoelectric figure of merit, ZT [1-3]. Recently, we developed the Au-based diffusion barrier for $\text{Cu}_{26}\text{Nb}_2\text{Ge}_6\text{S}_{32}$ single thermoelectric element, which provides low electrical and thermal contact resistances, leading to maximum conversion efficiency of 3.3% when the hot-side temperature (T_h) was kept at 570 K and cold-side temperature (T_c) at 297 K [4]. This work facilitated us to develop colusite-based thermoelectric power generation module. In this study, we successfully fabricated first prototype 2-pair thermoelectric module consisting of *p*-type colusite-based ($\text{Cu}_{26}\text{Cr}_2\text{Ge}_6\text{S}_{32}$) element with Au diffusion barrier and *n*-type PbTe-based element with $\text{Co}_{0.8}\text{Fe}_{0.2}$ alloy diffusion barrier. A maximum thermoelectric conversion efficiency (η_{max}) of $\sim 5.5\%$ was obtained when T_h and T_c were maintained at 673 K and 283 K, respectively.

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Preparation and thermoelectric properties of Sb substituted ZnTe alloys by melt-quenching method

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First time we prepare a novel compound i.e ZnSbTe alloy using melt quenching method for thermoelectric energy conversion. Five samples were prepared with various substitution ratio of Sb concentration in the host ZnTe compound. The prepared pure ZnTe alloy exposed cubic zinc blend structure along with some hexagonal Te phase. The ZnTe peak intensity was considerably decreased when increasing the substituted Sb% ions. Moreover, the Sb₂Te₃ peaks were systematically enhanced which confirms the presence of rhombohedral structure. FE-SEM images clearly indicate that all the prepared samples have similar morphological structures. From the EDX spectrum, the observed atomic composition percentages are very close to the used composition ratio for each alloy. The calculated bandgap decreased from 1.60 eV to 1.41 eV due to the barrier height change at grain boundaries. The observed bandgap for ZnTe (1.60 eV) is very close to that of previous reports, which indicates that there is no major change in the optical bandgap. From Seebeck coefficient (*S*) study, pure ZnTe sample showed *n*-type behavior, while all the other Sb substituted ZnTe shows *p*-type material. The substitution of Sb³⁺ in Zn²⁺ sites, increase the carrier concentration and decrease in electrical resistivity. The calculated power factor (*S*² σ) is 3.2 \times 10⁻⁹ for Zn_{0.25}Sb_{0.25}Te_{0.5} alloy; this value may be due to the less density of composite materials.

High-performance PEDOT:PSS flexible thermoelectric materials and their devices by triple post-treatments

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Searching an effective method to enhance the thermoelectric properties of flexible organic films can significantly widen the application of flexible thermoelectric devices. Tuning the microstacking structure and oxidation level can effectively optimize the thermoelectric properties of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) organic films. Here, we adopt triple post-treatments with formamide (CH_3NO), concentrated sulfuric acid (H_2SO_4), and sodium borohydride in sequence to engineer flexible PEDOT:PSS thermoelectric films. A high power factor of $141 \mu\text{Wm}^{-1}\text{K}^{-2}$ at 25°C has been obtained for the PEDOT:PSS film. Such a high power factor stems from the high σ (1786 Scm^{-1}) and S ($28.1 \mu\text{VK}^{-1}$) after posttreatment with CH_3NO , H_2SO_4 and NaBH_4 in order. The increased carrier mobility resulting from both the selective removal of excess insulating PSS within the films and the conformation transition after CH_3NO and H_2SO_4 treatments is responsible for the enhancement of σ , while the subsequent NaBH_4 treatment optimize the electrical properties (σ and S) by modulating the oxidation level. A homemade thermoelectric device has also been fabricated using the as-prepared flexible PEDOT:PSS films and had a high output power density of $\sim 1 \mu\text{Wcm}^{-2}$ with human arm as a heating source. This study indicates that flexible thermoelectric devices based on cheap conducting polymers have great potential in wearable electronics.

Morphology and texture engineering enhancing thermoelectric performance of solvothermal synthesized ultra-large SnS microcrystal

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With intrinsically strong anisotropy, layer-structured SnS and SnSe-based thermoelectric materials are attracting extensive attention. In this study, we synthesized ultra-large SnS microcrystal through a facile solvothermal method. It is found that the morphology of as-synthesized SnS powders can be tuned from plate into belt shapes with reducing the amount of NaOH. After sintering, the pellets sintered from larger SnS belts shows strengthened anisotropy due to texturing effect comparing with those sintered from SnS plates, and leads to enhanced electrical performance along the in-plane direction ($\{111\}$ -preferred). The tuned reaction condition with reducing the amount of NaOH also increases the Sn vacancies, leading to reduced band gap, shifted Fermi level and subsequently enhanced hole concentration. Consequently, the overall thermoelectric performance is enhanced with reducing the amount of NaOH. This study indicates texture engineering is effective in tuning anisotropy of polycrystalline SnS, enhancing the thermoelectric performance, and can be realized via morphology engineering.

Establishing the golden range of Seebeck coefficient for maximizing thermoelectric performance

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A net increase in zT requires the optimized Fermi level, which is determined by the coupling nature of thermoelectric properties. Commonly, the carrier concentration is the measurable parameter that reflects the variation of Fermi level. However, the carrier concentration also depends upon effective mass and temperature, leading to optimal carrier concentrations differing significantly from materials to materials. Consequently, it is difficult to decide whether the thermoelectric performance of a specific material has been optimized or not. To address such a basic but challenging issue, we survey reported thermoelectric properties from over 100 materials, which indicates that the maximized thermoelectric performance corresponds to a narrow range of Seebeck coefficient (S). Using a modeling study, we develop a golden S range of 202 – 230 μVK^{-1} for n/p -type thermoelectric semiconductors with lattice thermal conductivity of 0.4 – 1.5 $\text{Wm}^{-1}\text{K}^{-1}$. When the measured S reaches this range, the corresponding zT is maximized. Using this approach, we exemplarily analyze the characteristics of n -type $\text{Pb}_{1-x}\text{Bi}_x\text{Se}$ thermoelectric materials. Bi substitution significantly tunes S in a wide range. As a result, S of $\sim -230 \mu\text{VK}^{-1}$ in $\text{Pb}_{0.98}\text{Bi}_{0.02}\text{Se}$ is close to the golden range. Combining with the reduced thermal conductivity, an enhanced zT is achieved. This finding provides an intuitive metric to determine the optimization extent of thermoelectric performance.

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Nd doped TAGS-85 thermoelectrical materials

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The phase change material GeTe with high carrier concentration is modified by alloying with cubic AgSbTe₂ to optimize thermoelectric performance, nominated as (GeTe)₈₅(AgSbTe₂)₁₅, so-called TAGS-85. Herein, the Nd-doped TAGS-85 has been synthesized by the melting and quenching method. The Power factor was improved to 32 $\mu\text{W cm}^{-1}\text{K}^{-2}$ due to the increased Seebeck coefficient result from the reduction of hole concentration. Simultaneously, the thermal conductivity decreased at high temperature caused by the second phase compounds produced by Nd and Te as well as the decreased electrical thermal conductivity. Consequently, the figure of merit zT was optimized to 1.65 at 727 K in the composition of (Ge_{0.98}Nd_{0.02}Te)₈₅(AgSbTe₂)₁₅.

Optimization of sodium hydroxide for securing high thermoelectric performance in polycrystalline Sn_{1-x}Se

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In this study, we report a high figure-of-merit (ZT) of ~ 1.5 at 823 K in *p*-type polycrystalline Sn_{1-x}Se resulted from a synergy of morphology control and vacancy optimization, realized by carefully tuning the sodium hydroxide (NaOH) concentration during solvothermal synthesis. After a comprehensive investigation on various NaOH concentrations, it was found that an optimized NaOH amount of 10 mL with a concentration of 10 mol L⁻¹ can simultaneously achieve a large average crystal size and a high Sn vacancy concentration of $\sim 2.5\%$. The large microplate-like crystals lead to a considerable anisotropy in the sintered pellets, and the high Sn vacancy level contributes to an optimum hole concentration to the level of $\sim 2.3 \times 10^{19}$ cm⁻³, and in turn a high power factor of ~ 7.4 $\mu\text{W cm}^{-1}\text{K}^{-2}$ at 823 K, measured along the direction perpendicular to the sintering pressure. In addition, a low thermal conductivity of ~ 0.41 W m⁻¹K⁻¹ is achieved by effective phonon scattering at localized crystal imperfections including lattice distortions, grain boundaries, and vacancy domains, as observed by detailed structural characterizations. Furthermore, a competitive compressive strength of ~ 52.1 MPa can be achieved along the direction of high thermoelectric performance, indicating a mechanically robust feature. This study provides a new avenue in achieving high thermoelectric performance in SnSe-based thermoelectric materials.

A new approach to enhance thermoelectric figure of merit of polypyrrole - reduced graphene oxide hollow fibers mat - A flexible thermoelectric material

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Green energy harvesting by waste heat recovery using inexpensive and nontoxic thermoelectric (TE) materials have got much attention. These materials are characterized by dimensionless figure of merit $ZT = S^2\sigma T/\kappa$ where S is the seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and κ is the thermal conductivity respectively. In the present work, free standing and flexible composite of polypyrrole (PPy) and reduced graphene oxide (RGO) hollow fibers mat (PGHF) were fabricated by sacrificial removal of soft templates of electrospun polycaprolactone fibers with PPy and RGO coating through chemical polymerization of pyrrole monomer. Though RGO is beneficial with high σ , whereas it's extremely high κ limits its TE performance. PGHF composite may provide an attractive strategy to lowering $\kappa = 0.0213 \text{ Wm}^{-1}\text{K}^{-1}$ by an order of magnitude than pure PPy for which $\kappa = 0.2939 \text{ Wm}^{-1}\text{K}^{-1}$ because it has a large void fraction generated by the bulky fiber network and low-density structure. Furthermore the strong interfacial π - π interactions between PPy nanosphere and RGO nanosheets provides highly effective conducting pathways for electron transport which play a key role in significant enhancement of power factor ($P = S^2\sigma$) than that of pure PPy. Therefore, PGHF is expected to be a promising candidate for use as a flexible TE material, where ZT value with few order of magnitude higher than that of pure PPy.

Conducting polymers for room-temperature thermoelectric applications

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Room-temperature thermoelectrics, now-a-days is being focussed on conducting polymers to explore their potential in harnessing low temperature waste heat ($\leq 100^\circ\text{C}$). Conducting polymers (CPs) besides having many advantages such as very low thermal conductivity, tuneable electrical conductivity and nature friendliness, are also capable of being deposited over large and flexible surface-areas due to their flexibility and solution processability. In this work, we demonstrate the incorporation of nanostructures as a strategy to improve the thermoelectric performance of various CPs such polypyrrole (PPy), PEDOT:PSS and P3HT. For instance, introduction of Ag nanoparticles in PPy matrix reduced the thermal conductivity due to phonon scattering in spite of that Ag particles are known for their high thermal conductivity and thus, resulted in the record thermoelectric figure of merit of $\sim 7.4 \times 10^{-3}$ at 62°C . Further, composite of PEDOT:PSS with $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ not only resulted in enhancement of electrical conductivity but also improved Seebeck coefficient through energy filtering of charge carriers at organic inorganic interface. Whereas, doping of P3HT films with FeCl_3 resulted in the remarkable enhancement of Seebeck coefficient. In fact, the work reveals that blending of organic-inorganic components can be a promising approach for tuning the thermoelectric properties of conducting polymer based films/materials.

Investigating the thermoelectric properties of PANI/G nanocomposite coated carbon fabric for wearable TEGs

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A fabric based thermoelectric generators (TEGs) with great stability and flexibility would overcome the problems of existing all other self-powered TEGs by accumulating low-grade body heat to produce electricity. However, to fabricate a wearable fabric based TEGs, fabrics with thermoelectric properties are very essential for further formation of thermoelectric legs. With these, further to increase the thermoelectric properties of fabrics at room temperature, different PANI/G (graphene) nanocomposite (0.02, 0.04 and 0.06 wt%) was coated on conducting carbon fabric by drop casting method. Polyaniline (PANI) was synthesised by in-situ polymerization and graphene was taken as commercial product. The structural analysis confirmed the growth of PANI/G nanocomposite on carbon fabric. The thermoelectric properties of the bare carbon fabric and different PANI/G nanocomposite coated on carbon fabric have been investigated in the temperature ranging from 303 to 373 K. The electrical conductivity, Seebeck coefficient and power factor of 0.04 wt% of PANI/G was around 2.03 S/m, 18.3 mV/K and 0.68 nW/K²m at 273 K, which was comparably higher than bare carbon fabric. In the subsequent coating process, the synthesised PANI/G nanocomposite was successfully coated on commercial carbon fabric.

Thermoelectric properties of PEDOT under nanoconfinement

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Electrical transport of conducting polymer blends such as PEDOT:PSS exhibit significant enhancement when confined in an array of nanochannels. [1] We compare these results with that of PEDOT:Tos, another doped form of PEDOT having higher electrical conductivities. The rearrangement of interconnected microstructures of various forms of PEDOT under confinement opens up the scope to tune the electrical and thermal properties simultaneously. A combined effect of tunable Seebeck coefficient and low thermal conductivity will be useful in tailoring thermoelectric properties of thin-film conducting polymers. Improvements in the thermoelectric performance can also be engineered by nano-patterning. The three-dimensional ordered nanostructure is known to have reduced thermal conductivity. [2] We study the thermoelectric properties of PEDOT with different dopants under confinement at dimensions comparable to that of the polymer microstructures. Results from studies of device structures where thermal gradients are introduced pulsed IR excitation will be presented. Results from studies of device structures where thermal gradients are introduced by pulsed IR excitation will be presented. The thermal voltage response with different nanochannel dimensions is studied for two different dopant derivatives of PEDOT.

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Accelerated discovery of thermoelectrics by unravelling connections between electronic and thermal transport properties

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Development of high performance thermoelectrics requires simultaneously favourable electronic and thermal transport properties. These properties are often addressed independently via conventional approaches and there is lack of convincing connections between these two. In this presentation, power of machine learning will be demonstrated in uncovering the hidden connections between these otherwise independent electronic and thermal transport properties [1]. Analysis of independent machine learning models for thermopower, electrical conductivity, and lattice thermal conductivity reveals the role of bonding attributes in controlling both the electronic and thermal transport and hence establishes the connection. Using electronic transport parameters and bonding characteristics as descriptors, an accurate machine learning model for thermal transport properties is proposed. Among these descriptors, bond distance in conjunction with electronic transport properties seamlessly partitions the dataset into low and high lattice thermal conductivity regimes. Additionally, the use of only elemental and bonding descriptors in developing these models can lead to accelerated screening of efficient thermoelectric materials without the need for expensive first-principles calculations.

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Effect of electron-phonon coupling on transport properties: a thermoelectric perspective

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Performance of thermoelectric devices is measured by the figure of merit (ZT). Over the last several years there has been lot of efforts to design novel materials with large value of ZT . Computational design of materials plays a crucial role in screening them. Usually density functional theory along with semiclassical Boltzmann transport (BT) theory is used to compute transport properties of materials. BT equations are usually solved within the constant relaxation time (RT , τ) approximation. Computing τ itself is challenging since it is not possible to estimate τ ab initio for all possible scattering mechanisms. Amongst the different scattering mechanisms, τ due to electron-phonon (EP) coupling has usually been estimated using the deformation potential (DP) theory. With new computational methods, τ can be computed from first principles. Recent calculations by Bolin et al. [1] show that the values of τ obtained from first principles calculations and those computed within the deformation theory for phosphorene differs significantly. In this work, we studied the effect of the accuracy of the estimations of τ on ionic solids ZrS_2 , PbI_2 and BiI_3 . Our calculations show that τ determined from explicit EP calculations differs by two orders of magnitude compared to those estimated from DP theory. Further, we have also studied the validity of the constant RT approximation and their implications on the computed values of electrical transport properties.

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Implication of local distortion in periodic crystals: use of pair distribution function (PDF) analysis

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Bragg's law is mainly restricted to crystalline solids with distinct ordering as it gives only the long-range average structure. With the advent of complex materials that are often characterized by varying degrees of disorder, the data obtained from normal powder X-ray diffraction can be deceiving. These disorderings bring forth interesting properties like low lattice thermal conductivity (κ_{lat}) which are often pivotal for applications like thermoelectrics; thus, making it essential to delve ourselves into understanding the local structure. One of the most powerful local probes is the atomic Pair Distribution Function (PDF); which provides complete structural information from local coordination to long-range arrangements of the solids. Herein, I will demonstrate how the local distortion in an apparent periodic global structure brings forth ultra-low κ_{lat} in materials like AgPbBiSe_3 , $\text{Sn}_{0.7}\text{Ge}_{0.3}\text{Te}$, and AgSbSe_2 . We will observe the effectiveness of PDF in arresting local distortion and finally its implication in the field of thermoelectrics.

Multiscale modeling of unsteady non-equilibrium Boltzmann transport equation

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The thermoelectric materials could complement the renewable energy extraction from sources like solar energy and can act as an alternative to heat engines harvesting waste heat from electronic devices and boilers. The figure of merit ZT responsible for the thermal efficiency of TE can be increased by decreasing lattice thermal conductivity, which has been

enhanced in nano-structured grains with small mis-orientations. Also, nano-composites like optimally doped Bi_2Te_3 and its solid solution with silica powder can further enhance ZT . These grains and nano-inclusions range from nano to micrometer scale for which first principle calculations and molecular dynamics (MD) based calculations become computationally expensive however solutions to Boltzmann Transport Equation (BTE) promises the problem to be tractable. A multi-scale modeling of BTE will help understand thermal and electrical transport across these defects and composites at several length and time scales. We aim to develop a multi-scale framework where the phonon and electron information coming from MD/DFT simulations will be coupled with finite element methods (FEM) for solving BTE. This will have certain advantages such as constructing a well

defined boundary of complex geometries for studying thermal transport across the grain boundaries or phase and interface boundaries for nano-inclusions. This will be cross verified by the experiments involving nano-composites of $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$.

MBE deposited scandium nitride (ScN) for thermoelectric applications

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Scandium nitride (ScN) is an emerging rocksalt III-nitride semiconductor and has attracted significant interests in recent years for its potential thermoelectric applications, as a substrate for high-quality epitaxial GaN growth and as a semiconducting component for epitaxial single-crystalline metal/semiconductor superlattices for thermionic energy conversion. In this poster, we show high mobility and high thermoelectric power factor in epitaxial ScN thin films deposited on MgO substrates with plasma-assisted molecular beam epitaxy (PAMBE). Structural and microscopic characterization showed epitaxial 002 oriented ScN film growth on MgO (001) substrates and the presence of extended defects including dislocations and grain boundaries. Electrical measurement exhibited high room-temperature mobility of 127 cm²/Vs and temperature-dependent mobility from 50-400 K temperature range that is dominated by dislocation and grain boundary scattering. Due to the high mobility and a moderately large carrier concentration (8.6×10^{19} cm⁻³), ScN films exhibit high Seebeck coefficients (180 μ V/K at 950 K) and a large thermoelectric power factor (2.3×10^{-3} W/m K² at 500K). The thermal conductivity measured with a time-domain thermoreflectance (TDTR) measurement system exhibit a value of 7.33 W/m K at 500 K that results in a maximum ZT of 0.2. Further research on alloy formation as well as nano-structuring is currently underway to reduce the thermal conductivity and improve the ZT .

Multi-probe measurement technique for accurate measurement of seebeck coefficient of thermoelectric materials from 300-700 K.

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An apparatus for sequential measurement of Seebeck Coefficient (S) and Electrical Conductivity (σ) of thermoelectric (TE) samples have been designed and developed. The measurement setup facilitates the accurate characterization of S and σ for n - and p -type of TE samples of various compositions in the temperature range 300-700K. The unique design of the sample holder with pressure probes allows for measurement of Seebeck coefficient from both the top-side and bottom-side of the sample simultaneously, which helps to qualitatively estimate the effect of Cold-Finger Effect in the Seebeck measurement. Electrical conductivity utilizes the DC 4-probe Van der Pauw configuration of probes from the top-side of the sample. The sample holder can accommodate samples in the form of cylindrical pellets of various thicknesses, without the need of sample cutting unlike many of the commercial systems. The measurement setup is housed within a high-temperature furnace under inert atmosphere (Argon/Helium gas). Further, the setup has two additional gradient heaters to create the temperature difference across the TE sample required for the Seebeck measurement. The entire system is automated and programmed in MATLAB to obtain S and σ as a function of temperature. The effect of heating-rate, thermal coupling and isolation of the TE sample were studied in detail, and error analysis was done to determine the accuracy and precision of the S and σ measurements on various standard samples.

Realization of *n*-type stable Cu-based ternary compound and the effect of densification technique on its thermoelectric properties

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The primary challenge in Cu-based thermoelectric (TE) elements is realized as the production of *n*-type material which should be stable even for elevated temperatures. The intrinsic Cu-vacancies cause the holes as majority carriers and the research towards to reduce these vacancies by involving the foreign atoms in the Cu-matrix was enthused. In this context, we successfully substituted Ni-ions on Cu-site in order to form *n*-type Cu-based TE material. The product was prepared by optimizing the reaction parameters in solid-state ball-milling method and identified as ternary non-stoichiometric $\text{Cu}_{1.45}\text{Ni}_{1.45}\text{Te}_2$ compound. Various analytic techniques have been performed to analyse its thermal behavior and chemical states of the material which confirmed that Te states significantly contributed to the DOS at Fermi level. The effect of densification techniques on its TE properties was also studied in which the conduction type was unmodified in SPS technique whereas cold-pressing technique can change its conducting nature from *n*-type to *p*-type at elevated temperatures. SPS sample exhibited 80% increased electrical conductivity and 167% increased *zT* when comparing to cold-pressing sample.

Waste heat driven microporous-carbon thermocells

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Solid state thermoelectrics have been the focus of thermal to electrical energy conversion for many decades. Nevertheless, thermoelectric energy conversion efficiency is limited by the coupling between material properties such as electrical conductivity and the Seebeck coefficient that reduces its efficiency despite much progress in this field. Here, we demonstrate a simple, cost effective platform for harvesting waste heat to electricity via the use of thermo-electrochemical cells (or thermocells) that utilize the temperature gradient of electrochemical redox potentials (i.e., the Seebeck effect). Electrodes composed of different microstructures of carbon black, carbon nanotubes and graphene with a large specific surface area are used in conjunction with aqueous potassium ferri/ferrocyanide solution in a thermally conducting coin-cell configuration. Performance of our thermocells will be presented, and their ability to directly power small electronic devices will be discussed.

Development of thermoelectric power generator using SiGe alloy

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SiGe alloy has been receiving extensive attention as an eco-friendly emerging thermoelectric material for high temperature (up to 800 - 1000 °C) usages and space missions. Usually the Si_{0.8}Ge_{0.2} has a classic band convergence in conduction band. This enhances the effective mass of the carriers and thus increasing the Seebeck coefficient for n-type material resulting in high figure of merit ($ZT \sim 1.8$ at ~ 850 °C). For synthesis of *p*- and *n*-type Si_{0.8}Ge_{0.2}, Boron and Phosphorus are used as dopants and the amount has been optimised. The enhanced ZT of the synthesized Si_{0.8}Ge_{0.2} alloy is attributed to strong suppression of lattice thermal conductivity due to defects produced in mechanical alloying and improved Seebeck coefficient due to band convergence. Pellets of *n*- and *p*-type Si_{0.8}Ge_{0.2} alloy has been synthesized using hot press. A Si_{0.8}Ge_{0.2} thermoelectric power generator has been fabricated using *n*- and *p*-type pellets, zircar housing and Ag plates as electrodes, which exhibits conversion efficiency of $\sim 5\%$ at temperature difference of ~ 600 C.

Nanostructuring of Si-rich $MnSi_y$ composites for mid-temperature thermoelectric applications

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Thermoelectric (TE) technology is an eco-friendly energy conversion process with the advantages of smaller size, high reliability and feasibility in a wide temperature operation range. The heat to electricity conversion efficiency depends on materials' parameter called as figure of merit, $zT = S^2\sigma T/K_{total}$. Though the ηTE is product of Carnot efficiency and zT , the interdependency of the TE parameters makes the zT enhancement efforts more challenging.

Alloys of Bi_2Te_3 , $PbTe$, etc., have reported to exhibit the $zT > 1-2$ owing to high σ , large S and low K_{total} . However, mass production of TE devices using these materials has been limited due to their toxicity and expensive constituent elements. Thus, silicides are proposed to be the promising materials for mid-temperature TE application because of their structural and thermal stability at elevated temperature and highly abundant in nature. Amongst many silicides, higher manganese silicide (HMS) is well-known as it possess high σ and S with relatively high K_{total} which turns out to the moderate zT of ~ 0.7 at 773K. In this context, an attempt has been made to nanostructure the Si-rich HMS using high energy ball milling to embed nanostructured Si in the HMS matrix to reduce K_{total} value via increased phonon scattering to increase the zT . Further, roles of nanostructuring and Si nanoparticles on TE properties of HMS will be discussed in detail.

Novel multi-layer approach for contacting thermoelectric materials: case study for *n*- and *p*-type $\text{Mg}_2\text{Si}_{0.3}\text{Sn}_{0.7}$

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Fabrication of suitable electrode layers is essential for maximizing the conversion efficiency of thermoelectric (TE) power generators. Various approaches are reported in literature which have been successful for specific material systems. In this work, we report a generic approach which can be used to develop low resistance contact layers in TE materials. As examples *n*- and *p*-doped $\text{Mg}_2\text{Si}_{0.3}\text{Sn}_{0.7}$ were chosen for the study. Measurement of the electrical contact resistance (r_c) of the interface indicate values of $2.5 \mu\Omega \text{ cm}^2$ and $19 \mu\Omega \text{ cm}^2$ for the *n*- and *p*-type leg respectively. Further, long term thermal stability of the joints was tested by annealing the samples for 7 days at $400 \text{ }^\circ\text{C}$. Minor changes were observed in the electrical contact resistance indicating a stable interface. In this presentation, the approach for developing the contact layers will be presented along with the electrical and micro-structural characterization of the contacted $\text{Mg}_2\text{Si}_{0.3}\text{Sn}_{0.7}$ specimens.

One-step fabrication of low resistance contacts for $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ thermoelectric materials

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$\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ is a low cost, medium temperature thermoelectric material suitable for power generation in the 500-800 K range. An impressive figure of merit (zT) as high as 1.5 at 773 K is reported in *n*-type doped $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$. To translate such high zT into a module with high efficiency and power output, stable contacts with low resistance need to be developed. The present work describes the development of contact between $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ and Cu electrode in single-step monobloc sintering. The microstructure shows the presence of a continuous layer of $\text{Cu}_3\text{Mg}_2\text{Si}$ at the Cu/ $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$ interface. The specific contact resistance was evaluated to be $4.4 \mu\Omega \text{ cm}^2$ and found to be increasing when isothermally treated at 723 K. The thermoelectric properties of $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$ also degrade severely due to diffusion of Cu contact material with annealing time. However, in the presence of a diffusion barrier layer, the interface is free from any reaction products due to limited Cu diffusion into $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$. The specific contact resistance increases marginally to $6.3 \mu\Omega \text{ cm}^2$ and remains nearly the same even after isothermal annealing for 15 days at 723 K. The thermoelectric properties of $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$ also did not show any signs of degradation both after sintering as well as at the end of isothermal treatment. The study demonstrates by incorporating a suitable diffusion barrier, thermo-chemically stable interfaces can be made by a single step consolidation process for $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ materials.

Dependence of lattice thermal conductivity on doping in electron-poor semiconductors: case study in ZnSb-CdSb solid solution

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Zinc Antimonide (ZnSb) and Cadmium Antimonide (CdSb) are electron-poor (II-V group) semiconductors, familiar for their high thermoelectric (TE) conversion efficiency. The unique feature associated with these compounds is the presence of multi-centre bonds which result in low lattice thermal conductivity (κ_L) and high carrier mobility (μ). An intermediate ZnSb-CdSb solid-solution ($\text{Zn}_{0.625}\text{Cd}_{0.375}\text{Sb}$) was chosen for this study and doped with group IV (Sn, Ge) and group I (Ag) elements to attain a wide range ($0.4 - 2.2 \times 10^{19} \text{ cm}^{-3}$) of charge carrier concentration (n). TE properties have been measured between room temperature and 650 K. It is observed that a linear relationship exists between κ_L and n near room temperature with κ_L almost doubling on increasing n from $4 \times 10^{18} \text{ cm}^{-3}$ to $2 \times 10^{19} \text{ cm}^{-3}$. The material parameter β ($\mu_0 m_D^*{}^{3/2} T^{5/2} / \kappa_L$) also shows a systematic decrease with increasing n . Fourier charge density analysis from the synchrotron powder XRD data and Density Functional Theory (DFT) -based calculations disclose that the multi-centre bonds become more symmetric on increasing n , i.e. on making the system more electron-poor. In turn, this lowers the bond anharmonicity resulting in an increase of κ_L and lowering of the β parameter. This work highlights the importance of chemical bonding while targeting high thermoelectric performance in ZnSb-CdSb solid-solutions in particular and electron-poor semiconductors in general.

Effect of tantalum filling and nanostructuring on thermoelectric properties of CoSb_3 skutterudites

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Thermoelectric (TE) device converts heat into electricity when a temperature gradient is created across the device. The TE materials must have figure of merit $ZT \sim 1.5$ and above at the operation temperature. The $\text{Co}_4\text{Sb}_{12}$ based skutterudites are considered as promising candidates for waste heat recovery between the temperature range 573 K to 773 K due to their stable TE properties, flexibility of fabrication and cost effectiveness. We have investigated the effect of Ta atom filling in $\text{Co}_4\text{Sb}_{12}$ lattice on its structural, electrical, and thermal transport properties. The samples are of single phase and nanocrystalline in nature. The bi-modal distribution of grains is observed in some samples. There is a notable reduction in thermal conductivity and a sound enhancement of power factor with increase in Ta concentration. The highest $ZT \sim 0.39$ is achieved in $\text{Ta}_{0.6}\text{Co}_4\text{Sb}_{12}$ at 773 K, higher among single element filled skutterudites. The TE properties of the Ta filled skutterudites might be useful to replace the rare earth fillers in skutterudites. Detailed investigations of microstructure, electron-phonon and phonon-phonon scatterings on the thermophysical properties of Ta filled $\text{Co}_4\text{Sb}_{12}$ skutterudites will be discussed.

Enhanced thermoelectric performance and positive magnetoresistivity in *p*-type Mg_3Sb_2

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Thermoelectric (TE) materials have been considered as the sustainable and flexible source of electric energy that can be able to meet a wide range of power requirements. Due to the earth-abundant Mg and Sb elements, low thermal conductivity and high Seebeck coefficient, Mg_3Sb_2 -based Zintl compounds are potential TE materials for intermediate temperature range (450 - 650 K) power generation. To improve the TE efficiency in *p*-type Mg_3Sb_2 , Ag-doped Mg_3Sb_2 ($\text{Mg}_{3-x}\text{Ag}_x\text{Sb}_2$, $x = 0, 0.005, 0.008, 0.01$ and 0.012) samples processed by powder metallurgy route. Undoped Mg_3Sb_2 exhibits bipolar effect which reduces the Seebeck coefficient at 150 - 250 K. A remarkable enhancement in TE power factor upon the suppression of bipolar effect due to Ag-doping in Mg_3Sb_2 is established. The temperature dependent behavior of the Seebeck coefficient is explained by charge carriers scattering. The Ag-doped Mg_3Sb_2 shows strong positive magnetoresistivity ($\sim 47\%$) at 150 K. Our work sheds light on the magneto-transport and suppression of bipolar effect to enhance the thermoelectric properties in narrow band gap Ag-doped *p*-type Mg_3Sb_2 , which will be of interest for TE device to function above 300 K. Detailed investigation of the phase stability, thermoelectric and mechanical properties of the *p*-type Mg_3Sb_2 will be presented.

Enhanced thermoelectric properties of $\text{In}_{0.2}\text{Co}_4\text{Sb}_{12}$ by uniform dispersion of GaSb nano-inclusions

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Filling the voids of cage forming compounds by loosely bound electropositive elements and incorporating nano-sized secondary phases are promising approaches to enhance the thermoelectric figure of merit of these materials. Hence, in this work, by combining these two approaches - inserting In into the voids of skutterudite $\text{Co}_4\text{Sb}_{12}$ as well as dispersing nanoparticles (GaSb) - we have synthesized various samples via ball-milling and spark plasma sintering. InSb as secondary phase in the matrix, mixed with GaSb, formed the solid solution $(\text{Ga}_{0.5}\text{In}_{0.5})\text{Sb}$. Nanocrystalline grains of size 30 - 100 nm, together with a few larger grains (10 - 30 μm) are found to be spread in $\text{In}_{0.2}\text{Co}_4\text{Sb}_{12}$. The former are constituted either of InSb, GaSb or $(\text{Ga}_{0.5}\text{In}_{0.5})\text{Sb}$. Because of their same space group and same lattice parameters, InSb, GaSb and $(\text{Ga}_{0.5}\text{In}_{0.5})\text{Sb}$ could not be detected separately in EBSD. Scattering of charge carriers at the interfaces of InSb and GaSb as well as the matrix phases increased both the electrical resistivity and the Seebeck coefficient. The multi-scale size distribution of grains, of both the matrix phase and the secondary phases, scattered phonons within a broad wavelength range, resulting in very low lattice thermal conductivities. As a result, an enhanced figure of merit of 1.4 was achieved for $(\text{GaSb})_{0.1}+\text{In}_{0.2}\text{Co}_4\text{Sb}_{12}$ nanocomposite at 773 K.

Enhancing thermoelectric figure of merit in defect stabilized half-Heusler NbCoSb

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Engineering new materials or phases to enhance the figure of merit (ZT) is one of the key challenges in the area of thermoelectrics. Here, we focus on the half-Heusler alloys as potential high-temperature thermoelectrics. Their high structural symmetry leads to high thermopower. They have high electrical conductivity but high thermal conductivity limits ZT to less than 1. The earlier attention in this family was limited to the valence electron count (VEC) 18 compounds due to their semiconducting nature, which is one of the requirements for having sufficiently high thermopower. However, recently VEC 19 compounds have come to fore, which can be stabilized with some off-stoichiometry to fulfil the valence balanced condition. These are also referred to as defective half Heuslers as they have a vacancy disorder, further reducing thermal conductivity. In this work, we show that mere 1% Sn doping in defect-stabilized NbCoSb enhances the electrical conductivity considerably but with nearly the same total thermal conductivity, which gives 25% increment in ZT . Pisarenko plots for Sn doped samples show deviation from the single parabolic band (SPB) model for low concentration of Sn at Sb site, indicating that small Sn doping may have changed the band structure, pointing Sn as a possible resonant dopant. Our results suggest that half-Heusler VEC 19 compounds, with intrinsically low thermal conductivity, are promising thermoelectric materials where $ZT > 1$ can be achieved.

All-fiber based thermoelectric materials and generators toward wearable application

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With the escalating use of portable electronics, wearable thermoelectric generators (TEG) are highly desired as a potential power supply to harvest electricity from human body heat. Fibers, which are the fundamental building blocks of textiles, are skin-attachable, lightweight and thin, flexible and durable, making "smart fibers" well suitable for wearable application and become a research frontier for wearable thermoelectrics. In this context, the aim of our work is to develop high-performance all-fiber based thermoelectric materials and generators toward wearable application. Here, our recent works of PEDOT:PSS nanofiber based materials¹ prepared by electrospinning technology and three-dimensional carbon nanotube fiber based TEG² built via weaving technology are presented and analyzed in detail. A peak power density of the all-fiber based TEG can reach $35\mu\text{Wm}^{-2}\text{K}^{-2}$, and excellent stretchability ($\sim 80\%$ strain) with no output degradation can be achieved. Besides, the compatibility between body movement and sustained power supply is further displayed, demonstrating the wearable application prospect.

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Tuning Thermoelectric Performance of Poly(3,4-ethylenedioxythiophene): Poly (styrene sulfonate)/Polyaniline Composite Films by Nanostructure Evolution of Polyaniline

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The relation of molecular structures, morphologies, and thermoelectric (TE) properties of the poly(3,4-ethylenedioxythiophene): poly (styrene sulfonate)/polyaniline (PEDOT: PSS/PANi) composite films have been carefully investigated. Various nanostructured PANi were synthesized firstly. Then PEDOT: PSS were employed to prepare PEDOT: PSS/PANi composite films. The morphological and structural characterization reveal that PANi nanoflakes with planar molecule structure possess the most ordered chain stacking, resulting good crystallinity and the highest TE properties in PEDOT: PSS/PANi-nanoflakes composite films. The power factor of PEDOT: PSS/PANi composite films increases as follows, PEDOT: PSS/PANi-hollow spheres < PEDOT: PSS/PANi-nanotubes < PEDOT: PSS/PANi-nanoparticles < PEDOT: PSS/PANi-nanowires < PEDOT: PSS/PANi-comb-like sheets < PEDOT: PSS/PANi-nanoflakes. It was found that in PEDOT: PSS/PANi, the π -bonded surface of PEDOT induce PANi to arrange regularly along the PEDOT sheets, and enriched PEDOT-PANi region enhance the electrical conductivity of PEDOT: PSS/PANi films.

High-performance thermoelectric films and their efficient cooling technology

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High-efficiency heat dissipation of next-generation mobile terminals puts a great demand on high-performance thermoelectric films. However, how to greatly improve the thermoelectric conversion performance of low-cost thermoelectric films is a challenging problem faced by its efficient cooling applications. This study develops a new technology for the preparation of high-performance Bi_2Te_3 based thermoelectric films by hot-pressing curing process to realize the in-situ preferential orientation of crystals. Partially preferentially oriented $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ /epoxy flexible thermoelectric films with (0001) preferential orientation and power factor increased by 378% and 250%, respectively, had been successfully prepared. A flexible thermoelectric film cascade cooling device with average cooling temperature of 1.56 K had been designed and fabricated. Our work demonstrates that the preferential orientation produced by hot-pressing curing process can significantly improve the electrical transport properties of Bi_2Te_3 based flexible films and the as-developed high-performance Bi_2Te_3 based flexible film is expected to provide thermoelectric cooling core materials for efficient heat dissipation of mobile communication terminals.

Understanding interface role in flexible nanocomposites for high thermoelectric performance

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The interface is always a critical factor affecting thermoelectric performance in composite systems. However, understanding the electrical and thermal transport behaviors at the interfaces has been a long-standing challenge. Here, we advance this understanding by using spatially resolved current and thermal measurements in single wall carbon nanotubes (CNTs)-Tellurium-poly(3,4-ethylenedioxythiophene): poly(4-styrenesulfonate) (PEDOT:PSS) nanocomposites. Our results indicate that the obtained ultra-low thermal conductivity in such nanocomposites with high CNTs content can be understood by the interface thermal resistance and interface density, which is directly confirmed by quantitative mappings of thermal conductivity in the micro-scale interface regions via scanning thermal microscopy. Furthermore, the highly conductive layers can be formed at the interfaces of Te - PEDOT:PSS and CNTs - PEDOT:PSS revealed by high-resolution local conductivity and topography mapping, leading to simultaneous enhancement of electrical conductivity and Seebeck coefficient. Ultimately, a power factor of $224 \mu\text{W}/\text{mK}^2$, as well as an ultralow in-plane thermal conductivity of $0.39 \text{ W}/\text{mK}$ at 410 K, has been achieved by tuning carrier mobility and phonon scattering using multiple polymer-inorganic interfaces. The ZT value reaches up to 0.24 at 410 K and a planar flexible thermoelectric generator exhibits the maximum output power of $1.33 \mu\text{W}$ at a temperature difference of 67.8 K. These approaches give deep insights to understand the interface role in nanocomposites, and also provide a promising method for developing high-performance thermoelectrics and other functional materials that can benefit from interface effect.

Novel high-power multilayer composite structured thermoelectric module

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Output power is an important criterion to evaluate the heat-electricity conversion capability of thermoelectric power generators (TEGs). In this work, a novel $(\text{Bi,Sb})_2\text{Te}_3$ -based multilayer composite structured thermoelectric module (MCTEM) with high power output is firstly proposed. For an n-type single-leg MCTEM composed of several alternately stacked thermoelectric slices and inner electrodes, parallel heat transfer and electrical parallel connection are simultaneously achieved. The extremely low inner resistance (R_{in}) and high current (I) are 0.03 and 12.7 times of those measured in a single-leg traditional module, respectively, then a maximum output power (P_{max}) of 5.8 mW is achieved at $\Delta T=35^\circ\text{C}$. The optimal P_{max} for n- and p-type single-leg MCTEMs have been obtained at slice number of 3. Based on the optimized single-leg MCTEMs mentioned above, a π -type MCTEM is designed and achieves a high V of 3.1 mV while keeping a low R_{in} of 0.94 m Ω and a large I of 3.3 A. Then a P_{max} of 10.5 mW is obtained, which is 4.2 times of traditional module at $\Delta T=35^\circ\text{C}$. This novel design of MCTEM provides new thoughts for the fabrication and commercialization through the development of high-power TEGs.

Thermoelectric properties of low dimensional telluride materials

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Because of the correlation between the Seebeck coefficient, electrical conductivity and thermal conductivity, there is an obstacle for researchers to optimize the thermoelectric figure of merit zT in bulk system. It was suggested that if the TE material have a length scale lowered down to nanometer length scale, the electronic Density of States will be changed, such that there is possibility on tuning the TE properties independently. In our work two systems are fabricated, the first one is the SnSe/SnTe multilayered structure, while the second one is ZrTe₂ thin film on STO. In the multilayered structure, a clear boundary is formed between the SnSe and SnTe layers, suggesting the limited interfacial diffusion. In the TE measurement, the multilayered structure shows a similar p-type Seebeck coefficient trend as SnTe film, but with an 1.75 times enhancement at high temperature, with a little decrease of electrical conductivity, the structure shows a 1.5 times higher power factor. In the ZrTe₂/STO system, a very large n-type Seebeck coefficient and extremely high electrical conductivity is observed, resulting in an enormous power factor ($3.3 \times 10^5 \mu W cm^{-1} K^{-2}$) at 10 K, the high carrier mobility, quasi-two-dimensional transport and phonon drag effect is believed to be the origin of such great power factor. These two works provides the feasibility on enhancing the thin film TE performances by utilizing the two-dimensional electronic transport.

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Self-powered Wearable Pressure Sensing System for Continuous Healthcare Monitoring Enabled by Flexible Thin-Film Thermoelectric Generator

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Flexible and portable pressure sensors with highly sensitive and cost-effective attributes are of great demand in wearable electronics, biomedical monitoring, and artificial intelligence. To realize portable pressure sensors with mobile operation, ultrathin, flexible, and sustainable power sources are highly desired. Here, a self-powered wearable pressure sensing system is developed by integrating a conductive elastomer-based pressure sensor with a flexible thin-film thermoelectric generator (tf-TEG) to harvest body heat. Laser engraving technique is adopted to achieve pressure sensor with tunable sensitivity through the controllable design of surface microstructures. To produce a reliable and renewable power supply for the pressure sensor, the flexible tf-TEG is constructed with high thermal-conductivity insulation films for heat absorbing and flexible hydrogels as heat sink, resulting in a large temperature gradient for high power generation. In particular, the pressure sensitivity of the self-powered system is independent of the temperature gradient across the tf-TEG, allowing it to maintain a stable performance under various temperature differences between human skin and surroundings. For the first time, the self-powered pressure sensing system proposed in this work enables continuous monitoring of human physiological signals and body motions entirely powered by the skin-attachable tf-TEG without an electronic boost circuitry.

Cross-plane thin-film thermoelectric generator with high power density assisted by advanced pulse laser ablation patterning technique

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The cross-plane thin-film thermoelectric (TE) device has drawn great attention due to its potential in microelectronic and wearable self-power system. However, the performance of thin-film TE generator has long been restricted by the incompatibility of the high-density integration and the high property TE material deposition process. Herein, to achieve a high-density TE arrays, rapid pulse laser ablation is introduced to pattern the TE pillars. In addition, to investigate the process window of pulse laser ablation patterning, a detailed analysis of threshold fluences from the pulse laser- materials interaction has been conducted. With the high patterning precision realized by pulse laser ablation, a thin-film TE generator with 200 pillars cm^{-2} is fabricated, which shows an output of 1 mW cm^{-2} when the temperature difference is 88 K. Furthermore, to explore the temperature drop raised by additional thermal resistance, a detailed investigation has been carried out.

Revealing the origin of thermoelectric sensing: From reverse temperature gradient to eigen-resolution

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Thermoelectric (TE) sensors/detectors meet diverse emerging demands including healthcare monitoring, infrared navigation, and industrial inspection, which have been attracting immense attention in recent years. The performance evaluation for conventional photothermal thermoelectric (PTE) sensors with typical thermopile and vertical forest architectures mainly focuses on responsivity, noise equivalent power (NEP), and detectivity. Nonetheless, for PTE-based sensors with dense detectors and various structures, the traditional criteria cannot fulfill the precise spatial resolution characterization as the structure-dependent neighboring heating leads to inevitable heat transfer and temperature-induced noise fluctuation along with the thermoelectric unit. In this work, aided by finite element analysis (FEA) and principal component analysis (PCA), the reverse temperature gradient and zero potential are observed in fiber-based plain weaving sensor and alloy-based serial detector. Importantly, a new descriptor named eigen-resolution is derived from a view of materials Seebeck coefficient and structure-dependent thermopower translation for evaluation of spatial resolution. Compared with conventional responsibility for PTE-based sensing analysis, the eigen-resolution indicates a liner variation in a wide temperature range. Ultimately, the preliminary guideline and strategy for high-eigen-resolution PTE-based sensors are delivered in view of materials genetic engineering. This work paves a new insight into the origin of thermoelectric sensing and facilitates the co-design of diverse sensors/detectors with high responsivity and eigen-resolution.

The reliability experiment study of mini thermoelectric cooler under extreme working condition

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Thermoelectric cooler (TEC) is a promising solid-state active heat pump, it has been widely used for cooling and heating in the military, aerospace, commercial devices, and industry fields for its compact size and environmentally friendly. With the development of highly integrated and miniaturized micro-electronic devices, increasing interest is focused on the micro-TEC for its ultra-small size and capability to handle higher heat flux. However, the reliability of TEC naturally gets the concern for the practical application. In this work, we built a test rig to conduct the temperature cycling, power cycling and high temperature storage experiments. To assess the reliability of TEC, the electrical resistance is selected as the evaluation index in analogy with semiconductor device. Due to the influence of Seebeck effect, ohmic voltage cannot be directly measured through the voltmeter. The DC transient method can be used to obtain the total voltage U_t and Seebeck voltage U_s in the circuit, and their difference ($U_t - U_s$) is ohmic voltage U_R . The current I in the circuit is known, and then according to Ohm's law, the internal resistance can be directly calculated. Then, the performance degradation characteristics of TEC are investigated through the experiment method. The results show that the deviation of electrical resistance of TEC is smaller than 5% when TEC stored at high temperature of 150°C for 1000h or experienced 100 temperature cycles from -50°C to 150°C. But the deviation of electrical resistance of TEC is the largest when TEC experienced power cycling, and the deviation changes with the given cooling load, input electrical current and hot-side temperature. It finds that the TEC is damaged when TEC experienced 20 power cycles with $T_h=150^\circ\text{C}$, $Q_c=0\text{W}$ and $I=1\text{A}$. The crack-formation near the solder/ceramic interface is mainly due to the severe thermal stresses for overwhelming temperature gradient.

Dynamic research of on-Chip hot spot removal with micro-thermoelectric cooler

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Micro-thermoelectric cooler has been widely used to cool the electronic devices with high heat flux. However the combination of micro-contact structure and micro-thermoelectric cooler under dynamic working load of chip still needs to be further explored. This paper aims to establish a model of dynamic working load of chip integrated with micro-thermoelectric cooler and explore the performance of this system under various micro-contacts, heat fluxes of hot spot, interfacial effects and insulation materials. The simulation results of micro-thermoelectric model consisting with 3×3 pairs of thermoelectric elements matches well with the experiment's. The cooling performance of micro-thermoelectric cooler with or without contact resistance and solder materials are discussed under dynamic heating load. The influence of different insulation materials is also discussed. The results indicate that the contact resistance, solder materials and insulation materials are crucial in building an accurate simulation model. The maximum temperatures of hot spot without contact resistance, without solder materials and with different insulation materials are 87.38°C, 98.98°C, and 117.9°C respectively. However, the maximum temperature of accurate model is 104.15°C. Furthermore, the influence of micro-thermoelectric cooler and mini-contacts are also discussed under dynamic heating load. The results indicate that the maximum temperature of hot spot and background without micro-thermoelectric cooler are 109.61°C and 104.57°C, with micro-thermoelectric cooler are 114.59°C and 108.96°C, with micro-thermoelectric cooler and mini-contact are 102.48°C and 99.89°C, respectively. The simulation indicates that the combination of mini-contact and TEC will not only reduce the hot spot temperature but also the background temperature. This dynamic research will provide a real-time simulation under different working load of chip.

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Thermal-Electrical Transport Characteristics and Structure Optimization of Thermoelectric Coolers

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With the development of technology, the requirements for temperature control are becoming higher. People hope to find an efficient, clean, fast, and accurate method. Thermoelectric cooling technology has been widely studied and applied by its advantages of small size, no moving parts, fast response, small pollution, wide application range and so on, but it is also limited by its shortcomings such as low efficiency and limited cooling capacity. Based on this, in order to improve the performance of the thermoelectric cooler, an L-shaped thermoelectric arm structure is proposed. A multiphysics model is established to analyse the influence of the structural parameters on the performance, and the steady-state performance, starting characteristics and start-up characteristics of the L-shaped thermoelectric cooler are also studied. The research shows that the L-shaped thermoelectric cooler can change the heat transport and electric transport path in the thermoelectric leg to be L-shaped, significantly reducing the flow length, so that the L-shaped thermoelectric cooler can obtain the performance close to the thin film thermoelectric cooler. Under the premise of processing using traditional technology, the maximum cooling flux of L-shaped thermoelectric cooler can be increased by 76.30% compared with the optimal design of Π -shaped thermoelectric cooler. In comparison with the performance of the same size Π -type thermoelectric cooler, the maximum cooling flux and COP of the L-shaped thermoelectric cooler are significantly improved, and better performance can be obtained under different input currents, cold end load, and hot end heat exchange conditions. At the same time its startup time can be reduced by 58.78%. The supercooling performance of the L-shaped thermoelectric cooler has a significant advantage, which is manifested in the larger supercooling temperature drop, the smaller the superheating temperature rise, and the faster speed to reach the coldest minimum temperature. This study provides a new idea for the structural optimization design of thermoelectric coolers.

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Enhancing the thermoelectric performance of $\text{Cu}_{1.9}\text{S}$ by transition elements doping

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Recently, Cu-S based thermoelectric (TE) material has drawn boosting attention due to its ultralow lattice thermal conductivity, abundant elements and low toxicity. However, due to high sensitivity between phase composition and Cu/S ratio, the majority of binary Cu-S based TE materials research is concentrated on the pure-phase $\text{Cu}_{1.8}\text{S}$ and Cu_2S , while the mixed-phase Cu_xS materials, such as $\text{Cu}_{1.9}\text{S}$, have rarely been studied. Thus, we studied the phase composition, microstructure, carrier transport properties and TE properties of $\text{Cu}_{1.9}\text{S}$ in detail and enhanced its TE properties via different transition elements doping including Ag, Ni and Co. Furthermore, considering the number of effective and high quality microstructure characterization in Cu-S based TE material is not enough, we also use amounts of clear and effective HRTEM images to directly display the line defects, stack fault and amounts of nanopores in $\text{Cu}_{1.9-x}\text{M}_x\text{S}$ ($M=\text{Ag, Ni and Co}$) samples, and explain the reason of lattice thermal conduction reduction. In addition, the relationship between the valence state of doping element and TE properties of $\text{Cu}_{1.9-x}\text{M}_x\text{S}$ is also investigated. From the valence state, microstructure analysis and TE properties measurement of $\text{Cu}_{1.9-x}\text{M}_x\text{S}$, it indicates that Ag, Ni and Co doping can gradually optimize thermoelectric performance and all effectively reduce thermal conductivity of $\text{Cu}_{1.9}\text{S}$. By comparing their TE properties, Co-doped $\text{Cu}_{1.9}\text{S}$ samples have most excellent TE properties. Among the $\text{Cu}_{1.9-x}\text{Co}_x\text{S}$ samples, a low κ of 0.88 W/mK was obtained for $\text{Cu}_{1.86}\text{Co}_{0.04}\text{S}$, which is less 54.7% than that of the $\text{Cu}_{1.9}\text{S}$ at 773K, leading to the highest $ZT \sim 1.0$ at 773K and highest $ZT_{\text{ave}} \sim 0.48$ from 323K to 773K. This work proves that element doping with higher valence state is an effective method to enhance thermoelectric properties of mixed-phase Cu_xS materials.

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Defect engineering for realizing p-type AgBiSe₂ with promising thermoelectric performance

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Realization of ambipolar doping (n- and p-type) in thermoelectric materials is highly critical for module design. However, many thermoelectric materials can only be doped into one type, due to the Fermi-level pinning by intrinsic defects, or have poor performance for one doping type. AgBiSe₂ is a typical case that shows persistent n-type doping while p-type AgBiSe₂ has been predicted to exhibit higher thermoelectric performance but has not been reliably obtained nor has the performance been demonstrated. Here, we demonstrate the successful experimental synthesis of p-type AgBiSe₂ by suppressing Se vacancies *via* adding an excess amount of Se. In addition, we show that Pb doping at the Bi site can effectively increase the hole concentration and optimize the power factor of p-type AgBiSe₂. This leads to promising thermoelectric performance close to room temperature. Our work demonstrates the importance of defect engineering for overcoming the doping bottleneck, thus promoting the discovery of new thermoelectric materials.

Modulation of thermoelectric performance for superionic conductor AgCrSe_2

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The superionic conductor AgCrSe_2 is considered as a promising thermoelectric material due to its intrinsic ultralow lattice thermal conductivity. What is the physical essential of its ultralow lattice thermal conductivity has attracted great attention. However, its inferior electric performance creates a bottleneck for improving its thermoelectric performance. This motivates us to enhance electric performance without appreciable rise in lattice thermal conductivity. Two strategies for dealing with inferior electric property are developed in our work. For one thing, carrier concentration is optimized through the modulation of defects. For another, higher power factor is achieved by manipulating band effective mass. The single parabolic band (SPB) model gives a good clarification regarding the increased electronic performance. Moreover, Ag vacancy is found to be critical for maintaining ultralow thermal conductivity ($\sim 0.25 \text{ W m}^{-1} \text{ K}^{-1}$). Eventually, a maximum figure of merit zT of ~ 0.7 is realized for AgCrSe_2 compound at 750 K. The present findings may shed light on the improvement of thermoelectric performance in AgCrSe_2 materials.

High Thermoelectric Performance in Sulfide-Type Argyrodites Compound $\text{Ag}_8\text{Sn}(\text{S}_{1-x}\text{Se}_x)_6$ Enabled by Ultralow Lattice Thermal Conductivity and Extended Cubic Phase Regime

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Argyrodites with a general chemical formula A_8BC_6 are known for complex phase transitions, ultralow lattice thermal conductivity, and mixed electronic and ionic conduction. The coexistence of ionic conduction and promising thermoelectric performance have recently been reported in selenide and telluride Argyrodites, but scarce in sulfide Argyrodites. Here the thermoelectric properties of $\text{Ag}_8\text{Sn}(\text{S}_{1-x}\text{Se}_x)_6$ are reported. Specifically, Ag_8SnS_6 exhibits intrinsically ultralow lattice thermal conductivities of $0.61\text{--}0.31\text{ W m}^{-1}\text{ K}^{-1}$ over the whole temperature range from 32 to 773 K due to distorted local crystal structure, relatively weak chemical bonding, rattler-like Ag atoms, low-lying optical modes, and dynamic disorder of Ag ions at high temperatures. Se doping shifts the orthorhombic-cubic phase transition from 457 K at $x = 0$ to 430 K at $x = 0.10$, thereby expanding the temperature range of the thermoelectrically favored cubic phase. A figure of merit zT value ≈ 0.80 is achieved at 773 K in $\text{Ag}_8\text{Sn}(\text{S}_{1-x}\text{Se}_x)_6$ ($x = 0.03$), the highest zT value reported in sulfide Argyrodites. These results fill a knowledge gap of the thermoelectric study of Argyrodites and contribute to a comprehensive understanding of the chemical bonding, lattice dynamics, and thermal transport of Argyrodites.

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Enhanced thermoelectric properties of p-type Argyrodites Cu_8GeS_6 through Cu vacancy

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Cu_8GeS_6 compound with room temperatures orthorhombic phase, high-temperature cubic phase and the low intrinsic lattice thermal conductivity is a potential thermoelectric material. However, its performance is limited by low electrical conductivity. In this study, p-type polycrystalline $\text{Cu}_{8(1-x)}\text{GeS}_6$ ($x = 0.03, 0.05, 0.08, 0.10$) are successfully synthesized through solid-phase reaction and hot pressing. The electrical conductivity of the wide band gap semiconductor Cu_8GeS_6 as verified by the density functional theory (DFT) calculation can be greatly enhanced by intentionally introduced Cu vacancy. Also, the calculation indicates that the top of valence band is mainly comprised of the Cu 3d orbitals. As a consequence, the Hall carrier concentrations are significantly enhanced to $\sim 10^{18} \text{ cm}^{-3}$ with Cu vacancy. Owing to the improved electrical conductivity, the compound with nominal composition of $\text{Cu}_{7.36}\text{GeS}_6$ reaches a maximum $zT \sim 0.29$ at 819 K.

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Microstructure and thermoelectric properties of $[00]_c$ grain-aligned $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramics

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$\text{Ca}_3\text{Co}_4\text{O}_9$ -based ceramics along $[00]_c$ crystallographic orientation were prepared using template grain growth method with different sintering temperature and soaking time. The mechanism of epitaxial growth was observed through the SEM and EDX analysis. The effect of texturing evolution on the microstructure and thermoelectric properties were investigated. Optimized sintering parameters led to the great changes in the degree of texturing. A high degree of texturing of 92.5% was obtained for the sample sintered at 1273 K for 20 h, giving rise to large thermoelectric properties of electrical resistivity ($\rho = 10.7 \text{ m}\Omega\cdot\text{cm}$), Seebeck coefficient ($S = 202.1 \text{ }\mu\text{V}/\text{K}$), and power factor ($PF = 0.38 \text{ mW}/(\text{m}\cdot\text{K}^2)$) at 1073 K. The controlled crystallographic and morphologic orientation opens the possibility of achieving the high thermoelectric properties.

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Enhanced thermoelectric properties of La and Sr dual doped CaMnO₃ ceramics

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Perovskite-type $\text{Ca}_{1-x-y}\text{La}_x\text{Sr}_y\text{MnO}_3$ ($x=0, 0.02, 0.03, 0.04, 0.05$, $y=0.02, 0.03, 0.04, 0.05$) are synthesized by co-precipitation method and conventional sintering. Based on $\text{Ca}_{1-x}\text{La}_x\text{MnO}_3$ with optimized carrier concentrations, enhanced thermoelectric performance has been achieved by co-doping with Sr. Through detailed structural investigation and theoretical analysis, we find that the enhanced thermoelectric properties of CaMnO_3 ceramics are mainly benefited from the optimized carrier concentration, electronic structure near Fermi surface, and enhanced phonon scattering by dual doping of La and Sr. This study provides a potential strategy to further optimize the thermoelectric performance of CaMnO_3 .

Candidate for Magnetic Doping Agent and High-Temperature Thermoelectric Performance Enhancer: Hard Magnetic M-type BaFe₁₂O₁₉ Nanometer Suspension

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How to prevent the agglomeration of nanoparticles in nanocomposites remains a key challenge. Using nanometer suspension as a doping agent provides an effective approach to solve this challenge. A new technique that consists of chemical coprecipitation, ball milling and sedimentation separation methods was developed for preparing hard magnetic M-type BaFe₁₂O₁₉ nanometer suspension. The single-phase BaFe₁₂O₁₉ nanoparticles dispersed uniformly in alcohol have been prepared by this new technique. Magnetic nanocomposite thermoelectric materials with a homogeneous dispersion of BaFe₁₂O₁₉ nanoparticles were prepared through a combination process of an ultrasonic mixing of BaFe₁₂O₁₉ nanometer suspension and In-filled CoSb₃ thermoelectric matrix material and spark plasma sintering. The microstructure analysis of magnetic nanocomposite thermoelectric materials confirmed that using the nanometer suspension as a doping agent is an effective way to solve the agglomeration phenomenon of nanoparticles in nanocomposites. In addition, the decline of thermoelectric performance in the high-temperature intrinsic excitation region of In-filled CoSb₃ can be effectively suppressed by the magnetic phase transition of BaFe₁₂O₁₉ nanoparticles dried by nanometer suspension from ferromagnetism to paramagnetism. It is also confirmed that using the BaFe₁₂O₁₉ nanometer suspension as a thermoelectric performance enhancer is an effective way to solve the challenging problem of performance deterioration of thermoelectric materials at high temperature

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Research progress on Seebeck effect of cement-based composites

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By incorporating a second phase (carbon material, metal material, metal oxide) into the cement matrix, the cement-based composite material has the Seebeck effect and has been extensively studied. The cement-based composite material has the Seebeck effect and can be applied to fields such as outdoor heat conversion and collection, building material structural health monitoring sensors, and road deicing. The influence of adding different admixtures on the Seebeck effect of cement-based composites, the strengthening method of its Seebeck effect and its application prospect are analyzed, and it is of great significance to further improve the thermoelectric properties of cement-based composites.

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Dramatically Improved Thermoelectric Properties by Defect Engineering in Cement-Based Composites

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Expanded graphite/cement-based composites (EGCC) have received much attention for their ability to convert heat from solar radiation directly into electricity for large-scale energy harvesting. In this paper, the highest power factor in cement-based composites at present was reported for the first time. Zinc oxide powder was treated by reducing atmosphere to increase the content of oxygen defects and thus improve the electrical conductivity. Pretreated ZnO powder of 5wt% was added to EGCC and exhibited excellent thermoelectric properties. The results show high conductivity (12.78 S/cm), Seebeck coefficient (-419 $\mu\text{V}/^\circ\text{C}$) and the power factor (224 $\mu\text{Wm}^{-1}\text{K}^{-2}$), which facilitates future large-scale applications. This study will therefore shed light on future proposals of cement-based composites showing good thermoelectric.

Discussion on Phonon Scattering and Confinement, and Thermal Conductivity Optimization

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The theoretical fundamental of thermal conductivity and phonon transport is of utmost importance for thermoelectrics. Finite-temperature leads to anharmonicity, which significantly affects predictions of thermal conductivity and phonon properties. We apply a temperature-dependent effective potential method with first principle calculations to extract finite-temperature force constants for rutile TiO_2 . Compared to the large underprediction using 0 K force constants, the finite-temperature force constants predict thermal conductivity of rutile accurately. The thermal conductivity underprediction is attributed to the underprediction of phonon lifetimes through phonon mode level analysis. Beyond the study of bulk materials, we propose an effective strategy to reduce thermal conductivity by introducing a new concept of local angle, which is defined as the angle between directions of the total heat flux and its component along temperature gradient, and a larger local angle always corresponds to a smaller thermal conductivity. A significantly enhanced reduction of thermal conductivity is achieved in silicon nanoporous films and nanocomposites based on the local angle analysis. Considering that optimization of carrier concentration plays an important role in thermoelectrics, we also investigate electron-phonon scattering effect on thermal conductivity of nanostructures. The thermal conductivity reduction due to the electron-phonon scattering decreases as the feature size goes down and could be ignored at low feature sizes. As the feature size decreases to the magnitude of phonon wavelength, we study phonon transport in films with thicknesses of less than 10 nm using two-dimensional lattice dynamics calculations and the Boltzmann transport equation. We rigorously identify signatures of confinement and determine the transition point from phonon-boundary scattering regime to confinement regime in ultrathin films. This work was supported by the National Natural Science Foundation of China under Grant No. 51825604 and 51721004, and the 111 Project under Grant No. B16038.

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Routes for suppression of thermal conductivity in Yb-filled skutterudites to improve thermoelectric performance

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Filled skutterudites are one group of the most promising thermoelectric materials in the real power generation application. However, in classic skutterudite system, $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12}$, high thermal conductivity is difficult to achieve a breakthrough at figure of merit ZT . Such a high thermal conductivity mainly derives from high electronic thermal conductivity accompanied by high filling fraction and lattice thermal conductivity above the amorphous limit. Herein, Sn acceptor doping and constructing CoSi nanoparticles routes are adopted to attempt to weaken the contribution of carriers and phonons to thermal conductivity, respectively. As the Sn doping, the ratio of κ_e/κ gradually decreases, resulting in the higher ZT and ZT_{ave} , which reveals that the critical role of electronic thermal conductivity on the enhanced thermoelectric performance. Meanwhile, the significant amount of interfaces and lattice misfits generated by the *in situ* precipitated multi-scale CoSi nanoparticles cause a remarkable suppression on the lattice thermal conductivity, approaching the theoretical limit. In addition, the interfaces between the matrix and CoSi nanoprecipitates can screen somewhat low-energy electrons, leading to enhanced Seebeck coefficient and power factor. As the combination of the synergistic optimized electrical and thermal properties, an enhanced peak ZT value of ~ 1.5 at 873 K for the $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12}/0.05\text{CoSi}$ composite is achieved. This work proposes two effective routes to reduce thermal conductivity for Yb filled skutterudites.

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Synthesis and properties of $\text{Ni}_{0.3}\text{Co}_{3.7}\text{Sb}_{12}$ skutterudite filled with electronegative element Se

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The electronegative element can be introduced into the voids of skutterudite by doping electron donors in the framework of skutterudite. This method has been considered as a promising method to improve thermoelectric properties. In this study, $\text{Se}_y\text{Ni}_{0.3}\text{Co}_{3.7}\text{Sb}_{12}$ ($x=0, 0.025, 0.1, 0.125, 0.15, 0.2$) compounds were prepared by the traditional metal melting method and spark plasma sintering technology. Phase, microstructure, thermoelectric properties and thermal transport properties were studied. The results show that the charge compensation between Ni doping and Se filling is the basic reason for the formation of thermodynamically stable $\text{Se}_y\text{Ni}_{0.3}\text{Co}_{3.7}\text{Sb}_{12}$ compound. The electronegative element Se as a filling atom can effectively reduce the lattice thermal conductivity. At the same time, the filling of Se increases the number of holes, resulting in a decrease in carrier concentration. Finally, the zT of the $\text{Se}_{0.15}\text{Ni}_{0.3}\text{Co}_{3.7}\text{Sb}_{12}$ sample can reach a maximum of 0.81 at 825K.

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Effects of sintering temperature on microstructure and thermoelectric properties of Ce-filled $\text{Fe}_4\text{Sb}_{12}$ skutterudites

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The improvement of thermoelectric properties of *p*-type iron-based skutterudites is limited due to the present of more ironrich impurity phases induced by the inherent structural instability of Fe-containing skutterudites. How to reduce the content of the impurity phase in *p*-type Fe-based skutterudites is a key to obtain high *ZT* value. $\text{Ce}_{1.25}\text{Fe}_4\text{Sb}_{12}$ materials with different sintering temperatures (723 K, 773 K, 798 K, 823 K and 848 K) have been prepared by a traditional melting-quenching-annealing process coupled with spark plasma sintering (SPS) technique. The results of XRD and EPMA analysis indicate that all the SPSed samples consist of the main skutterudite phase and impurity phases of FeSb_2 , Sb, CeSb_2 and oxides of Ce and Sb. Compared with other SPSed samples, the SPS-773 K sample has the best thermoelectric properties due to the relatively fewer impurity phases, a large number of micro-nanoscale particles at the grain boundary and more voids. The SPS-773 K sample shows the largest *ZT* value over the entire test temperature range due to the higher power factor and lower lattice thermal conductivity. The maximum *ZT* value reaches 0.81 at 800 K. This indicates that thermoelectric properties of Ce-filled $\text{Fe}_4\text{Sb}_{12}$ skutterudite materials can be effectively improved by reducing impurity phases induced by the optimization of the sintering temperature.

Synergistic tuning of carrier mobility, effective mass and point defects scattering triggered high thermoelectric performance in *n*-type Ge-doped PbTe

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Most achievements on remarkable thermoelectric performance have been made in the intermediate-temperature *p*-type PbTe. However, the *n*-type PbTe exhibits a relatively poor figure of merit ZT , which is urgently expected to be enhanced and compatible with *p*-type counterpart. Here, we report that the introduction of excessive Pb can effectively eliminate cation vacancies in *n*-type $\text{Pb}_{1+x}\text{Te}-0.4\%I$, leading to a considerable improvement of carrier mobility μ . Moreover, further Ge doping induces a large enhancement of thermoelectric properties due to the combined effect of improved electrical transport properties and increased phonon scattering in *n*-type $\text{Pb}_{1.01}\text{Te}-0.4\%I-y\%Ge$. The Ge doping not only contributes to the increase of Seebeck coefficient owing to the increased effective mass m^* , but also gives rise to the dramatic decrease of lattice thermal conductivity due to the strengthened point defects scattering. As a result, a tremendous enhancement of ZT value at 723 K reaches ~ 1.31 for *n*-type $\text{Pb}_{1.01}\text{Te}-0.4\%I-3\%Ge$. Particularly, the average ZT_{ave} value of ~ 0.87 and calculated conversion efficiency $\eta \sim 13.5\%$ is achieved by Ge doping in a wide temperature range from 323 to 823 K. The present findings demonstrate the great potential in *n*-type $\text{Pb}_{1.01}\text{Te}-0.4\%I-y\%Ge$ through a synergistic tuning of carrier mobility, effective mass, and point defects engineering strategy.

Thermoelectric Enhancements in PbTe Alloys Due to Dislocation-Induced Strains and Converged Bands

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In-grain dislocation-induced lattice strain fluctuations are recently revealed as an effective avenue for minimizing the lattice thermal conductivity. This effect could be integratable with electronic enhancements for a great advancement in thermoelectric performance. This motivates the current work to focus on the thermoelectric enhancements of PbTe alloys, where a dynamic doping approach and band convergence are used for optimizing electronic performance and aliovalent defects are used for a manipulation on dislocation. As is confirmed by synchrotron X-ray diffractions and Raman measurements, the resultant dense in-grain dislocations induce lattice strain fluctuations for broadening the phonon dispersion, leading to an exceptionally low lattice thermal conductivity. Eventually, the integration of both electronic and thermal improvements lead to a realization of an extraordinary figure of merit zT .

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Microwave hydrothermal synthesis and thermoelectric properties of n-type $\text{Pb}_{1-x}\text{Bi}_x\text{Te}$ alloys

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In order to improve the thermoelectric conversion effective, the figure of merit of n-type PbTe must be enhanced to the thermoelectric level of p-type ones. In this work, n-type $\text{Pb}_{1-x}\text{Bi}_x\text{Te}$ alloys was rapidly synthesized by microwave hydrothermal method followed by hot pressing and their microstructure and thermoelectric performance has been studied. Single cubic crystal structure, compacted microstructure and homogenous element distribution have been formed for all samples. The solid solubility limit of Bi can be reached in $x=0.02$ and 0.03 range. With increase of Bi, the carrier concentration is improved in the solubility limit. This leads to low electrical resistivity and higher power factor at high temperature. The maximum value of power factor about $8.5 \mu\text{W}/\text{cmK}^2$ has been achieved at 623 K for $\text{Pb}_{0.98}\text{Bi}_{0.02}\text{Te}$ alloy. In addition, the introduction of Bi effectively prohibit the p-n transition and bipolar thermal conductivity of pristine of PbTe, and the scattering of alloys, grain boundaries and point defects are introduced and strengthened. Thus, a lowest lattice thermal conductivity of $0.68 \text{ Wm}^{-1}\text{K}^{-1}$ has been obtained for $\text{Pb}_{0.98}\text{Bi}_{0.02}\text{Te}$ alloy. As a result, the highest peak zT value of 0.62 has obtained at 673 K for $\text{Pb}_{0.98}\text{Bi}_{0.02}\text{Te}$ sample, which is comparable with that of Bi doped PbTe alloys synthesized by conventional melting method. Therefore, the microwave hydrothermal method at right synthesis conditions can rapidly prepare n-type $\text{Pb}_{1-x}\text{Bi}_x\text{Te}$ alloys with comparable thermoelectric performance.

Identifying the origins of high thermoelectric performance in group IIIA elements doped PbS

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Comparing with PbTe and PbSe, the development of much cheaper and more chemically stable PbS-based compounds seems to be stagnant for its low thermoelectric performance. Here, thermoelectric properties of group IIIA elements (Al, Ga, In) doped PbS are systematically investigated. Al shows a low solubility limit (<1 mol%) in PbS, whereas Ga and In are soluble up to 2 mol%. Both experimental results and theoretical calculations suggest that Ga or In doping introduces strong gap states in PbS, which are the physical origins of enhanced effective mass and Seebeck coefficients. Meanwhile, a subtle simulation of carrier concentration dependent mobilities under single Kane band model clearly reveals that, Ga doping significantly lowers the deformation potential of n-type PbS while In does not. This lower deformation potential yields higher electrical conductivities at the same doping levels. The weakened electron phonon coupling phenomenon by Ga doping in PbS is further verified by our first-principles calculations. The rare combination of large effective mass and low deformation potential in Ga-doped PbS contributes to a high ZT value of ~ 0.85 at 723 K, $\sim 40\%$ higher than that of Cl-doped PbS control sample. Combining with alloying with Se and Te, which lower the lattice thermal conductivity obviously, higher ZT value are obtained in Ga-doped PbS samples.

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Realizing high thermoelectric performance in Ag-doped PbSe bulk by morphology engineering

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Thermoelectric power generation requires high application temperature as well as materials with outstanding figure of merit. Here we report an efficient strategy of morphology engineering used for breaking through the obstacle of achieving high power factor and low thermal conductivity simultaneously in lead selenide with earth-abundant elementals. With enormous Ag₂Se nanofibers assembled by excessive Ag doping and ultrafast synthesizing process, the parallel connection built with Ag-doped PbSe make the comprehensive electrical properties be successfully improved with smaller effective mass as well as high hole mobility. Meanwhile, additionally multi-sized pores are formed during the period of violently reaction, further lead to much lower lattice thermal conductivities among Ag-doped materials by reducing both velocities of sound and phonon mean free paths (MFP). Ultimately, a high figure of merit (ZT) ~ 1.2 at 773K and average value of ~ 1.1 between 523K - 823K are achieved for p-type lead selenide. These findings combined with energy- and time-saving properties of fabrication highlight the prospective commercialization of PbSe-based thermoelectric materials in the future.

Enhanced Comprehensive Performance of Thermoelectric SnTe via In-Li Codoping

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SnTe-based thermoelectric materials are regarded as environment-friendly alternative of PbTe in large scale commercial power generation applications. In addition to conversion efficiency, output power density is also an important consideration for practical applications in generating electrical energy from solar or waste heat. Improving these two key performance indicators simultaneously in SnTe system is of great significant. In this study, Indium doping is adopted to enhance the Seebeck coefficient and Lithium is innovatively added to further improve electrical conductivity, in contrast to the traditional way. The combination of these two mechanisms results in an ultrahigh PF_{ave} of $\sim 28 \mu\text{W cm}^{-1} \text{K}^{-2}$ from 300 K to 873 K. On the other hand, dispersive LiTe_3 nano-precipitates (5~10nm) are constructed to sharply reduce the lattice thermal conductivity. Taking into account the cumulative temperature dependent thermoelectric properties, Joule and Thomson heat, high output power density of $\sim 5.53 \text{ W cm}^{-2}$ and high conversion efficiency of $\sim 9.6\%$ are achieved for $(\text{SnTe})_{2.94}(\text{In}_2\text{Te}_3)_{0.02}(\text{Li}_2\text{Te})_{0.045}$, assuming a leg length of 4 mm, cold-side temperature $T_c = 300 \text{ K}$ and hot-side temperature $T_h = 870 \text{ K}$.

Ultra-low lattice thermal conductivity of SnTe due to enhanced lattice anharmonicity

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Lattice anharmonicity enlargement is reported as an effective way to achieve low lattice thermal conductivity thus good thermoelectric performance for kinds of materials. Herein, enhanced lattice anharmonicity has been achieved in Cu and Mn dual doped SnTe. Thermal expansion measurement varified increased linear thermal expansion parameter. More importantly, higher order lattice variation parameter was proved to contribute to the lattice anharmonicity. Enhanced lattice anharmonicity leads to stronger phonon-phonon interaction thus shortened phonon lifetime which was proved by the Brillouin and Raman scattering spectrometers. Consequently, an ultra low lattice thermal conductivity 0.47 W/mK was achieved in Cu and Mn dual doped samples. Combining with the increased Seebeck coefficient due to band convergence, a zT around 1.3 was obtained which 225% improvement than pristine sample.

Multiple Effects of Ag(Bi/Sb)Se₂ on thermoelectric properties of SnTe

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SnTe is an emerging lead-free IV–VI thermoelectric compound, but the high hole concentration, low Seebeck coefficient and high thermal conductivity limit its thermoelectric performance. Over the past five years, researchers have achieved a series of successful band engineering and phonon engineering to improve the thermoelectric performance of SnTe. In this work, we systematically investigated the effect of AgBiSe₂ and AgSbSe₂ on the electronic and thermal transport of SnTe. It was found that the introduction of AgBiSe₂ reduced the hole concentration significantly, and improved the Seebeck coefficient in a wide temperature range. The density functional theory calculations confirmed that AgBiSe₂ alloying led to a moderate band convergence and an increase in density of state effective mass. The AgBiSe₂ alloying also decreased the lattice thermal conductivity due to the enhanced phonon scattering by point defect and nanoscale precipitates. In SnTe alloyed AgSbSe₂ system, the total thermal conductivity exhibited a significant reduction from 3.37 to 1.27 Wm⁻¹K⁻¹ at 850 K, even though the hole concentration was at a high-level of 10²¹ cm⁻³. Combining the density functional theory calculations, it was unraveled that the decreased thermal conductivity is due to the nonmonotonic dependence of electron-phonon coupling on the lattice constant. These works will provide new insight into the thermoelectric enhancement of SnTe and similar IV-VI compounds.

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Synergistic Manipulation of Transport Properties for Advancing Thermoelectric Performance in SnTe Alloys

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The rich capabilities for both electronic and phonon engineering in SnTe are highly desirable for achieving high thermoelectric performance. Alloying SnTe with 5% GeTe increases the solubility CdTe/MnTe up to ~20%, triggering an inherent decline of valence band offset effectively, and thus, an improvement of thermoelectric performance in SnTe is realized. However, to what level an additional element doping in low-solubility SnTe-CdTe/MnTe alloys can play a role in enhancing the thermoelectric performance still remains a mystery. Here, a strategy is shown that unexpected Bi doping, by alloying with low solubility CdTe/MnTe, induces a significant enhancement of the thermoelectric figure of merit zT . Combining the experimental evidence and the first-principles calculations, we demonstrate that the prominent enhancement of electronic performance arises from the Bi-doping-driven transport valence band convergence and the carrier concentration optimization. Moreover, the Debye-Callaway model verifies that the reduction in lattice thermal conductivity is dominated by the Bi substitutional defects. Furthermore, the Bi substituted samples show an superior average zT_{avg} compared to high solubility SnTe-CdTe/MnTe thermoelectrics. The present findings reveal the significance of Bi in synergistically manipulating transport properties for promoting the improvement of thermoelectric performance.

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Optimized thermoelectric performances of highly dense Ag doped SnSe polycrystal

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SnSe is a remarkable thermoelectric material due to its ultralow thermal conductivity and giant phonon anharmonicity^[1,2]. However, stoichiometric SnSe compounds possess very low charge carrier density ($\sim 10^{17} \text{ cm}^{-3}$) and poor electrical transport properties limit its thermoelectric transport performances^[3]. Herein, we report that the p-type Ag doped SnSe polycrystal and their thermoelectric performances. A series of $\text{Ag}_x\text{Sn}_{1-x}\text{Se}$ ($x=0$ to 0.05) polycrystals were synthesized through melting and annealing process followed by spark plasma sintering for compaction, eventually the relative density of all sample estimates >98% of its theoretical value. Ag:SnSe exhibits in distorted orthorhombic crystal structure and negligible lattice constant change was observed with different Ag doping. The neutron powder diffraction reveals the temperature dependent inter-orthorhombic structural transition from low symmetry Pnma phase structure to high symmetry Cmcm phase. The thermoelectric properties of $\text{Ag}_x\text{Sn}_{1-x}\text{Se}$ polycrystal was studied in the range of 323 K to 773 K. The electrical conductivity (σ) of Ag:SnSe was increases with Ag doping and +Ve sign of Seebeck co-efficient (α) indicates the p-type SnSe leading to the maximum power factor ($\alpha^2\sigma$) of $\sim 0.3 \text{ mW m}^{-1} \text{ K}^{-2}$ at 773 K for Ag:SnSe samples. The thermal conductivity (k_{Total}) for $\text{Ag}_x\text{Sn}_{1-x}\text{Se}$ ($x=0$ to 0.05) samples follow T^{-1} dependence in the umklapp phonon scattering region and then reaches minimum of $< 0.5 \text{ W m}^{-1} \text{ K}^{-1}$ at higher temperature with major contribution from k_{Lattice} and negligible $k_{\text{Electronic}}$ counterpart. The marginal increment of average figure of merit (ZT) from 323 K to 673 K for Ag:SnSe over than pristine SnSe and ZT_{max} about ~ 0.6 at 773 K for $\text{Ag}_{0.005}\text{Sn}_{0.995}\text{Se}$.

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Optimization of thermoelectric properties of monolayer SnSe doped with Mn nanowires

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Two-dimensional SnSe monolayers have an excellent prospect in thermoelectric applications. It has been proven that the doping of transition metal atoms can significantly affect the electronic and magnetic structures, which motivated us to investigate whether it is effective in thermoelectric performance optimization of the monolayer SnSe. In this work, we systematically investigated the structure, electron and phonon properties of 2D monolayer SnSe doped with 1D Mn nanowires using the first principle calculation within density functional theory (DFT). The Boltzmann theory for electrons under relaxation time approximation (RTA) was employed to obtain the Seebeck coefficient and electrical conductivity. The lattice thermal conductivity was calculated using the Boltzmann Transport Equation (BTE) method and the Debye-Callaway model. The results show that the doping of 1D Mn nanowires can enhance the phonon scattering process by introducing wire defects, and future reduce the lattice thermal conductivity by up to $\sim 0.17 \text{ W m}^{-1} \text{ K}^{-1}$. The lower energy level of Mn 3d electrons reduces the band gap value of the monolayer SnSe. When the width between adjacent nanowires is relatively small, the band degeneration of spin-up and spin-down CBMs can be observed. In addition, the 2D-1D composite structure can directionally enhance the electron transport in the armchair direction, leading to a high electron mobility and electrical conductivity. By adjusting the width between nanowires, record high ZT values from 0.71 at 200 K to 3.76 at 650 K are achieved, 37.8% larger than the intrinsic monolayer SnSe on average. The strategy demonstrated in this work is effective to optimize the thermoelectric performance of 2D SnSe and could be extended to other low-dimensional thermoelectric materials. This work was supported by the National Natural Science Foundation of China under grant numbers of 51825604 and 51721004, and 111 Project under grant number of B16038.

Facile Solution Synthesis of SnSe/rGO Nanocomposites and Impurity-Removed SnSe Nanorods with Enhanced Thermoelectric performance

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Bottom-up solution synthesis has been considered as a facile, controllable and energy efficient approach for SnSe thermoelectric materials. In this study, we have synthesized a series of SnSe/reduced graphene oxide (rGO)- x ($x = 0.1, 0.3, 0.5, 0.7$ wt%) nanocomposites based on an *in-situ* aqueous solution strategy. High-density SnSe/rGO interfaces were formed due to the uniformly distributed rGO in SnSe matrix, which enhance phonon scattering and reduce the lattice thermal conductivity (κ_L). Meanwhile, the increased carrier concentration in the SnSe/rGO composites improves the electrical conductivity. Finally, SnSe/rGO-0.3 composite obtains a figure of merit (zT) of 0.91 at 823 K.¹ In addition, SnSe nanostructures with different sizes have been synthesized *via* a microwave-assisted hydrothermal method by adjusting the NaOH concentration. It is found that a NaOH:SnCl₂ molar ratio of 30 leads to the formation of phase-pure SnSe nanorods. The significantly reduced fraction of SnO₂ in the pellet results in an enhanced power factor and a sharply diminished thermal conductivity, which in turn lead to a maximum zT of 0.78 at 773 K. These results prove essential for thermoelectric performance enhancement by designing composite microstructures and decreasing impurity contents.

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Thermoelectric Transport Properties in Bi-Doped SnTe-SnSe Alloys

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Numerous endeavors have been made to advance thermoelectric SnTe for potential applications. Effective strategies focus on the manipulation of transport properties, including valence band convergence, resonant state and defect engineering. It has been demonstrated that alloying trivalent Bi or chalcogenide SnSe alone in SnTe can trigger an inherent enhancement of thermoelectric performance. However, what the critical role on transport valence band by co-doping Bi and Se in SnTe plays is still unclear. Particularly, fully evaluating the effect of band convergence on the carrier concentration-dependent weighted mobility, which dominates the electronic performance, is of primary and essential for designing excellent thermoelectric materials. Here, we report that Bi doping in SnTe-SnSe alloys can derive a distinct decrease of energy offset between the two valence bands, thus improving the density-of-state effective mass with only slightly deteriorating the mobility. The well-established theoretical model reveals that the Bi-doping-induced band convergence and the optimized carrier concentration actually enhance the weighted mobility, contributing to the improvement of electronic performance. Moreover, the Debye-Callaway model demonstrates the origin of the reduced lattice thermal conductivity. The present results confirm the potential of transport engineering in promoting thermoelectric performance.

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Ge-vacancy Engineering of GeTe-based Alloys for Enhanced Thermoelectric Performance

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GeTe-based alloys have shown great promise as mid-temperature TE materials with superhigh TE performance, mostly due to their relatively high-degeneracy band structures and low lattice thermal conductivity. Ge vacancies is one of the most important factors influencing the thermoelectric properties of GeTe-based alloys. Due to the high hole-carrier concentration induced by the frequently observed Ge vacancies, many studies of GeTe-based alloys have taken Ge vacancies as negative effects for improving the ZT and have also demonstrated various strategies for suppressing the high-density Ge vacancies. However, in this presentation, we have demonstrated that the Ge vacancies can also have great positive effects on enhancing the ZT of GeTe-based alloys when the hole concentration falls into the optimal range, e.g., introducing stacking faults for the reduction of lattice thermal conductivity, increasing the band convergence, suppressing the bipolar transport, enhancing the low-temperature thermoelectric performance of GeTe-based alloys. The summarized strategies in this presentation can also be used as a reference for guiding the further development of GeTe-based alloys and also other TE materials.

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Leveraging on Quality Factor as a Guide Towards Enhancing Thermoelectric Performance: A Case Study of GeTe

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In recent years, GeTe has received tremendous attention from the research community because of its favorable electronic and thermal properties which make it one of the best performing medium-temperature thermoelectric compounds.^{1,2} However, due to the *p*-type tendency of this compound, the primary focus in many studies is to optimize its carrier concentration. In many reports, high performance has often been achieved via various doping/alloying methods, which typically involve more than one type of dopants. Consequently, the origin of *zT* enhancements in this compound has always been due to a confluence of a set of factors (*i.e.* carrier concentration optimization, lattice thermal conductivity reduction, band-convergence, as well as resonant doping).

This work sought to systematically unravel the role of various parameters in determining the overall thermoelectric performance. Specifically, the discussion will be focused on the efficacy of various strategies to enhance the thermoelectric performances of GeTe from the point of view of quality factor (*B*), which represents a holistic account of all the parameters such as lattice thermal conductivity and weighted-mobility that independently contribute to high *zT* values.³

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High performance GeTe thermoelectrics in both rhombohedral and cubic phases

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Although GeTe has been known as thermoelectrics since 1960s, it has attracted intensive renewed attention recently. Historically, cubic GeTe has been mostly focused on, with electronic performance as good as the analogue PbTe and SnTe. GeTe undergoes a phase transition from a high- T cubic (c-GeTe) to a low- T rhombohedral structure (r-GeTe), through slightly distortion along the [111] direction at ~ 720 K. This work utilizes the symmetry breaking of GeTe, which electronically enables a diversified rearrangement of split bands for a high band degeneracy, and thermally allows hierarchical bonds and microstructures for a low lattice thermal conductivity. This reveals low-symmetry r-GeTe show a thermoelectric figure of merit zT as high as that of c-GeTe. However, the intrinsic Ge-vacancies in GeTe leads the hole concentration to be much higher than the optimum. The existing efforts on advancing GeTe thermoelectrics (both rhombohedral and cubic) largely involve a very high concentration of impurities for a reduction in hole concentration. This usually leads to the significant changes in band structure and scattering processes of electrons and phonons, leaving the inherent thermoelectric nature of GeTe unveiled. This work uses Cu_2Te as effective dopant, consequently, an inherently high mobility has been revealed that has never been realized in the literature. This talk involves our recent efforts on advancing thermoelectric GeTe in both rhombohedral and cubic phases, as well as fundamental evaluation on the inherent thermoelectric potential of GeTe alloys.

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Discovery of low-temperature GeTe-based thermoelectric alloys with high performance competing with Bi_2Te_3

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Much effort has recently been put in developing high-performance low-temperature thermoelectric materials for waste-heat recovery and thermoelectric cooling. Here, we report an unusual enhancement of low-temperature figure of merit (ZT) in quenched p-type GeTe-based alloys. The average ZT within low-temperature range (300-473 K) for our quenched GeTe-based alloys can reach to 1.1, which is even better than the state-of-the-art commercial $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ ingots. Moreover, our samples also show superior thermoelectric performance in mid-temperature range, demonstrating great promising for thermoelectric applications in broad-temperature range. The microstructures of Ge-vacancy arrays can be responsible for serving as high-speed channels with low effective mass for carrier transport but obstacles for phonon transport, resulting in increased carrier mobility and reduced lattice thermal conductivity simultaneously for high ZT in our quenched GeTe-based alloys. These findings provide an intriguing way to enhance ZT and to develop low-temperature thermoelectric materials beyond Bi_2Te_3 -based alloys.

The Study of GeTe-based Compounds with Inelastic Neutron Scattering

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Understanding the microscopy of the bulk thermal conductivity is crucial to develop the efficient thermoelectric materials. GeTe is currently one of the leading thermoelectric materials, thanks to its superior electronic performance as well as the low thermal conductivity. The high electronic performance arise from the multiple valence bands and highly degenerated band on high symmetric points of Brillouin zone¹. However, the origin of the low thermal conductivity has so far been elusive. PbTe, one of the group IV monotellurides analogous to GeTe, has been identified a strong anharmonic coupling between the ferroelectric transverse optic mode and the longitudinal acoustic modes. The anharmonicity directly affects the heat-carrying longitudinal acoustic phonon². The longitudinal acoustic-transverse optic anharmonic coupling is likely to play a central role in explaining the low thermal conductivity of PbTe. Similar to the thermal transport mechanism in PbTe, the low thermal conductivity in GeTe is likely related to the acoustic and optical phonon coupling³. Moreover, GeTe is a ferroelectric material with a phase transition around 700K. the ferroelectric instability is believed to be the indicator of low thermal conductivity. Therefore we conduct inelastic neutron scattering experiments with $\text{Ge}_{0.9}\text{Bi}_{0.1}\text{Te}$ and $\text{Ge}_{0.9}\text{Sb}_{0.1}\text{Te}$, to have a sight of the lattice dynamic of GeTe for further analysis of thermal conductivity.

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Vacancy-based Defects Regulation for High Thermoelectric Performance in $\text{Ge}_9\text{Sb}_2\text{Te}_{12-x}$ compounds

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Defect engineering is the core strategy for improving thermoelectric properties. Herein, cation doping along with modulation of cation vacancy have been developed in GeTe based materials as an effective method to induce vacancy-based defects to boost its thermoelectric performance. A series of ternary compounds of $\text{Ge}_9\text{Sb}_2\text{Te}_{12-x}$ ($x = 0, 0.03, 0.06, 0.09, 0.12, 0.15$) was prepared by vacuum melting and annealing combined with the SPS process. The role of Sb doping and the cation vacancy on the thermoelectric properties were systematically investigated. It is found that alloying Sb_2Te_3 with GeTe increases the concentration of cation vacancies, which is corroborated by both positron annihilation measurements and theoretical calculations. The vacancies and planar defects interaction determines the thermoelectric transport properties. Adjusting the deficiency of Te effectively tunes the concentration of cation vacancies and dopant defects in the structure. In turn, this tunes the carrier concentration close to its optimum. A high power factor of $32.6 \mu\text{W cm}^{-1} \text{K}^{-2}$ is realized for $\text{Ge}_9\text{Sb}_2\text{Te}_{11.91}$ at 725 K. Moreover, large strains induced by the defect structures including Sb dopant, vacancy as well as planar defects intensify phonon scattering, leading to a significant decrease in the thermal conductivity from $7.6 \text{ W m}^{-1} \text{K}^{-1}$ for pristine GeTe to $1.18 \text{ W m}^{-1} \text{K}^{-1}$ for $\text{Ge}_9\text{Sb}_2\text{Te}_{11.85}$ at room temperature. All the above contribute to a high ZT value of 2.1 achieved for $\text{Ge}_9\text{Sb}_2\text{Te}_{11.91}$ sample at 775 K.

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Establishing the carrier scattering phase diagram for ZrNiSn-based half-Heusler thermoelectric materials

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Manipulation on the carrier and phonon transport mechanisms is crucial for optimizing the thermoelectric performance of solid materials. In recent years, good thermoelectric materials have been discovered in systems with multi-element, complex crystal structure, and multiple chemical bonds. Their carrier transport mechanism could be more complicated than the simply acoustic phonon scattering picture, requiring thorough and deep studies. Herein, with high-quality single and polycrystalline crystals, various probes, including electrical transport measurements, inelastic neutron scattering measurement, and first-principle calculations, have been performed to identify the carrier transport behavior of ZrNiSn-based half-Heusler thermoelectric materials. The carrier mobility in this system exhibits non-monotonous dependence on carrier concentration over a broad temperature range. In lightly doped region, the ionized impurity and grain boundary scatterings are thought to dominate the carrier transport at low temperature, while phonon DOSs analysis demonstrated a polar-optical-phonon predominant scattering at high temperature. These three kinds of scattering resources could be well screened by electron doping, leading to a crossover to acoustic phonon scattering, at which the optimal thermoelectric performance is obtained. All the findings make up a carrier scattering “phase diagram”, which could serve as a guide for choosing reasonable strategy targeting the optimization of thermoelectric performance.

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Electronic Quality Factor for Thermoelectrics

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Development of thermoelectrics usually involves trial-and-error investigations, including time-consuming synthesis and measurements. Here, we identify the electronic quality factor for determining the maximum thermoelectric power factor, which can be conveniently estimated by a single measurement of Seebeck coefficient and electrical conductivity of only one sample, not necessarily optimized, at an arbitrary temperature. We demonstrate that thousands of experimental measurements in dozens of materials can all be described by a universal curve and a single material parameter BE for each class of materials. Furthermore, any deviation in B_E with temperature or doping indicating new effects such as band convergence or additional scattering. This makes B_E a powerful tool for evaluating and guiding the development of thermoelectrics. We demonstrate the power of B_E , to show that both p-type GeTe-alloys and n-type Mg_3SbBi -alloys as highly competitive materials, at near room temperature, to state-of-the-art Bi_2Te_3 -alloys used in nearly all commercial applications.

High-performance p-type elemental Te thermoelectrics enabled by synergy of carrier tuning and phonon engineering

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Elemental Te is the focus of much research interest due to its multi-functional physical properties, such as semiconducting, photoconductive, thermoelectric, piezoelectric, etc. Nonetheless, owing to its highly interdependent thermoelectric parameters and unfavorably high reactive activity, it is still challenging to advance the figure of merit (zT) through traditionally single doping/alloying approaches. In the present work, we show that an outstanding peak zT of ~ 1.06 (at 600 K) and an average zT as high as ~ 0.69 can be achieved in $\text{Te}_{0.985}\text{Sb}_{0.015}$ -2%SmSe₂ system based on an ingenious multicomponent alloying strategy. Importantly, for the first time, we report the detailed structural characterizations to correlate microscopic nature with thermoelectric transport mechanisms in the Te system, rendering more fundamental interpretations of our developed multifunctional alloying approach. Meanwhile, the remarkably enhanced mechanical stability makes Te a promising candidate to practical device applications.

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Carrier Grain Boundary Scattering in Thermoelectric Materials

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Reducing the grain size to lower the lattice thermal conductivity, is widely used in many thermoelectric (TE) materials. However, recently it's found that in materials where grain boundary scattering (GBS) dominates the carrier transport, reduction of grain size could result in the deterioration of TE performance, especially at a lower temperature, yet the detailed discussion is lacked. Hence, it's significant to have a comprehensive understanding on GBS. This review recalls the origin of grain boundary resistance and focuses on the recent progress in TE materials from the perspective of carrier GBS. Temperature dependence and energy dependence of carrier transport along with their underlying physical mechanisms are discussed and some limitations are pointed out. The strength of GBS could be manipulated by three main parameters (grain size, carrier concentration and static dielectric constant) and their relating factors. As stronger charge carrier screening could weaken both the ionized impurity scattering (IIS) and GBS, the ratio of effective Bohr radius to Debye screening length is recommended used as a criterion to exclude the possibility that IIS dominates the carrier transport. In conclusion, we provide an overview of recent progress of GBS in TE materials and gives some approaches to distinguish and manipulate GBS. It's of great importance to understand scattering mechanism for further TE performance optimization.

Enhanced thermoelectric performance of n-type PbTe through the introduction of low-dimensional C₆₀ nanodots

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Lead telluride (PbTe) has long been considered as an ideal p-type thermoelectric material at an intermediate temperature range. However, the relatively low thermoelectric performance of n-type PbTe largely limits the commercial applications of integral PbTe devices. In current work, we report that a significant enhancement of the ZT value of ≈ 1.3 can be achieved at 823 K in PbTe_{0.998}I_{0.002}-0.5%C₆₀ by adding low-dimensional C₆₀ nanodots. This remarkable improvement in thermoelectric performance is attributed to the incorporation of C₆₀ in n-type PbTe matrix, which creates dense nanodots that can simultaneously manipulate electron and phonon transport. On one hand, the dispersion of C₆₀ nanodots in n-type PbTe matrix leads to highly depressed lattice thermal conductivity (κ_{lat}) ($\sim 52\%$) due to the refinement of grains and the extra phonon scattering centers. On the other hand, the introduction of C₆₀ nanodots increases the scattering parameter α , and brings about the overall improvement of Seebeck coefficient S , especially at room temperature. This work demonstrates the great potential of lowdimensional dopant in optimizing PbTe thermoelectric materials, which should be equally applicable in improving the performance of other thermoelectric materials.

Revealing the origin of dislocations in $\text{Pb}_{1-x}\text{Sb}_{2x/3}\text{Se}$ ($x=0\sim 0.09$)

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Physical/chemical properties of materials critically depend on the microstructure. In the thermoelectric material $\text{Pb}_{1-x}\text{Sb}_{2x/3}\text{Se}$, a large number of dislocations are reported, which enhance intermediate-frequency phonon scattering, and then improve the zT value. However, the microstructural origin of dislocations remains unclear. In this paper, aberration corrected electron microscopy observation is combined with the density function theory to study the microstructure of $\text{Pb}_{1-x}\text{Sb}_{2x/3}\text{Se}$ ($x=0\sim 0.09$) for indepth understanding of the formation mechanism of the dislocations. Plenty of zinc blende (ZB) nanostructures are found in the PbSe matrix with rock salt (RS) structure, and the theoretical calculations confirm its reasonability from the point view of formation energy. The similar ZB structure is identified at dislocation cores in the Sb-doped materials as well, so that the direct relationship between nanostructures and dislocations can be obtained in this PbSe system. This result provides important guidance to understand the structural evolution in the compounds with the RS structure, especially in the high-performance lead chalcogenide thermoelectric materials.

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Thermal stress analysis of thermoelectric cooler

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Thermoelectric cooler (TEC) is a solid state device, which can provide cooling without the use of refrigerants. TECs can be an alternate solution for the conventional vapour compression refrigeration systems, if the thermoelectric material with higher figure of merit is found. Though, TECs have advantages such as it can be operated with solar energy and there are no moving parts, but due to their lower efficiencies, TECs are not widely used. Studies reported that the shape of the thermoelements have impact on their thermal performance. Therefore, In this paper, the TECs with different geometry of thermoelectric legs are being studied including cuboidal, annular, pin and trapezoidal geometries to evaluate the thermal performance and induced thermal stress during its operation. In addition to that, the thermal stress of different thermoelectric cooler geometries have also been evaluated and compared for varying cooling load, operating current, and hot side heat transfer coefficient. The results of this study will help in designing of thermoelectric modules.

Imparting multifunctionality by utilizing biporosity in a Zr-Based MOF

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An elegant design strategy of selectively incorporating conducting polymers inside Metal-Organic Framework (MOF) was introduced, which resulted in decoupling of electrical and thermal conductivities along with significant retention in porosity. Using a well-known Zr-based bi-porous MOF (UiO-66), herein, we have introduced specialty monomers 3,4-ethylenedioxythiophene (EDOT) and pyrrole (Py) selectively inside one of the pores, which were then polymerized by using extraneous oxidizing agents. An electrical conductivity enhancement of $\sim 10^6$ times was observed in both the nanocomposites compared to pristine MOF bringing them into semiconducting regime. Alongside, there was a significant decrease in thermal conductivity. Overall, the process resulted in loading of ~ 12 wt% of polymers inside the voids, creating a balance between the electrical and thermal conductivities as well as simultaneous porosity retention up to $\sim 70\%$.

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One-pot synthesis of thermoelectric oxide $(\text{ZnO})_k\text{In}_2\text{O}_3$ ($k= 3, 5$ and 7) – a potential photocatalyst

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Homologous $(\text{ZnO})_k\text{In}_2\text{O}_3$ ($k= 3, 5$ and 7) ceramics were synthesised by glycine nitrate combustion method. Variation in structural, optical and morphological properties with respect to change in k was recorded using X-Ray Diffraction, UV-Visible Spectroscopy and Scanning Electron Microscopy. Structural studies revealed a rhombohedral structure with crystallite size within a range of ~ 18 to ~ 25 nm. Broad and strong absorption was noticed in the UV region for pristine ZnO. However, some amount of visible light absorption was also seen for the rest of the series which would open doors for possible photocatalysis. Bandgap was found to be between 2.95 eV to 3.21 eV as calculated by tau'c method. Typical agglomerated particles were visible on studying the scanning electron micrographs which is a characteristic of this method.

Role of In doping on enhanced thermoelectric properties of Cu_2SnSe_3

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Cu_2SnSe_3 has been considered as a potential thermoelectric material owing to its tunable transport properties and its phonon-glass-electron-crystal (PGEC) characteristics. In this work *p*-type pristine and In doped Cu_2SnSe_3 bulk samples are prepared by solid state sintering technique. Cubic structure with $F\bar{4}3m$ space group is maintained for all the samples and a linear increase in lattice parameter with In concentration has been observed. The nature of electrical resistivity changes from semiconducting to metallic behavior for $x > 0.10$. The decrease in electrical resistivity as well as Seebeck coefficient with increase in x is attributed to the increased hole concentration and is confirmed from the room temperature Hall effect measurements. In doping also reduces the thermal conductivity of Cu_2SnSe_3 system as the result of increased phonon scattering due to the mass fluctuation introduced by In doping. Concurrently, successful enhancement of PF and ZT is achieved with In doping at Sn site of Cu_2SnSe_3 . The maximum ZT is attained for $x = 0.25$ at 400 K which is six times than that of pristine.

Effect of unidirectional solidification in the microstructure and thermoelectric power factor of $\text{Cu}_2\text{Te-Sb}_2\text{Te}_3$ pseudo-binary alloys

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Tuning microstructural features of a composite material offer improved thermoelectric power factors ($PF=S^2\sigma$) and plays a vital role in controlling the inherent transport processes. Therefore, in the present study, we explore in-situ composites of $(\text{Cu}_2\text{Te})_{62.02}-(\text{Sb}_2\text{Te}_3)_{37.98}$ produced by directional solidification using a modified-Bridgman apparatus. We investigated the variation of the electrical conductivity, the Seebeck coefficient and the thermoelectric power factor for the different structural morphologies of the two phases (i.e. Cu_2Te and Sb_2Te_3) that are obtained by varying solidification velocities. By measuring the transport properties along the growth direction (longitudinal direction) and perpendicular to growth direction (transverse direction), we observed that there is a variation in the properties due to anisotropy induced by the directional growth of the phases. PF has been improved to $1.4 \text{ mW m}^{-1}\text{K}^{-2}$ by tuning eutectic colony structures (observed at higher solidification velocities as well in furnace cooled samples) to uniform fibre composites (at $1 \mu\text{m/s}$) by reducing the solidification velocity below the critical velocity for instability formation. Moreover, the PF did not vary much across the temperature range of measurement in this eutectic system. This is a significant result that may have a profound influence in thermoelectric applications.

Doped ZnO nanosheets towards the realization of high thermoelectric performance

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Thermoelectric materials which can convert thermal energy directly into electrical energy. The performance of a thermoelectric (TE) material is quantified by a dimensionless figure of merit, $ZT = (\sigma S^2 / \kappa)$, where σ , S , T and κ are the electrical conductivity, Seebeck coefficient, temperature and thermal conductivity respectively. Power factor is defined as $P = \sigma S^2$. ZnO is a promising *n*-type oxide thermoelectric material having high figure of merit. In our present investigation, we report 1 at% Sn-doped ZnO and 1% Sn - 2% Al-codoped ZnO nanosheets which exhibit large power factor of $\sim 1.3 \text{ mW/K}^2$ and 2.0 mW/K^2 . This is the highest power factor reported so far for ZnO based materials. This behaviour can be attributed to the synergistic effect of codoping of Sn-Al on the electronic structure and non polar facet growth which causes simultaneous increases in S and σ at high charge carrier concentrations. This unique behaviour does not obey conventional band theory and mainly originates from substantial changes in the electronic band structure as indicated by doping-induced multifold increases in the effective localized density of states near Fermi level. Our findings opens up a new pathway in ZnO based materials.

A novel thermoelectric generator module along with thermo-mechanical properties

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To simplify the research and outcome of the practical TEG device on the real condition, this paper proposes a real-time simulation model, consequently the model is divided into three parts: 1) ideal model 2) segmented model 3) hybrid model. The ideal model consisted of bismuth telluride as the *p*-type and the *n*-type materials. The segmented and the hybrid models consisted of different combination of materials such as lead telluride and antimony telluride. The optimisation of the length of the thermoelectric module was carried out to achieve the highest power output and it was observed to be at 2 mm. This paper also investigates the thermo-mechanical stress distribution analysis in the module to find the maximum load the thermoelectric device can withstand before undergoing fracture, depending upon the yield strength of the material. The stress was analyzed in all the three thermoelectric modules and the results are evaluated. Results are observed from the optimized length at 2 mm. The conventional, hybrid and segmented module showed the highest power output of 147.122 mW, 198.82 mW and 171.934 mW respectively at the temperature difference at 50 K.

Development of thermoelectric power generator using SiGe alloy

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SiGe alloy has been receiving extensive attention as an eco-friendly emerging thermoelectric material for high temperature range (up to 800 – 1000 °C) usages and space missions. Usually the $\text{Si}_{0.8}\text{Ge}_{0.2}$ has a classic band convergence in conduction band. This enhances the effective mass of the carriers and thus increasing the Seebeck coefficient for *n-type* material resulting in high figure of merit ($ZT \sim 1.8$ at ~ 850 °C). For synthesis of *p-* and *n-type* $\text{Si}_{0.8}\text{Ge}_{0.2}$, Boron and Phosphorus are used as dopants and the amount has been optimised. The enhanced ZT of the synthesized $\text{Si}_{0.8}\text{Ge}_{0.2}$ alloy is attributed to strong suppression of lattice thermal conductivity due to defects produced in mechanical alloying and improved Seebeck coefficient due to band convergence. Pellets of *n-* and *p-type* $\text{Si}_{0.8}\text{Ge}_{0.2}$ alloy has been synthesized using hot press. A $\text{Si}_{0.8}\text{Ge}_{0.2}$ thermoelectric power generator has been fabricated using *n-* and *p-type* pellets, zircar housing and Ag plates as electrodes, which exhibits conversion efficiency of $\sim 5\%$ at temperature difference of ~ 600 °C.

Study on microstructural evolution at PbTe/(Ni-XFe) interfaces using diffusion couple technique

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In this study, we investigate phase evolution at Ni/PbTe thermoelectric joints using diffusion couple technique and compare the effect of Fe addition on microstructural evolution at the interface. Ni_(x)Fe (x = 0, 1, 5 at%) discs were successfully diffusion bonded with PbTe disc for $t = 15, 30, 45$ and 60 minutes at $700\text{ }^{\circ}\text{C}$. Three product phases were observed β_2 ($\text{Ni}_{3-x}\text{Te}_2$), Pb and a ternary with approximate composition $\text{Ni}_5\text{Pb}_2\text{Te}_3$ for all couples. Thermodynamic calculation showed such ternary phase decomposes into Ni_3Te_2 and PbTe via eutectic reaction when samples were furnace cooled. It was observed that minor Fe addition in Ni considerably reduces Ni-PbTe reaction by forming Fe enriched Ni precipitate layer at the interface. No Fe-Te intermetallics were observed for any of the samples irrespective of Fe content in Ni. In PbTe/Ni-Fe joints two distinct layer were observed at the interface. Layer 1 consists of primarily Fe enriched Ni precipitates. Layer 2 consists primarily of product phases coming out of reaction between PbTe and Ni. The best optimized interface was obtained for Ni-5%atFe/PbTe joints diffusion bonded for 15 mins at $700\text{ }^{\circ}\text{C}$. The best optimized interface was obtained for Ni-5%atFe/PbTe joints diffusion bonded for 15 mins at $700\text{ }^{\circ}\text{C}$.

Influence of In doping on the thermoelectric properties of AgSbTe₂ compound with enhanced figure of merit

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More than 60% of heat is wasted while burning fuel. This waste heat can be utilized as a source of free energy. Thermoelectric materials can convert this waste heat from different sources directly into electricity. Thermoelectric materials are environmentally friendly, have no moving parts and are light weight, which make them excellent energy harvesting materials. Their efficiency is represented by the dimensionless figure of merit (ZT) that depends on high electrical conductivity and seebeck coefficient and low values of thermal conductivity. We report a maximal ZT value of 1.1 at 600 K was obtained for the sample of which $x = 0.03$, representing an enhancement greater than 20% compared with a pristine AgSbTe₂ sample. This favorable thermoelectric performance originated from the optimal Sn²⁺ substitution for Sb³⁺ in AgSbTe₂, which not only increased electrical conductivity but also led to a substantial reduction in thermal conductivity that was likely caused by an enhanced phonon-scattering mechanism through the combined effects of lattice defects and the presence of Ag₂Te nanoprecipitates dispersed in the matrix.

Understanding the conduction mechanism in N ion implanted SrTiO₃ thin films from electrical and thermoelectric properties

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Present study focuses to understand the conduction mechanisms in the N ion implanted SrTiO₃ thin films fabricated by pulsed laser deposition using electrical and thermoelectrical properties. The Ion implantation is a technique that offers precise control of implanted ion/dopant species, profile and temperature. N ion implantation with 60 keV N ions at two different fluences 1×10^{16} and 5×10^{16} ions/cm² followed by annealing was carried out. It is observed that the electrical conductivity and Seebeck coefficient (*S*) of these films are significantly enhanced for higher N ion fluence. It is revealed that the band conduction mechanism dominates at high temperature regime and in low temperature regime, there is a crossover between NNH and VRH. The *S* has been analysed using the relaxation time approximation model and dispersive transport mechanism in the temperature range of 300 - 400 K. Due to improvement in electrical conductivity and thermopower, the power factor is enhanced to $15 \mu\text{W m}^{-1}\text{K}^2$ at 400 K at the higher ion fluence which is in the order of ten times higher compared to the pristine films. X-ray absorption spectroscopy reveals the change in the t_{2g}/e_g ratio resulting from the local distortion of TiO₆ octahedra and introduction of oxygen vacancies due to N implantation. This study suggests that ion beam can be used as an effective technique to selectively alter the electrical transport properties of oxide thermoelectric materials.

Enhanced thermoelectric performance of Yb filled CoSb_3 due to Type-I clathrates addition

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Filled skutterudites such as $\text{Yb-Co}_4\text{Sb}_{12}$ have a high potential for medium temperature thermoelectric energy conversion due to their high power factor. In order to enhance both power factor and figure of merit of Yb-filled $\text{Co}_4\text{Sb}_{12}$, type-I clathrates and modified type-I clathrates $\text{Ba}_8\text{Al}_{16}\text{Si}_{30}$ and $(\text{DyBa})_8\text{Al}_{16}\text{Si}_{30}$ which also exhibits open cage structure have been added. The skutterudite and clathrates were synthesized separately by vacuum alloying, and the mixed materials were obtained by hot pressing. All the materials, $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12}$, $(\text{Ba}_8\text{Al}_{16}\text{Si}_{30})_x(\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12})_{100-x}$ and $(\text{Ba}_{7.5}\text{Dy}_{0.5}\text{Al}_{16}\text{Si}_{30})_y(\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12})_{100-y}$ with $x = 2, 4$ and $y = 1, 2$ wt.% respectively, exhibit a single phase X-ray diffraction pattern corresponding to the skutterudite phase. The materials with 1 wt.% Dy- modified clathrates addition has the highest Seebeck coefficient at all temperatures and has a peak value of $210 \mu\text{V K}^{-1}$ at $\sim 725 \text{ K}$, 15 % higher than $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12}$. The electrical conductivity of this materials is lowest compared to other materials, 1150 S cm^{-1} at room temperature, which decreases to $\sim 700 \text{ S cm}^{-1}$ at 750 K . The high value of Seebeck coefficient coupled with good electrical conductivity results in good power factor of $3.2 \text{ mW}^{-1}\text{K}^2$, 25 % increase compared to single filled skutterudite at 650 K . The power factor for $T > 650 \text{ K}$ decreases due to the onset of bipolar conduction.

Molten flux synthesis and characterization of thermoelectric material – $\text{Ca}_{3-x}\text{Y}_x\text{Co}_4\text{O}_9$

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Synthesis and characterization of $\text{Ca}_{3-x}\text{Y}_x\text{Co}_4\text{O}_9$ ($x = 0.0 - 1.0$) by one step molten salt method. Yttrium substitution on calcium site increases the electrical resistivity due to reduction in the concentration. Resistivity plots show semiconducting behavior for all the compositions, particularly in the low temperature regime. The seebeck coefficient and figure of merit of $\text{Ca}_2\text{YCo}_4\text{O}_9$ at 1000 K are $180 \mu\text{V K}^{-1}$ and 0.23 respectively. The grain size of the parent and substituted products are in the range of 1-2 μm . The particle morphologies investigated by SEM indicate irregular platelet-shape microstructures.

Role of Se non-stoichiometry in enhancing thermoelectric performance of Cu_2SnSe_3 system

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We have attempted to tune selenium content in $\text{Cu}_2\text{SnSe}_{3-\delta}$ ($-0.04 \leq \delta \leq 0.1$) compounds synthesized via the conventional solid-state reaction, in order to investigate the thermoelectric behavior. Electrical and thermal properties are presented in the low and near room temperature regime (10 - 350 K). The lowest electrical resistivity is observed for the compound with $\delta = 0.08$. A decrease in the Seebeck coefficient along with carrier concentration is observed, verifying the linear electron band dispersion. A downward shift of the Fermi level deep into the valence band is realized in the case of non-stoichiometric samples, thereby reducing the Seebeck coefficient. A maximum power factor of $\sim 50 \mu\text{W m K}^2$ is achieved for the sample with $\delta = 0.04$, which is about twice that of the pristine compound. The highest ZT of ~ 0.01 is obtained for the compound with $\delta = 0.08$. The observed results suggest that Se nonstoichiometry plays a significant role in modifying the thermoelectric properties of Cu_2SnSe_3 compound.

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Thermoelectric properties of Bi_2Te_3 nanostructures

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Nanostructures are of great interest for thermoelectric application as presence of the large phonon scattering and high Seebeck coefficient would result in the enhancement of figure of merit (ZT). Bismuth telluride (Bi_2Te_3) is best suited material for the thermoelectric applications due to large carrier effective mass, good electrical performance and low value of thermal conductivity and has superior heat to electrical energy conversion efficiency at room temperature

In this study, we probe the effect of synthesis parameter on morphology of Bi_2Te_3 . Various nanostructure dimensions are categorized according to synthesis parameter. The controllable Bi_2Te_3 nanorods, nanoflowers, and nanosheets morphology are obtained by hydrothermal method, which provides the opportunity for synergistically structure.

Thermal properties of mixed valence manganites

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Among the complex oxides, the doped Rare Earth manganites ($R_{1-x}A_xMnO_3$, where R and A are trivalent and monovalent/bivalent/trivalent/tetravalent cations), Cobaltates and Vanadates exhibit enormous variety of fascinating physical properties. They are potential candidates for new magnetic recording devices, cathode materials for Solid Oxide Fuel Cells (SOFC), gas sensors, magnetic refrigerant and thermoelectric materials.

We have investigated the various lattice distortions in complex oxides induced by varying the valence of doped cation at A-site in $RMnO_3$, $RCoO_3$ and RVO_3 where R is rare earth cation. The main focus of the present paper is to describe the various distortions induced due to varying valence at A-site and its effect on the thermal properties, especially Debye temperature and specific heat of these complex oxides. The specific heat of these complex oxides $R_{1-x}A_xMnO_3$ with doping at the A-site is studied as a function of temperature (1 K – 500 K) using Rigid Ion Model (RIM) after modifying its framework to incorporate the van der Waals interactions. The Debye temperatures are found to be in somewhat closer agreement with the available experimental data. The specific heat values revealed by using modified RIM are in closer agreement with the available experimental data for some concentrations (x) of $R_{1-x}A_xMnO_3$.

Synthesis and characterisation of polypyrrole-Ce_{0.05}CoSb₃ nanocomposites

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Filled Skutterudite Ce_yCoSb₃ (y = 0.05) nanoparticles synthesized by solvothermal method are incorporated into conducting polypyrrole (PPy) via in-situ chemical polymerization technique to form Polymer Inorganic Nanocomposites (PINs). Further, studies on different weight percent (10, 20, 30 and 40%) of the nanocomposites with respect to pure PPy are conducted. Field Emission Scanning Electron Microscopy (FE-SEM) equipped with Energy

Dispersive X-Ray Spectrometer (EDS), powder X-Ray Diffractometer (pXRD), Fourier Transform Infrared (FTIR) Spectroscopy techniques were employed to study morphological, structural and optical properties of as synthesized PINs. FESEM confirms uniform distribution of nanoparticles in polymer matrix and increase in atomic weight % of Ce_yCoSb₃ (y = 0.05) shown in EDS analysis confirms the successful fusing of nanoparticles into the PPy chains. pXRD analysis justifies the formation of PPy-Ce_{0.05}CoSb₃ nanocomposites indicating the presence of Ce_{0.05}CoSb₃ diffraction peaks with broad amorphous background of polypyrrole. FTIR spectra reveal the vibrational modes and the chemical bonds of pure PPy and PPy fused with Ce_{0.05}CoSb₃ justifying the formation of expected nanocomposites.

Searching for a high performance thermoelectric material from large-scale materials database

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To find environmentally-friendly thermoelectric (TE) materials showing high performance enough for a practical use is difficult because materials that have a band gap and electronegativity suitable for high performance TE materials contain toxic elements normally. The purpose of the present study is searching environmentally-friendly TE materials having optimal band gap and electronegativity from the materials database called Materials Project [1]. This database stores results of first-principle calculations for almost eighty thousand compounds. However, it is impossible to estimate the TE properties of all the compounds stored in the database. Therefore, materials screening was performed for efficient materials search by the following three steps; (1) select materials which fulfill conditions of low toxic and high chemical stability; (2) pick up semiconductor materials with the band gap between 1.0×10^{-3} and 3.0 eV; (3) choose rock-forming elements based binary alloys with the electronegativity difference less than 1 and the weighted average electronegativity between 1.75 and 2.25. As a result, binary compounds composed of Ru and Si were selected because one of them is expected to show high power factor reaching 10 mW/m K² at 700 K at optimized carrier concentration, which is confirmed by the Boltzmann transport calculations performed in this study.

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Excimer laser irradiation of amorphous IGZO thin films for thermoelectric device applications

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Amorphous InGaZnO (a-IGZO), a well-established channel material for thin film transistors, has also been recently explored for thermoelectric (TE) applications owing to low thermal conductivity and relatively high mobility. However, annealing at high temperatures ($T > 300^{\circ}\text{C}$) typically needs to be employed for several hours to significantly enhance its TE performance. Excimer laser annealing (ELA) was previously reported to instantly enhance the electrical conductivity (σ) of IGZO at a low substrate T . In this work, ELA was utilized to improve the TE power factor of the a-IGZO thin films. The a-IGZO thin films (200 nm thick) deposited on glass were irradiated with a single shot of KrF excimer laser ($\lambda = 248$ nm, *pulsewidth* = 9 ns) throughout the sample surface at varying fluence ($F = 100, 120$ and 140 mJ/cm²) under air. After metal electrode deposition following a typical four-point probe configuration, TE properties were measured using a physical properties measurement system at 1 Pa from 100 – 400 K. Compared to the as-deposited a-IGZO, an about fifteen-fold increase in σ was observed even at 100 mJ/cm², but Seebeck coefficient (S) dramatically decreased. Increasing the fluence to 120 mJ/cm² led to insignificant changes in values. However, when 140 mJ/cm² was used, further increase in σ was observed, but no change in S occurred. ELA irradiation is therefore successfully demonstrated as an ultrafast, near RT treatment for future IGZO transparent and flexible thermoelectric devices.

Fabrication of lotus-type porous thermoelectric materials by continuous casting method

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Lotus-type porous materials can be fabricated by unidirectional solidification under hydrogen atmosphere. The formation of pores is due to a gap of hydrogen solubility at the melting point, that is, a sort of an invariant reaction, $L \rightarrow S + G$. It has been confirmed that we can fabricate lotus-type porous thermoelectric materials such as Si, Mg_2Si , and Constantan. In this study, we have tried to fabricate lotus-type porous thermoelectric materials by continuous casting method in order to develop new thermoelectric devices. The continuous casting method can fabricate a large amount of lotus-type porous thermoelectric materials that are long in the pore direction. In this study, we have attempted to fabricate lotus-type porous Si, $Al_2Fe_3Si_3$ and Constantan by continuous casting. In the experiments, the transference velocity and the partial pressures of the H_2 -Ar atmosphere were varied to examine their effects on pore formation.

Existing composition range of the $\text{Al}_2\text{Fe}_3\text{Si}_3$ phase and its composition dependent thermoelectric properties

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Recently, $\text{Al}_2\text{Fe}_3\text{Si}_3$ (τ_1 phase) has been suggested to show excellent thermoelectric properties near room temperature by first-principle calculation and Boltzmann transport equation. Al, Fe and Si are abundant and non-toxic elements. The Al-Fe-Si ternary system has many intermetallic compounds and hence it shows a complex phase diagram.

In this work, the equilibrium phase diagram of the Al-Fe-Si system was examined. We made samples that are supposed to have compositions within two phase regions between the τ_1 phase and other phases. They were annealed for long time to investigate the equilibrium phase boundaries at 900°C. It has been found that the τ_1 phase lies as a line at an iron concentration around 39 at.% extends in aluminum/silicon ratio from 0.53 to ~1.90. These results are similar to a reported phase diagram.

We also investigated the composition dependence of thermoelectric properties of the τ_1 phase using a composition-graded diffusion couple, which were made by diffusion bonding between an Al rich and Si rich samples of the τ_1 phase. It has been found that the τ_1 phase exhibits a variation in the Seebeck coefficients from positive to negative values as the Si concentration increases. We will also report results of the electrical resistivity and the thermal effusivity of the τ_1 phase.

Structure optimization of thin film thermoelectric generator

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Since the thin film thermoelectric generator (TEG) can be fabricated by semiconductor process, it is suitable for large area, low cost and mass production. Therefore, the thin film TEG can be applied as a power source of self-powered IoT devices including wearable devices. However, a novel method to control the heat flow in the thin film is required to drive the device. Thus, optimizing the device structure is more important than bulk devices. In this study, structural optimization of the thin film TEG were performed. In our proposed structure, the optimization of material and size is particularly important, and the simulation results show that the output power density is $0.67 \mu\text{W}/\text{cm}^2$ for a thin film with $\text{PF}=1.0 \text{ mW}/\text{mK}^2$ at a temperature difference of 10 K. Thus, if a thin film material with a PF of about $15 \text{ mW}/\text{mK}^2$ can be realized, it is possible to generate up to $10 \mu\text{W}/\text{cm}^2$, which is sufficient to power IoT devices.

Development of multiple diffusion method to facilitate phase diagram investigations

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In recent years in material development, the number of constituent elements has increased to improve performance. On the other hand, it increases efforts required to examine phase diagrams necessary for material research. Examples include thermoelectric materials such as $\text{Al}_2\text{Fe}_3\text{Si}_3$, which has recently been found to show excellent thermoelectric properties at room temperatures, and high entropy materials such as CrMnFeCoNi , which are defined as solid solution alloys composed of five or more elements. The Al-Fe-Si system has many intermetallic compounds and hence it shows a complex phase diagrams. Large number of constituent elements makes it difficult to know phase diagrams if one uses a conventional experimental technique such as annealing many samples with various compositions. Therefore, a method that can easily examine a phase diagram is desired. In this work, we propose a multiple diffusion method that can easily study phase diagrams of multicomponent systems. We have developed analyses to obtain tie lines and phase boundary compositions and applied them to the Al-Fe-Si system and high entropy materials.

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Synthesis and transport study of bulk polycrystalline molybdenite

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Molybdenite or Molybdenum disulfide (MoS_2) is an indirect gap semiconductor in bulk morphology with the gap of 1.4 eV. Bulk polycrystalline Molybdenite sample prepared through Plasma Spark Sintering technique have been studied through structural analysis and transport measurements. The prepared sample is in amorph phase, *n-type* doped with the carrier density of $1.7 \times 10^{18} \text{ cm}^{-3}$. We plan to present our findings through a poster at the VCT2020 virtual conference.

Determination of the thermoelectric figure of merit using the peltier cooling effect

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The maximum temperature depression, ΔT_{max} , that can be obtained using the Peltier effect is simply related to the figure of merit, ZT , of a thermocouple and can, in principle, be used to determine that quantity. However, for good thermoelectric materials, with ZT of the order of unity or greater, this temperature depression, ΔT_{max} , can be very large and it is difficult to assign the measurement to a particular temperature. This is less of a problem if the thermocouple consists of a semiconductor and a metal since ZT and ΔT_{max} are then much smaller. We have been developing a procedure for the measurement of the dimensionless figure of merit of a semiconductor using semiconductor-metal thermocouples in which the relative form factors of the two branches are optimised. We also show that there are attractive features in the measurement of ΔT_{max} when the ratio of the form factors for the two branches is very far from being optimised. Our experiments on couples consisting of a bismuth telluride alloy and constantan show that radiation losses are significant at ordinary temperatures.

Europe Program

Development of thermoelectric sensors based on GaN for measuring the thermal flux of High Electron Mobility Transistors

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High power output can be obtained with new generation “High Electron Mobility Transistors” (HEMTs) which use AlGaN on GaN heterostructures, however, the high power dissipated by HEMTs can lead to them overheating (150°C - 300°C) and cause their degradation.

Integrated thermoelectric (TE) sensors have been developed to manage the HEMT’s thermal flux and prevent them from reaching critical temperatures and deteriorating. The temperature gradient within the sensor, due to the hot HEMT at one side and a cooler ambient temperature on the other side, creates a voltage due the material’s thermoelectric properties directly proportional to the HEMT’s temperature.

In-situ TE sensors are fabricated simultaneously with HEMTs, in order for them to be located closest to the transistors for a more precise and faster thermal measurement. They use the same materials as the HEMTs – GaN and AlGaN – and must follow exactly the same fabrication steps. A computerised model of the sensor was created using a finite element programme to simulate the device with the best compromise between the highest output signal and smallest response time, and the lowest resistive geometry. This was done using the material’s previously-measured thermoelectric property values. Sensors are fabricated in our clean rooms and electrically tested in our laboratories. Results from the characterisation of our TE sensors will be presented.

Towards Efficient Waste Heat Recovery in Aircrafts using Thermoelectrics

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Emissions from the passenger aircrafts result in 2.4% of total, global CO₂ emission in 2018. The amount of these emission is predicted to grow and reach 25% of the global carbon budget. Additionally, the increasing demands for on-board electrical power require aircrafts to be more fuel efficient. Thermoelectric generators (TEGs) have been identified as a possible means of aircraft Waste Heat Recovery (WHR) which can help reduce fuel consumption in aircrafts by 0.5% , saving \$12 M monthly in operating costs. However, owing to the requirement of large heat transfer surfaces and heavy heat spreaders, TEG based WHR systems with high power density (kW/kg) is challenging to achieve. The present study seeks to exploit the temperature difference that exists between the cold (~-50°C), ambient air of an aircraft and the high temperature (~200°C), waste heat from a Turbo-fan engine. With consideration to spatial, thermal fluid and weight constraints; three distinct heat exchanger designs were studied by developing and comparing their engineering models. The most efficient of these systems was developed into a lab-scale TEG based WHR system for a 1 m² fuselage wall. The experimental results were used to verify the analytical model and gain insights into the system that may not have been captured using modelling.

Autonomous volcanic monitoring stations: combination of thermoelectric generators and Internet of Things (IoT)

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Although there is a lack of commercial thermoelectric applications mainly due to their low efficiency, there exist some cases in which thermoelectric generators are the best option thanks to their well-known advantages: reliability, lack of maintenance and scalability. This work develops a novel application to supply power to volcanic monitoring stations, making them completely autonomous. These stations are indispensable in any volcano, since they can predict eruptions. However, they present energy supply difficulties due to the absence of power grid, the remote access, the climatology and the corrosion. As a solution, this work proposes the combination of thermoelectric generators and IoT technologies. Thus, the heat emitted from volcanic fumaroles is transformed directly into electricity with thermoelectric generators with passive heat exchangers based on phase change, leading to a continuous generation without moving parts that powers different sensors, whose information is emitted via LoRa. The viability of the solution has been demonstrated both at the laboratory and at a real volcano, Teide (Spain), where a compact prototype has been installed in an 83°C fumarole. The results obtained during more than 5 months of operation prove the robustness and durability of the developed generator, which has been in operation without maintenance and under all kind of meteorological conditions, leading to an average generation of 0.54 W and a continuous emission over 14 km.

Impact of BG+H₂ flames in thermoelectric power generation

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The economic development at a global scale led to an increased demand for electricity in activities from isolated communities and rural areas (not connected to the grid). Being a technology in constant improvement, thermoelectric devices might soon integrate solutions for this demand. Renewable fuels (such as biogas and H₂) are energy sources valued for having a high energy density and yet a reduced carbon footprint. Considering that biogas (BG) has a high CO₂ content, the effects that the addition of small amounts of H₂ can produce in BG combustion have been a focus of study in recent years.

In this work, the viability of using premixed BG+H₂ flames combined with thermoelectric devices (for direct heat-to-electricity conversion) was studied. In the setup used, the major challenges for power and efficiency optimization were related to heat transfer from flame and burnt gases to the device. Therefore, the flow velocity field and flame-wall interaction were studied via experimental techniques.

Results showed the benefic impact that H₂ can have as a biogas dopant. Even in reduced amounts (up to 20% in volume), the power yielded increased by 10%. The improvements observed in flame stabilization and quenching distances (to typical levels of pure methane) prove that H₂ would enable this concept in smaller, portable applications, with downsized combustion chambers. If a final concept is to be implemented, key aspects inferred from the obtained results should be considered.

Design and optimization of a thermoelectric generator for the high enthalpy superficial geothermal anomalies of Timanfaya National Park

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Thermoelectricity applied to geothermal energy has great future potential due to its robustness, reliability and it needs no maintenance since it is a technology with no moving parts. However, the efficiency of a thermoelectric generator highly depends on heat exchangers.

The aim of this project is to develop a prototype of a thermoelectric generator which transforms the heat in the ground of the Timanfaya National Park into electricity. Therefore, heat exchangers are designed and built specifically for this application. The function of these exchangers will be to transport the heat with the maximum possible efficiency from the inside of the well (hot side) until the thermoelectric modules, using a part of this heat to generate electricity and another part to dissipate it into the environment through exchangers on the cold side. The principle of operation of all these exchangers will be the heat exchange by thermosiphon and phase change.

During the study, different designs and improvement possibilities were evaluated, the prototype was built and it was finally experimented in the laboratory with different conditions, temperatures and heat flows. The prototype will be located in a well in the Timanfaya National Park, Lanzarote, reaching temperatures between 200°C and 500°C in just a few meters inside the ground.

Performance Prediction of a Temperature-controlled Thermoelectric Generator Recovering the Exhaust Heat of medium Duty Vehicle during Driving Cycles

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The automotive industry is pressed with increasingly stringent efficiency and emissions goals. Medium and Heavy-duty vehicles are having increasing degrees of hybridization. Therefore, on-board electricity production seems highly attractive.

Thermoelectric (TE) generators are able to directly convert the exhaust heat into electricity with no moving parts and unlike competing technologies, need little to no maintenance if carefully designed. They are temperature limited, and their electric output is very sensible to the thermal level. It is a challenge to design a system so that it provides an optimized operation under the wide range of operating conditions found in realistic driving.

The present work assesses the performance of a TE generator incorporating thermal control through the use of a phase change heat spreading device incorporated into the exhaust heat exchanger (HE). Whenever the temperature limit is exceeded at the hotter upstream regions of the HE, the device absorbs heat by vaporization and spreads this heat by condensation at the colder regions of the heat exchanger.

Driving cycles were simulated with a medium-duty vehicle using the software ADVISOR for the vehicle energy model and a thermoelectric and a heat transfer model described in previous work. Results indicate that the system is able to achieve an efficiency that is close to the maximum efficiency of the TE modules and with an output level that seems to be a breakthrough for road vehicle TE generators.

Development of a computational model that simulate a thermoelectric subcooling system in a supercritical CO₂ refrigeration cycle

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Nowadays, due to the increasing climate change problem, several sector regulations in the refrigeration market are leading to the use of natural refrigerant fluids such as CO₂ with very low impact on global warming. These systems operate under transcritical conditions most of the time at warm climates resulting high working pressures. It has been demonstrated that under this conditions when a subcooling system is introduced in to the cycle the efficiency of the cycle rises.

In this work, a computational model that simulate a thermoelectric subcooling system in a supercritical CO₂ refrigeration cycle has been developed. The model represents the vapour compression equipment and a subcooling system powered by thermoelectric modules that takes into consideration thermal resistances of the heat-exchangers, thermal losses, thermal contact resistances and every thermoelectric phenomena.

On the Relevance of Defects for the Selection of Contacting Electrodes: Ag for Mg₂(Si,Sn)-based Thermoelectric Generators

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In developing thermoelectric generators, optimizing the interfaces between thermoelectric materials and contacting electrodes is a crucial step. Among the tested electrodes for Mg₂X (X = Si,Sn)-based generators, Ag shows a controllable interface and low electrical contact resistance. However, it induces changes in the Seebeck coefficient of *n*-type samples, while no change is observed in *p*-type. To understand this, Ag-contacted Bi-doped Mg₂Si, Mg₂Sn and their solid solutions are compared with predictions based on defect formation energies obtained within hybrid-density functional theory (DFT).

The calculations show that Ag-induced defects have formation energies low enough to influence charge carrier concentrations, particularly Ag on Mg site. It acts as acceptor and causes a compensation of the Bi electrons. However, in *p*-type, as Li defects have the lowest formation energies, no charge compensation is predicted to occur, which fits experimental observations. As for solid solutions, a rough interpolation of the binary results predicts a similar behavior where the Seebeck would only be affected in *n*-type, which also meets experimental data.

This work proves the importance of defects in electrode selection. Such correlation between thermoelectric data and defect formation energies will be investigated in a future work to study the interactions between potential electrodes and Mg₂X, which would provide a first screening of contacting electrodes for technological applications.

Aluminium as an electrode for Mg₂(Si,Sn)-based thermoelectric generators

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Mg₂(Si,Sn) is an excellent thermoelectric (TE) material in the mid- to high temperature range, which has advantages with respect to cost, toxicity and abundance. Several attempts at finding a good electrode for this material are reported, without complete success due to mismatching coefficient of thermal expansion (CTE) (Ni) or an induced change in the transport properties of the TE material (Ag, Cu).

In this work, aluminum is evaluated as electrode material for Mg₂(Si,Sn) due to its low cost and matching CTE. The synthesis of functionalized legs is a two-step process where the joining step is made with a pressure of 28 MPa at 500°C for 10 min. The specific contact resistance r_c of the Mg₂Si_{0.3}Sn_{0.7} pellets joined with Al is measured using a Potential & Seebeck scanning Microprobe and corresponds to $9 \pm 5 \mu\Omega \text{ cm}^2$ (*p*-type) and $3 \pm 2 \mu\Omega \text{ cm}^2$ (*n*-type). No change is observed in the TE properties, nor is the formation of secondary phases between the TE material and the electrode, which makes aluminum the current best electrode for a Mg₂(Si,Sn)-based thermoelectric generator.

In order to test the long-term stability of the contacts, the samples were annealed for 1 and 2 weeks at 450°C under argon atmosphere. It is found that the contact resistance of the junction does not deteriorate and that a Sn-rich phase appears in the TE material at the interface. The *n*-type Seebeck coefficient is altered, but it is suspected to be due to Mg evaporation rather than an effect of the Al electrode.

FEM Simulation of thermal response of thermoelectric Bi₈₈Sb₁₂ thin films under the terahertz irradiation

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Terahertz (THz) devices can be used for imaging, sensing, security systems, safe medical diagnostics, and other promising applications. The effect of electromagnetic heating due to THz irradiation absorption can be used as the basis for thermoelectric (TE) sensors development. Bi and Bi-Sb thin film structures seem to be promising materials for THz detecting due to the relatively small overlap between energy bands compared to THz emission energy. The study of electrical conductivity and relative permittivity of Bi and Bi₈₈Sb₁₂ films on mica substrate in THz frequency range (0.3 - 0.8 THz) has been carried out. Films thickness was 70 and 150 nm. The simulation of electromagnetic heating under the THz irradiation power from 1 μ W to 50 mW has been performed using a finite elements method. The possible heating up to 0.1 - 1 K has been shown. The responsivity of several mV/W has been calculated.

Thermoelectric Generator Concept Suitable for Large-scale Industrial Waste Heat Recovery

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The industrial sector wastes a large portion of its process energy through the form of waste heat. Thermoelectric (TE) generators are known for their capacity to directly convert heat into electricity without moving parts and thus with little to no maintenance. They are also highly scalable due to their modularity. However, their deployment in large-scale Industrial Waste Heat Recovery applications has still not been effectively achieved. Actually, the viability of large-scale applications requires reducing substantially the degree of complexity and cost per unit power found in conventional thermoelectric modules.

The authors have been developing promising, non-hazardous earth-abundant materials, namely, p-tetrahedrites (pT) and n-magnesium silicides (nM), which reach figures of merit (ZT) around unity, a very good prospect for cheap materials, as well as geometries suited for up scaled systems.

The present work proposes and assesses a concept suitable for large-scale industrial applications. A generator composed of large pT-nM pairs connected with cheap aluminium connectors is assessed. The connectors also act as a heat transfer medium between the heat source and the TE elements, with their size being optimized for the specific thermal resistance of the heat source and the resulting optimal fill factor.

Bulk simulations were performed to optimize the geometry using simplified TE analyses and refined simulations were made using multiphysics approaches.

Assessing the transition from Si to SiGe nanowires as TE materials for MEMS-based microgenerators

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The thermoelectric performance of nanostructured silicon and silicon-germanium have been compared. Arrays of nanowires of both materials, grown by a VLS-CVD method, have been monolithically integrated in a silicon micromachined structure in order to exploit the thermoelectric properties of nanostructured silicon-based materials. The device architecture helps to translate a vertically occurring temperature gradient into a lateral temperature difference across the nanowires. Such uni-leg thermocouple is completed with a thin film metal leg. Despite showing a lower Seebeck coefficient and a higher electric resistance, the device with SiGe nanowires exhibited a much better performance leading to larger open circuit voltages and larger overall power. This was possible due to their lower thermal conductance of the nanostructured SiGe that enabled a much larger internal temperature difference, so that power densities in the $\mu\text{W}/\text{cm}^2$ could be obtained for such devices when heated in the 50-200°C range under natural convection without the presence of a heat exchanger.

Scalable Fabrication of Thermoelectric Generators by Combining Spray-Coating and Laser Structuring

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Thermoelectric energy conversion has become an important topic in energy research for utilization of wasted heat. Thermoelectric generators (TEGs) are capable of direct energy conversion of thermal energy into electrical energy consistently and without moving parts. Next to optimizing material's properties, there is an increasing interest in alternative additive and subtractive scalable manufacturing methods for easy and less costly device fabrication.

Here, a scalable manufacturing process for TEGs, which consists of spray-coating of the thermoelectric materials and subsequent laser structuring to control the resulting design, is presented. With this combination of additive and subtractive manufacturing, the resulting layer thickness as well as the structuring and the final design of the layers can be precisely controlled. The presented process is capable of fast fabrication of TEGs and on a large scale. A prototype device with ceramic $\text{Ca}_3\text{Co}_4\text{O}_9$ (front side) and Ag (back side) as thermoelectric materials was prepared and characterized. Here, a subsequent sintering step ensures the thermoelectric properties of the porous ceramic layers and leads to a rigid TEG. Due to the use of ceramic and/or metallic components, the prototype exhibits a high thermal stability up to 900 K. The universal fabrication method can be further extended to different kinds of thermoelectric materials and generator designs.

Practical development of efficient thermoelectric – photovoltaic hybrid systems

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Silicon solar cells dominate the photovoltaic (PV) market. Their high efficiencies, along with their low cost, make them the most valuable solution nowadays. However, it is well known that silicon solar cells are extremely sensitive to temperature, and they can lose up to 20% of their room temperature efficiency under operating conditions. In this perspective, less sensitive solar cells such as amorphous silicon (a-Si), Gallium Indium Phosphide (GaInP), and Perovskites, have been proposed as alternative solutions. However, the room temperature efficiencies of these candidate materials are still lower than silicon based devices. Hybrid Thermoelectric-Photovoltaic (HTEPV) systems, which recover solar cell heat losses to produce an additional power output, can be a suitable option to enhance the competitiveness of these kind of solar cells.

In this communication we report on the development and the characterization of home-made bismuth telluride thermoelectric generators, optimized to be hybridized with aSi, GaInP or Perovskites solar cells. The results showed in all three cases, efficiency gains ranging between 1.5 and 3.5%. These gains, in some cases were found to happen at typical operating temperatures of PV. For Perovskites solar cells the efficiency of the hybrid device was found to be higher than typical silicon solar cell efficiency. This experimental evaluation demonstrated in an accurate fashion the real potential of thermoelectric hybridization of solar cells.

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Performance of oxide thermoelectric generator based on hybrid p-n junction

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Most of the available oxides used today for fabrication of thermoelectric generators (TEGs), exhibit poor durability at high temperature caused by instability of the metal-oxide interfaces at the hot side. Here we demonstrate a concept of an all-oxide TEG based on a hybrid p-n junction, fabricated in one step by spark plasma co-sintering of $\text{Ca}_3\text{Co}_{4-x}\text{O}_{9+\delta}$ (CCO, *p*-type) and $\text{CaMnO}_{3-\delta}/\text{CaMn}_2\text{O}_4$ (CMO, *n*-type). Interestingly, we observed time-enhanced performance of the TEG attributed to the in situ formation of $\text{Ca}_3\text{CoMnO}_6$ (CCMO, *p*-type) and Co-oxide rich phases (*p*-type) at the p-n junction ($>700^\circ\text{C}$), hence the notation hybrid p-n junction. The TEG demonstrated a power density of $\sim 29 \text{ mW/cm}^2$ (7.2 mW) at $\Delta T \sim 650^\circ\text{C}$ after two-days of isothermal hold (hot side 900°C). This new concept of high-temperature TEGs by utilization of a hybrid p-n junction provides an easy-processing, cheap and high-performance high-temperature TEGs.

High-performance polycrystalline SnSe prepared by arc-melting: Pristine SnSe with negative Seebeck coefficient

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Recently, the SnSe semiconductor was identified, in single-crystal form, as a mid-temperature thermoelectric material with record-high figure of merit, high power factor and surprisingly low thermal conductivity, with the figure of merit ZT exceeding 2.5. It can also be doped appropriately to obtain both p - and n -type behavior.

Polycrystalline SnSe has similar excellent p -type properties when all contact with oxygen is avoided, and it has been demonstrated that the Sn and Se vacancies influence the transport properties. However, doping SnSe with donor or acceptor elements is more challenging than in other IV-VI chalcogenide semiconductors, like PbTe or GeTe. Thus, obtaining an n -type SnSe polycrystal is not an easy task.

Here we show that a straightforward, fast, and inexpensive arc-melting procedure followed by simple cold-pressing produces excellent n -type thermoelectric pellets. Neutron powder diffraction (NPD) reveals a slight Sn deficiency, probably affecting the transport properties. Additionally, X-ray photoelectron spectroscopy (XPS) confirms the effect over time of oxygen from ambient atmosphere on tin selenide surface. Although at lower temperatures this material has poor thermoelectric performance, it shows an exponential increase of the electrical conductivity with temperature, which along with the reasonably high Seebeck coefficient and the low thermal conductivity leads to the high $ZT \sim 1.8$ above 800 K.

Thermopower anomalies induced by resonant dopant Indium in thermoelectric SnTe

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Over the past few decade SnTe has re-emerged as a promising thermoelectric material due to its potential as an efficient thermoelectric materials. Being lead free, this makes it an interesting candidate for further thermoelectric investigations. Indium is a known resonant dopant that distorts the valence band structure in SnTe, thereby markedly enhancing the thermopower at high temperature. Nevertheless, a detailed study of the resonant effect at low temperature has never been performed.

In this work, we report on the synthesis and characterization of the thermoelectric properties of polycrystalline $\text{Sn}_{1.03-x}\text{In}_x\text{Te}$ ($0 < x < 0.02$). The synthesis was realized using the conventional power metallurgy method. Influence of excess Sn and In at low temperatures (5 – 300 K) on the thermopower, electrical resistivity, thermal conductivity and Hall effect was investigated. The results confirm the distinct role of In on the thermopower with room-temperature values that are higher than those measured in the binary $\text{Sn}_{1.03}\text{Te}$. An anomaly is observed in the form of a clear crossover from positive to negative value of thermopower for particular values of x with various scenarios possibly explaining this behaviour. The valence of In atoms in this system will be also discussed. The favourable influence of Indium, which results in an enhanced power factor, has also an impact on the residual electrical resistivity due to enhanced scattering by the resonant level.

Detailed structure and chemistry of structural defects in PbTe based alloys

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In a previous work,[1] the lattice thermal conductivity of the *p*-type $\text{Eu}_{0.03}\text{Na}_{0.025}\text{Pb}_{0.945}\text{Te}$ compound was reduced to the amorphous limit of $0.36 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, and a high zT of 2.2 was achieved at 850 K. Nevertheless, the responsible microstructure on the observed low κL , beside the generation mechanism of dislocations and its relationship with the dopant (Eu/Na) are still ambiguous. To that limit, we focus in this work on determining the number density and distribution of the dislocations and nanoprecipitates in the millimetre scale, using electron-channelling contrast imaging (ECCI) technique.[2] In the nanometre-scale, we use atom probe tomography (APT) to reveal that the dislocation cores are decorated by Na. We demonstrate the effect of the alignment and chemistry of dislocations on the low thermal conductivity by the Debye-Carruthers model.

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High-efficient n-type PbTe developed by advanced electronic structure engineering

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Lead telluride is one of the most attractive state-of-the-art thermoelectric (TE) materials. Therefore, any improvement of its average thermoelectric figure of merit $(ZT)_{av}$ over a broad temperature range is a great challenge. Here, we propose a new strategy of advanced electronic structure engineering using the In quasi-local level with simultaneous optimized EF for a significant enhancement of energy conversion. Electronic structure calculations confirmed the formation of a half-occupied indium quasi-local level in PbTe, which, together with I-implemented electrons, provides the optimal chemical potential in terms of energy conversion, near the conduction band edge over the entire temperature range. As a result, an extremely high average thermoelectric figure of merit $(ZT)_{av}$ of up to ~ 1.05 for temperature difference $\Delta T = T_h - T_c = 475$ K ($T_h = 773$ K, $T_c = 298$ K) was achieved. Thermoelectric efficiency was enhanced up to 14.2% for an n-type PbTe-based leg, which is a record-high value for a single-phase TE material. Moreover, as a result of the independence of the TE properties from the concentration of impurity for In-doped PbTe samples, the lifetime of the TE devices can be significantly elongated, making evident the great potential of this material for the construction of a new generation of energy conversion devices.

Strategies for the stabilization of mixed ionic-electronic conductors as thermoelectric materials: chances and limitations

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Mixed ionic-electronic conductors (MIECs) like Cu_2Se , $\text{LiGe}_{3.5}\text{Sb}_2\text{Te}_7$ or $\text{Zn}_{13-6}\text{Sb}_{10}$ (zT of ~ 1.5 at 1000 K, ~ 2 at 773 K and of ~ 1 at 400 K, respectively) have attracted much interest as they seem to exhibit excellent thermoelectric properties. However, electromigration is a problem as it leads to metal deposition and secondary phases. Investigations on $\text{Zn}_{13-6}\text{Sb}_{10}$ revealed decomposition already at voltages of ~ 0.01 V which is one magnitude lower than e.g. for Cu_2Se . Zn deposition and the formation of ZnSb with minor thermoelectric efficiency lead to increased Seebeck coefficients in parts of samples with decreased Zn concentration as shown by spatially resolved chemical analysis and Seebeck microprobe measurements.

3D X-ray diffraction computed tomography delivers insight concerning structural changes linked to transport properties and material degradation. Once $\alpha\text{-Cu}_2\text{Se}$ decomposes, a Cu-deficient phase with less favorable thermoelectric properties forms. The phase boundary between $\alpha\text{-Cu}_{2-6}\text{Se}$ and the HT modification moves along thermal gradients when Cu deposition occurs.

In order to stabilize MIEC materials, coating those aims at a fast syntheses of heterostructures consisting of particles covered with diffusion barrier layers. This technique does not require mechanical preparation steps after material synthesis in contrast to the fabrication of segmented thermoelectric legs, where slabs of conventional materials are sandwiched by additional carbon layers.

Understanding why disorder boosts the thermoelectric properties of kesterite $\text{Cu}_2\text{ZnSnS}_4$

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The crystallographic complexity of quaternary chalcogenides provides an opportunity for engineering defects and disorder to achieve specific properties. Kesterite (CZTS, $\text{Cu}_2\text{ZnSnS}_4$) seems to be particularly inclined to this: it displays several types of structural defects and can be stabilized in different crystallographic polymorphs.[1] This leads to a wide spectrum of consequences on thermoelectric properties, which physical origin is unveiled by experimental analyses and ab initio calculations. A remarkable case is the order-disorder transition of CZTS from *I-4* to *I-42m* crystal structures, which produces a sharp enhancement in the Seebeck coefficient.[2] Indeed, the increase of crystal symmetry in the disordered polymorph leads to a favorable electronic band structure characterized by flat and converged bands. Experiments prove the mechanism as a sharp drop in mobility and increase in carrier concentration are observed at the transition.[3] This, other than providing new understanding of the material, can cast light on profitable mechanisms to enhance the thermoelectric performance.

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Time-resolved in situ neutron diffraction study of solid-liquid-gas reaction in sulfides

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Structural and chemical transformations of mineral-derived materials have been achieved by solid state reaction in sealed silica tubes for a long time, making those reactions omnipresent in many research laboratories. Nevertheless, solid state transformations in sealed silica tubes are usually complex to monitor in real time, which leaves a large gap in the mechanistic understanding necessary for their improvement. We now report the real-time study of a solid state synthesis from elementary precursors transformations in a sealed tube by means of in situ diffraction of neutron. Focusing on the synthesis of synthetic germanite $\text{Cu}_{22}\text{Fe}_8\text{Ge}_4\text{S}_{32}$, we have directly monitored solid-liquid-gas reactions, the formation of intermediates, and conversions of similar space group. Our results reveal that sealed tube synthesis is highly dynamic, with reaction times much shorter than what actually used and revealed the importance of the cooling conditions. The technique also enabled us to probe directly the temperature stability.

Scaling-up the production of the promising copper sulfide thermoelectric colusite, $\text{Cu}_{26}\text{V}_2\text{Sn}_6\text{S}_{32}$

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Recently, derivatives of the natural mineral colusite, $\text{Cu}_{26}\text{V}_2\text{Sn}_6\text{S}_{32}$, have been studied for their outstanding thermoelectric properties. In particular, a large reduction in the lattice thermal conductivity has been observed in samples presenting process-controlled cationic disorder, reaching ZT values near unity at intermediate temperature. Because this material is composed of light, non-toxic, widely-available and inexpensive elements, we have begun to adapt the synthesis and consolidation of cost-efficient “V-Sn” colusite for large scale production. We demonstrate that high-purity colusite with good repeatable thermoelectric performance can be obtained from the scaled-up mechanical alloying of industrial-grade binary precursors and metal vanadium. In the same time, we introduce a series of multiscale defects linked to the synthesis mechanism, that depends on the SPS sintering conditions. Owing to the high sensitivity of the transport properties of colusite toward sintering temperature, we are able to observe and correct issues related to the scaled-up sintering of large monoliths of colusite materials. In particular, we use theoretical modeling of electrical and thermal fluxes to predict and observe experimentally the formation of temperature gradients within the samples. Finally, we demonstrate the feasibility of large, homogeneous and robust samples of “V-Sn” colusite for thermoelectric application.

Processing of tetrahedrite-based thermoelectric materials using tetrahedrite-tennantite copper ores

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Tetrahedrite-based compounds are considered a promising thermoelectric material. The tetrahedrite-tennantite series, that can be generically expressed as $\text{Cu}_6[\text{Cu}_4(\text{Fe,Zn})_2](\text{Sb,As})_4\text{S}_{13}$, is one of the most abundant sulfosalt minerals in the earth's crust. The Iberian Pyrite Belt (IPB), located in southern Portugal and Spain, is the host of the largest concentration of massive sulfide deposits worldwide, where the tetrahedrite-tennantite series mineral is one of the constituents. In this work we evaluate the effectiveness of combining synthetic tetrahedrite (ST) with tetrahedrite-tennantite ore samples (TTOS) in the mechanochemical synthesis (MCS) process of tetrahedrite-based compounds. The ore samples were collected from two distinct deposits within the Portuguese part of the IPB, the Neves Corvo mine and the abandoned Barrigão copper mine. The ST, also produced by MCS, were mixed with the TTOS in different mass ratios ranging from 20-80%. The influence of the chemical composition and phase constitution of the ore samples and of the mixing ratios will be presented in relation to the micro-structural properties of the obtained materials. The results here described are part of a broader study dedicated to the development of energy-harvesting applications based on tetrahedrite. This work is funded by national funds through the FCT – Fundação para a Ciência e a Tecnologia, I.P., under the project PTDC/EAM-PEC/29905/2017 (LocalEnergy project, <http://localenergy.lneg.pt>).

Protective coatings for thermoelectric tetrahedrites

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Thermoelectric generators (TEGs) are devices able to generate electricity directly from heat using the Seebeck effect. They are light and easy to transport, have no moving parts and can generate energy from waste heat.

Many materials used on TEGs contain toxic or rare elements, as Bi, Te, Pb, and exhibit small efficiencies (<10%). To change this tendency, it is important to discover new and more “greener” materials for TEGs. Recently, tetrahedrites have received great attention, especially due to their low cost and reduced toxicity, relatively high figures of merit and large natural abundance. To develop reliable TEGs, able to work without maintenance, it is fundamental that the materials are stable, have a high-performance and the capacity to maintain the efficiency at the working temperatures for long periods. However, previous studies indicated that tetrahedrites have a limited phase stability and suffer from oxidation and sulfur sublimation at high temperatures, which pointed to a maximum working temperature of 723 K and the need of apply protective coatings.

In this work, the tetrahedrites stability at medium temperatures was investigate under coated conditions. The materials were coated with 3 different coatings and exposed to air at 648 K for 500 h and 1000 h. The structural, microstructural and electrical transport characterization of aged materials was performed to examine if they decompose, oxidize, or if a significant change in Seebeck coefficient occurs.

Deciphering enhanced thermoelectric performance in disordered $\text{Cu}_2\text{ZnSnS}_4$ through ab initio calculations

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Variations of sintering temperature during the synthesis of the quaternary chalcogenide kesterite $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) give rise to different crystallographic polymorphs. These polymorphs can be differentiated by their thermoelectric (TE) performance as a function of the degree of disorder present within the crystal structure.[1] The characterization of these materials and measurement of their TE properties require experimental techniques; however, to obtain a fundamental understanding of the mechanisms responsible for their behavior requires theoretical analysis based on ab initio calculations. A remarkably increased Seebeck coefficient in the disordered polymorph of CZTS can be explained by observing the steeper slope of the calculated electronic density of states (DOS) at the Fermi energy, while experimentally observed decreases in mobility and increases in carrier concentration may be explained by the reduced curvature and increased degeneracy of the top of the valence band.[2] Additional information regarding thermal conductivity can be obtained by calculating phonon properties through the density functional perturbation theory (DFPT) formalism, while the calculated charge density and electron localization function (ELF) can be used to determine the nature of bonding within the disordered crystalline structure.

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Improved thermoelectric performance of Copper tin sulphide (Cu_2SnS_3 , CTS) via structural disorder

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CTS is a promising *p*-type thermoelectric material. CTS is reported in polymorphic crystal structure cubic (SG: *F-43m*) and monoclinic (SG: *Cc*). These polymorphs are identified as disordered and ordered structures, respectively. In the literature, the disordered-structured CTS has been reported only via acceptor doping, basing materials preparation on high-temperature Solid-State Reactions (SSR). Our approach, instead, relies on reactive ball milling, which is a bottom-up technique that helps to preserve the nanostructure, keeping a high density of crystalline defects with a non-homogeneous distribution of finely dispersed crystalline grains.

Binary sulfides CuS and SnS were milled in 2:1 for 30 minutes. Using XRD, SAED, and Raman spectroscopy, we observed that as-milled CTS shows a disordered structure, preserved with thermal treatment up to 500°C. By increasing the thermal treatment temperature, CTS gradually evolves towards the ordered structure, reaching complete order at 650°C. The disordered CTS has several times higher *zT* than the ordered CTS. This has been related to lower electrical resistivity and ultra-low thermal conductivity ($k \sim 0.26$ W/m-K), resulting from the disordered structure, promoting Phonon-Glass-Electron-Crystal (PGEC) characteristics. In our best knowledge, *zT* ~ 0.30 above 700 K is the highest in CTS samples without acting on the chemistry of the system.

Effect of the thermal disorder on the electronic and thermoelectric properties of Fe₂VAl

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Heusler-type Fe₂VAl compounds attract much interest for their application in waste heat conversion systems. The conversion efficiency of a thermoelectric module depends mainly on the thermoelectric properties of its components. This efficiency is proportional to a dimensionless quantity called figure of merit ZT ($Z = S^2\sigma / \kappa$).

Although the Fe₂VAl compound has a decent power factor $PF = S^2\sigma$, its conductive nature (semimetal or semiconductor) is not yet clarified especially at low temperature. In this study, DFT and AIMD are used to prior calculate the electronic properties then, the Boltzmann transport equations implemented in the Boltztrap code are employed to calculate the thermoelectric properties.

Our study shows that, in contrast to what is usually observed, both the increase in temperature and the formation of thermally activated Al/V inversion defects open the bandgap. This unusual behaviour is beneficial for the thermoelectric efficiency because an increase of the bandgap leads generally to an increase of the power factor and limits the effect of minority charge carriers at high temperature. Moreover, such an unusual behaviour is the key for reconciling all bandgap measurements performed on the Fe₂VAl compound using a standard generalized gradient approximation functional. Finally, we show that synthesizing a material containing Al/V inversions could be an efficient way for improving the thermoelectric properties of this family of materials.

Effect of microstructure on the thermoelectric properties of Ti(Co,Fe)Sb half Heusler

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Growing energy demand and climate change require the development of green energy sources. Thermoelectrics can contribute by generating electricity from any gradient of temperature without any movable parts. Establishing microstructure-property relationships is fundamental to the rational design of thermoelectric materials. In this work, the microstructure of a Ti(Co,Fe)Sb half Heusler thermoelectric is studied to understand the effect of grain boundaries, pores and precipitates on their thermoelectric properties.

The material is synthesized by arc melting, ball milling, hot pressing and annealing to ensure homogeneity. Characterization by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) reveals microscopic and nanoscopic pores and precipitates. In addition, elemental segregation at grain boundaries is investigated by TEM and atom probe tomography (APT). The observed microstructure is then related to the transport properties of Ti(Co,Fe)Sb.

Remarkable *n*-type thermoelectric performance in heavy-band half-Heusler phase ScNiSb

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Half-Heusler (HH) phase ScNiSb was synthesized by arc-melting combined with spark plasma sintering. X-ray diffraction revealed slight deviation from the MgAgAs prototype structure of HH phases, where Ni atoms in ScNiSb are off-centered from nominal 4c ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) Wyckoff site to quarterly occupied position 16e (x, x, x) $x = 0.256(2)$ [1]. Analysis of bipolar thermal conductivity uncovered curious feature of the investigated material, namely electrons in ScNiSb possess 8-times higher mobility than holes, which hampers thermoelectric performance of naturally *p*-type specimen. In order to benefit from unique characteristics of thermoelectric charge transport, we prepared *n*-type doped arc-melted samples ScNiSb_{1-y}Te_y. In close agreement to the expectation, the intrinsic mobility increased with doping by an order of magnitude. Simultaneously, with rising Te content we also observed increase in the effective mass of charge carriers from $0.7m_e$ for the valence band to $5.1m_e$ for the conduction band. The observation is in concert with ab-initio band structure of ScNiSb. Increase in both mobility and effective mass led to large weighted mobility of $334 \text{ cm}^2/\text{Vs}$ for ScNiSb_{0.9}Te_{0.1} at 300 K. Remarkably, the latter HH alloy showed enhanced thermoelectric performance, with the power factor attaining large value of $40 \mu\text{W}/\text{K}^2\text{cm}$ at 700 K. The project was supported by the National Science Centre (Poland) under research grant no. 2015/18/A/ST3/00057.

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Thermoelectric properties of self-substituted Fe₂VAl alloys

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Bi₂Te₃ is currently the best thermoelectric (TE) material in the market, displaying a dimensionless figure of merit $ZT = 1$ at 300 K. The Heusler alloy Fe₂VAl is a semi-metal and crystallizes at room temperature in the cubic *L21* structure. Fe₂VAl can either be doped as a *n*-type or a *p*-type conductor and its power factor (*PF*) is strongly improved – $PF_{\max} = 4.0 - 6.0 \text{ mW m}^{-1}\text{K}^{-2}$ at 300 K in *p*-type Fe_{2.04}V_{0.86}Ti_{0.1}Al [1] and *n*-type Fe₂VTa_{0.05}Al_{0.95} [2] respectively – to values which can be larger than that of Bi₂Te₃ ($PF_{\max} = 4.9 \text{ mW m}^{-1}\text{K}^{-2}$ at 300K). However, its TE performances are mainly hindered by its large thermal conductivity (λ) – $\lambda = 10 \text{ W m}^{-1}\text{K}^{-1}$ in *n*-type Fe₂VTa_{0.05}Al_{0.95} at 300K – conducting to values of $ZT \sim 0.2$ at 300 K. A reduction of thermal conductivity is thus necessary for the rise of Fe₂VAl.

Self-substitutions, which consist of the pure modification of the stoichiometry of raw elements was conducted. Self-substitutions introduce antisite defects, which modify the charge carrier concentration [3] and allow optimizing *PF*. These self-substitutions also give rise to atomic-scale mass defects which scatter the phonons and secondarily lead to a decrease of the lattice thermal. This presentation will focus on the alloy series Fe₂V_{1-x}Al_{1+x}, Fe_{2+x}V_{1-x}Al, and Fe_{2+x}VAl_{1-x} ($-0.1 \leq x \leq 0.1$).

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Segregation to crystal defects in Fe₂VAI Heusler compounds for improved thermoelectric performance

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The full-Heusler compound Fe₂VAI exhibits promising thermoelectric (TE) properties. By fast quenching, for example via melt spinning or surface laser remelting (SLR), a microstructure containing a hierarchy of defects can be generated. The defects include grain boundaries, antiphase boundaries (APB), and dislocations. The associated energy can drive chemical segregation, leading to a locally different composition. We report on the investigation of the microstructure of melt spun and SLR Fe₂VAI using scanning electron microscopy, atom probe tomography (APT), and field ion microscopy (FIM).

For melt-spun Fe₂VAI we observe platelet-shaped VC_xN_x precipitates located near {100}-APBs. The composition, determined by APT analysis, of these precipitates is V₆₃C₁₄N₁₀Fe₈Al₅ (at.%), which is close to a composition of (V,Fe,Al)₃(C,N). FIM micrographs are used to analyze an ordering of the Heusler phase.

Compared to melt spinning, SLR offers a more controlled manipulation of the microstructure and allows for facile systematic exploration of the influence of the quench conditions. We observe elongated grains growing nearly epitaxially from the heat-affected zone of the unmolten part. The grain size is strongly depending on the remelting parameters. At dislocations within the grain and at low-angle grain boundaries, we observe VC_xN_x precipitates.

Based on these findings, which can be linked to measurements of the TE properties, the microstructure-property relationship may be understood.

Enhanced thermoelectric performance of *p*-type nanostructured half-Heusler (Hf,Ti)Co(Sb,Sn) solid solutions fabricated by mechanical alloying

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Over the past decades, thermoelectric materials have attracted great interest due to their capability to reversibly convert heat into electrical power. Half-Heusler compounds were recently identified as promising, cost effective and environmentally friendly thermoelectric materials for medium-high temperature range applications. Reasonably high ZT s of up to ~ 1 , were achieved for both *n*- and *p*-type HH compositions which were mainly prepared by arc-melting method followed by several days of annealing. Even though the results are encouraging, the need for higher ZT values and more advantageous fabrication techniques still remains in order to use half-Heusler materials in large-scale thermoelectric applications.

The aim of this work is to investigate the thermoelectric properties of *p*-type (Hf,Ti)Co(Sb,Sn) solid solutions prepared by mechanical-alloying as an advantageous fabrication method. The temperature dependent thermoelectric properties (electrical conductivity, thermal conductivity and Seebeck coefficient) were measured on hot pressed pellets and the thermoelectric power factor and dimensionless figure of merit (ZT) values were estimated. In this presentation, our recent results on different compositions of (Hf,Ti)Co(Sb,Sn) based materials that were successfully prepared by mechanical alloying will be discussed.

Grain boundary engineering enhances the thermoelectric performance of *n*-type $\text{NbCo}_x\text{Pt}_{1-x}\text{Sn}$ half-Heusler alloys

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We reported on *n*-type half-Heusler (HH) alloys of $\text{NbCo}_{1-x}\text{Pt}_x\text{Sn}$ for thermoelectric (TE) applications. The microstructure was investigated at the nanometer scale by atom probe tomography (APT). Segregation of Pt is observed at grain boundaries. After annealing at 800°C for 7 days, the grain size of NbCoSn-Pt grows from 0.27 μm to 2.5 μm and the electrical conductivity is increased by ~50% at 296 K. The figure-of-merit (zT) increases after annealing and reaches ~0.6 at 773K.

The local enrichment of dopants at grain boundaries plays an important role as it could reduce the grain boundary resistance and thus improve the TE performance of NbCo(Pt)Sn HH alloy. This work reveals the complex interplay of structural defects and their individual chemical decoration states, allowing new insights into the underlying relationship between microstructure and TE performance.

Atomic and vacancy ordering in defective (V, Nb)CoSb and (V, Ta)CoSb half-Heuslers alloys.

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In this 12 minutes presentation, we report the current status of our studies in a relatively new class of half-Heuslers which have very promising thermoelectric properties, namely, defective half-Heuslers. Our results are based on DFT and Monte Carlo methods coupled throughout a cluster expansion. In particular, we focus on the effect of alloying in a sublattice corresponding to the atomic positions of Nb, V, or Ta in the presence of intrinsic vacancies, e.g the pseudo-quaternary $(\text{Nb}, \text{V})_x\text{CoSb}$ or $(\text{Ta}, \text{V})_x\text{CoSb}$. Here, x represents the total amount of vacancies in the material created by either the absence of any single atom (Nb, Ta, V) or the simultaneous absence of two of them (NbV or TaV). In our methodology, we first check the structural stability and electronical fingerprints of Nb_xCoSb , V_xCoSb , and Ta_xCoSb . Subsequently, we proceed to computationally alloy Nb/V and Ta/V over a wide range of vacancies in $(\text{Nb}, \text{V})_x\text{CoSb}$ and $(\text{Ta}, \text{V})_x\text{CoSb}$, correspondingly. We observe that the substitutions $\text{Nb} \leftrightarrow \text{V}$ or $\text{Ta} \leftrightarrow \text{V}$ in the presence of 20% of vacancies may open a semiconductor gap, similar to ones seen in $\text{Nb}_{0.8}\text{CoSb}$, $\text{V}_{0.8}\text{CoSb}$, and $\text{Ta}_{0.8}\text{CoSb}$. Indeed, we observe that for most of the atomic arrangements fulfilling the stoichiometry $(\text{V}, \text{Nb})_{0.8}\text{CoSb}$ and $(\text{V}, \text{Ta})_{0.8}\text{CoSb}$, the semiconducting gap remains, albeit some atomic geometries can reduce the width of the gap. We also analyze the short- and medium-range atomic ordering created by the vacancies and atoms.

Realizing *p*-type NbCoSn half-Heusler compounds with enhanced thermoelectric performance via Sc substitution

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N-type half-Heusler NbCoSn is a promising thermoelectric material due to favourable electronic properties. It has attracted much attention for thermoelectric applications while the desired *p*-type NbCoSn counterpart shows poor thermoelectric performance. In this work, *p*-type NbCoSn has been obtained using Sc substitution at the Nb site, and their thermoelectric properties were investigated. Of all samples, Nb_{0.95}Sc_{0.05}CoSn compound shows a maximum power factor of 0.54 mW/mK² which is the highest among the previously reported values of *p*-type NbCoSn. With the suppression of thermal conductivity, *p*-type Nb_{0.95}Sc_{0.05}CoSn compound shows the highest measured figure of merit $ZT = 0.13$ at 879 K.

Development of a New Low-Cost Measurement System for Electrical Conductivity, Hall Constant and Seebeck Coefficient at Temperatures up to 800°C

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The determination of the electrical transport parameters, such as electrical conductivity, charge carrier density, Hall mobility and the Seebeck coefficient over a wide temperature range and under different atmospheres are essential to characterize a material electrically. We report on a combined measuring device, which allows to measure all of these parameters within one measuring cycle up to 800°C.

The measurement device consists of two movable permanent magnetic yoke-systems of opposite polarity, as well as a fixed gas-floated measurement chamber in which a ceramic sample holder is installed. A screen-printed platinum heating structure on the bottom side of the Al₂O₃ sample holder was designed by FEM-Simulation allowing to heat a sample area of maximum 12.7 mm diameter up to 800°C by Joule heating. An additional screen-printed heater, also on the bottom side, is used to generate a temperature difference within the sample area. Thermal imaging validated a homogenous temperature distribution for Hall-measurements as well as a temperature difference for Seebeck-measurements. Four moveable electrodes on the top side allow measurements of any geometry according to van der Pauw's method. Two additional Au-Pt thermocouples were placed between the sample and the electrodes to determine the contact temperature and the occurring thermoelectric voltage. Measurements of known materials confirm the functionality of the measurement device.

Revealing nano-chemistry at lattice defects in thermoelectric materials using atom probe tomography

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The population of all non-equilibrium lattice defects in materials is referred to as microstructure. Examples are point defects such as substitutional and interstitial atoms, and vacancies; line defects such as dislocations; planar defects such as interfaces and stacking faults; or mesoscopic defects such as precipitates. These lattice imperfections are usually described in terms of their structural features, breaking the periodicity of the otherwise regular crystalline structure. Recent analytical probing at the nanoscale has revealed that their chemical features are likewise important and characteristic. The structure of the defects and their individual chemical composition, which results from elemental partitioning with the adjacent matrix, can significantly impact the electrical and thermal transport properties of thermoelectric materials. The emergence of atom probe tomography (APT) has now made routinely accessible the mapping of three-dimensional chemical composition with sub-nanometer spatial accuracy and elemental sensitivity in the range of tens of ppm. Here, we review APT-based investigations related to the local chemical decoration states of various lattice defects in thermoelectric materials. APT allows to better understand the interplay between thermoelectric properties and microstructural features, extending the concept of defect engineering to the field of segregation engineering so as to guide the rational design of high-performance thermoelectric materials.

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Coherent quasi-elastic neutron scattering and the phonon-liquid electron-crystal concept in AgCrSe_2

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Superionics have garnered much interest as thermoelectrics due to their ultra-low thermal conductivity. The proposed origin, the phonon-liquid picture can be tested by neutron scattering. Recent work on AgCrSe_2 has found contradictory evidence with very different diffusion rates. We have studied AgCrSe_2 using polarised neutrons and find the quasi-elastic response is dominated at low temperature by spin fluctuations and in the superionic phase by coherent dynamic disorder. We demonstrate that the diffusion is much slower than previously reported and confirm that it is not a phonon liquid.

Impedance spectroscopy as a tool for the detailed assessment of thermoelectric modules

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Impedance spectroscopy has been proved to be a useful method for the characterization of thermoelectric modules under suspended conditions. Although impedance models (equivalent circuits) have been recently advanced with the addition of different processes such as convection, radiation and spreading-constriction, we have found that deviations from these models still exist in experimental results, especially in the high frequency part of the impedance spectrum.

Here, we present a new more comprehensive equivalent circuit which covers all the key phenomena that affects the module performance. These new additions include the thermal contact resistance between the thermoelectric leg and the metallic strips (electrodes), the influence of the electrodes themselves, and the thermal contact resistance between the metallic strips and the ceramic layer. Moreover, a new spreading-constriction impedance element, which considers the variation of the heat flow in the radial direction at the outer ceramic surfaces, is obtained. This new equivalent circuit allows the qualitative analysis of different characteristic features that we have observed in modules fabricated by different manufacturers. The fact that impedance spectroscopy can identify all these phenomena opens the possibility of using this method as a tool to detect and monitor in great detail issues in thermoelectric modules.

Printing and Other Facile Fabrication Techniques for Chalcogenide Thermoelectric Materials

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The go to materials for thermoelectrics are Bi_2Te_3 and PbTe for room temperature and mid-temperature applications respectively. ZT was shown to be ~ 1 in these materials in the 1950s.[1,2] Te is, however, a rare element with an Earth abundance similar to Pt ($1 \mu\text{g kg}^{-1}$).[3] This along with the toxicity of Te, and the high embodied energy of material fabrication are some of the reasons that have prevented the wide scale use of thermoelectrics.

My recent work I have focused on facile fabrication techniques combined with more sustainable thermoelectric materials such as SnSe and Cu_{2-x}S . Printing has primarily focused on the production of films ($\sim 300 \mu\text{m}$), due to the limitations of printing techniques being studied for thermoelectrics, e.g. screen printing. Recent work I have conducted demonstrates that bulk printing can be achieved with ZT s in excess of 1.6.[3,4] Thermal evaporation is another facile technique. This has been used to evaporate films with unprecedentedly low thermal conductivity, below $0.1 \text{ W m}^{-1} \text{ K}^{-1}$. [5] Finally, I have successfully electrodeposited stoichiometric SnSe and measured the ZT of the electrodeposits.[6]

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Thickness dependence on the thermoelectric power factor of Nb doped SrTiO₃ thin films

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Transformation of the bulk properties into thin films is necessary for energy and niche application. However, thin films can accommodate high density of defects in the lattice and interfaces, which often reduces device performances. Here, we show a study on the thickness dependent thermoelectric power factor (PF) of Nb doped SrTiO₃ (Nb:STO) thin films grown by pulsed laser deposition technique on (LaAlO₃)_{0.3}(Sr₂TaAlO₆)_{0.7} - 001 substrates. As the films thickness decreases from 68 down to 5 nm, the electrical conductivity (σ) and thermopower (S) showed a systematic decrease in their respective values resulting in an overall decrease of the PF 6 to 1 $\mu\text{W}/\text{cmK}^2$ at 290 K. Our results indicate that the thermoelectric performance of Nb:STO thin films depends strongly on film thickness, and especially below a critical thickness of ~ 2 nm the films becomes almost inactive. The Seebeck coefficient is often inversely proportional to the electrical conductivity of the materials, however, interestingly this is not what we have observed in our samples. Origin of such trend is yet not clear, but we speculate that it is most likely due to the formation of defect states in the film lattice and at the substrate and film interfaces. This is currently investigated using DFT calculations.

Effect of Al and Bi dopants on thermoelectric properties of ZnO-based thin films

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This work reports on the optimization of the thermoelectric properties of ZnO-based thin films for applications that envisage coatings as transparent thermoelectric electrodes in devices. It has two main goals. One is to present a thermoelectric characterization of a 36 ZnO-based thin films batch produced by a custom-built d.c. magnetron sputtering setup. The other is to briefly describe the Frequency-domain thermoreflectance technique used to determine the thermal conductivity.

As previous studies reports, point defects are very effective in controlling the thermal conductivity on oxide-based thermoelectrics. Hence, the effect of Bi dopants on ZnO-based thin films was investigated for three concentrations of Bi, two thicknesses (500 nm and 250 nm) and for two types of based-films: ZnO and ZnO:Al. Three replicas of each described conditions were produced.

This design of experiment was drawn to minimize variability on analysis done. Thus, enabling an objectively evaluation the effect of thickness, Al and Bi doping on several properties of the films, namely on thermal conductivity, Seebeck coefficient, electrical conductivity and structural properties.

Results show that undoped ZnO has an almost zero Seebeck coefficient, which is enhanced, to $\sim 50 \mu\text{V}\cdot\text{K}^{-1}$, by dopants and that the introduction of Bi and/or Al dopants decrease the thermal conductivity to from 5 to $\sim 3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. In the best-case scenario, a thermoelectric figure of merit of ~ 0.01 was attained at room temperature.

Tuning ballisticity/diffusivity in asymmetric nanowire

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In the last decade, the improvement of elaboration processes allowed tailoring the physical properties of nanomaterials. Nanowires (NW) constitute a large group of nanomaterials, with a large potential for heat management and thermoelectric devices applications. Here, we studied different silicon NW with a crystalline core and an amorphous asymmetric shell for anisotropic thermal management. The core of the NW has a constant radius, while the shell radius increases either linearly, forming a conical shape, or in a step like manner forming a telescopic-like NW. The impact of this geometrical asymmetry on the thermal conductivity (TC) and vibrational properties has been studied. The wave-packets method was used to investigate the frequency dependence of phonon propagation within the NW. The effective TC has been also estimated in different directions, using the Non Equilibrium Molecular Dynamic method. We have observed a non-ballistic (diffusive) energy propagation both in the amorphous shell and in the crystalline core, with an influence of the distance to the free surface of the NW of the core/shell interface. Both the existence of the core/shell interface parallel to the heat flux and the thickness variation of the amorphous shells contribute to a direction dependent decrease of the TC, still keeping a large crystalline fraction useful to support the electronic transport. A forest of such asymmetric NWs would thus be an interesting candidate for thermoelectric devices.

Electrochemical deposition and thermoelectric characterisation of a semiconducting 2-D metal-organic framework thin film

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Conductive metal organic frameworks (c-MOFs) are hybrid materials composed of inorganic and organic building blocks, in which metal nodes are coordinated to highly conjugated organic linkers. The overlap between the metal and ligand frontier orbitals facilitates the charge transport in these materials. Porosity and heterogeneity in atomic species and linkers are features that have led to a predictably low thermal conductivity making c-MOFs potential candidates for thermoelectric generators (TEG). To implement their practical use, the synthesis and study of ultrathin c-MOFs nanosheets have recently been reported; however, the processing at large scale of these materials is still a challenge.

In this work we present an electrochemical approach to the growth of conducting thin films of the 2D c-MOF $\text{Cu}_3(\text{HHTP})_2$ (where HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene). Bulk $\text{Cu}_3(\text{HHTP})_2$ was synthesized solvothermally according to the literature and we have subsequently fabricated thin films of this important framework by anodic electrochemical synthesis. We report the first thermoelectric measurements of this framework both in bulk and thin film form which resulted in Seebeck coefficients of $-7.24 \mu\text{V/K}$ and $-121.4 \mu\text{V/K}$ with a power factor of $3.15 \times 10^{-3} \mu\text{W/m}$ for the film respectively. The study of conducting MOFs and their performance as TEG is expected to expand and offer alternatives to non-toxic, scalable and high-efficiency novel TEG materials.

Silicon Nanowires as antennas for thermal conductivity reduction in silicon thin films

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The reduction of thermal conductivity is a key point in the manufacturing of thermoelectric materials. Recently, it has been introduced the concept of nanophononic metamaterial (NPM), where material thermal conductivity may be reduced without affecting electron transport properties. Following the theoretical studies of Davis *et al.* and for both practical and functional purposes, silicon is the foundation material for the creation of a locally resonant NPM. The resonators take the form of an array of silicon nanopillars on top of silicon thin film surface. The phonon modes of the array may hybridize with the phonon dispersion of the underlying film, causing significant reductions in the group velocities of the film phonon modes – and consequently a reduction of its lattice thermal conductivity. In this work, we will present the development of a procedure introduced by Pennelli *et al.* to extrude Si nanopillars from a single-crystalline (100) silicon surface by Metal assisted Chemical Etching (MaCE). We will present the results of a systematic analysis of the interdependence among etching conditions, silicon doping and the microstructure of the nanopillars. An attempt will be made to provide a first interpretation of such interdependence based on the competing electrochemical mechanisms of etching. The results are expected not only to pave the way to the fabrication of Si NPM but might have relevance in view of the making of TEGs based on Si nanowires.

Morphologic effect of ZnO nanoparticles on the thermoelectric performance

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Nanostructure engineering has been extensively applied to the thermoelectric (TE) field due to the myriad of possibilities that arise to improve TE efficiencies. One of the materials that can benefit from this approach is Zinc Oxide (ZnO), having low toxicity, high thermal stability, reduced production costs, and very low environmental impact.

In this work, tailored ZnO nanoparticles were produced and studied to enhance their TE properties through the manipulation at the nanoscale. Nanometric phonon scattering effects were observed, arising from the morphology of the nanoparticles. The phononic phenomena was predominant on the thermal conductivity (k) where the structures are smaller (~ 50 nm), compared with the clusters formed afterwards (~ 4 μm). From the transport properties evaluation, it was possible to see the reduction of k by 30% (~ 0.5 $\text{Wm}^{-1}\text{K}^{-1}$) by quantum confinement. This approach arises from the that influence the heat diffusion, increasing the TE efficiency.

These ZnO nanoparticles were synthesized by a chemical co-precipitation route based on the addition of two solutions: $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and NaOH. It was possible to manipulate the structural and the morphological characteristics of ZnO (preferential direction and particles shape), by only varying the concentration of NaOH in the co-precipitation method. Discussion concerning the morphological effect on the transport properties will be addressed, to understand the phenomena involved.

Thin film Chalcogenide thermo-electric materials by CVD

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High performance thin film thermoelectric generators are a promising technique to produce sustainable power supply for the IoTs sensor networks. We have recently developed a series of novel single source precursors, $[\text{BiCl}_3(\text{EnBu}_2)_3]$ ($\text{E} = \text{Se}, \text{Te}$), which enable chemical vapour deposition of binary Bi_2Te_3 , Bi_2Se_3 , and ternary $\text{Bi}_2(\text{Se}_{1-x}\text{Te}_x)_3$ thin films with very good compositional, structural and morphological control [1]. As well as binary Sb_2Te_3 , and Sb_2Se_3 films from a single source precursor of $[\text{MeSb}(\text{EnBu})_2]$ [2,3]. Not only do these reagents produce high quality films with competitive thermoelectric properties but, they also permit highly selective deposition of the materials onto the conductive TiN surfaces of patterned substrates [2-4]. This selective deposition behaviour has enabled a novel processing method for the fabrication of material-efficient thin film thermoelectric micro-generators [3]. In this work, we report on the measurements of Seebeck coefficient, and electrical conductivity of those films. Thermoelectric characterisation reveals that Se content in $\text{Bi}_2(\text{Se}_{1-x}\text{Te}_x)_3$ thin films can optimise the carrier concentration to give a fourfold increase in power factor. Characterisation also shows that reducing deposition temperature can be used to improve the performance of Sb_2Te_3 .

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Seebeck coefficient in MgAgSb thin films elaborated by Magnetron sputtering

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In the case of technologies such as microelectronics integrated circuits (IC), for which a part of the energy is thermally lost, the integration of thermoelectric devices appears as a potential energy harvesting solution. these devices should be nanostructured, such as thin films, elaborated with industrial processes compatible with the complementary metal oxide semiconductor (CMOS) technology, and can be used at room temperature (RT). α -MgAgSb has attracted wide attention as promising thermoelectric compound for RT applications. It exhibits a ZT near to 1 at RT that can be increased by doping. but, the presence of secondary phases in the samples, such as Ag_3Sb , was found to mitigate the thermoelectric properties. Moreover, this material was only studied in its bulk state. This work reports for the first time Mg-Ag-Sb thin films fabrication and properties using the magnetron sputtering. The elaborated films contain principally two phases Ag_3Sb and α -MgAgSb approximately in the same proportions but exhibit different microstructures. The Seebeck coefficients measured on the different films was found to be identical despite their difference of microstructure and interface density. Theoretical Seebeck coefficient values of the main phases present in the films were studied within the framework of density functional and Boltzmann transport theories. The effective Seebeck coefficient depends only on the volume of each phase present in the film and their Seebeck coefficients.

CVD of Tin and Germanium Chalcogenide Thin Films for Thermoelectric Applications

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A number of exciting group 14 chalcogenide semiconducting materials have been identified for applications in thermoelectric devices and when nanostructured these materials are predicted to perform even more favourably. Using low pressure chemical vapour deposition (LPCVD) with single source precursors (SSPs) allows for a number of unique benefits when compared to other deposition techniques for the production of thin films. One of these benefits is the potential for selective deposition, whereby film deposition occurs onto one substrate material type preferentially over another; thus patterned substrates can yield patterned depositions. This may enable much simpler fabrication of thermoelectric microgenerators, without the need to etch (and thus waste) the thermoelectric materials and reducing the processing costs.

The work described will detail the synthesis for a family of compounds that are effective single source precursors for SnE and GeE (E = S, Se, Te), their application for thin film deposition and characterisation of the resulting thin films using grazing incidence X-ray diffraction, scanning electron microscopy with energy dispersive X-ray spectroscopy and Raman spectroscopy and measurement of both their electrical and thermoelectric properties.

The tin and germanium chalcogenide films show promising properties for thermoelectric applications.

Insight into the templating effect of PEDOT:PSS on Te nanowires

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Progress in hybrid thermoelectrics has been driven by the developments of composites based on poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), which have shown high thermoelectric performances at room temperature, as seen in hybrids of tellurium nanowires (Te NWs) coated with PEDOT:PSS. This enhanced performance has been attributed to a templating effect of the organic component on the inorganic surface, creating an interfacial region of high local ordering and contributing to an enhanced carrier transport. Theoretical descriptions of this templating effect have been presented in the literature, but experimental reports are lacking. In this work, we investigate this templating effect by analyzing the interaction of PEDOT:PSS and Te NWs by X-Ray Absorption Near Edge Structure measured at the four-crystal monochromator beamline of PTB at BESSY II. We analyze the hybrid system at different stages during synthesis in order to observe the evolution of the interactions between PEDOT:PSS and the Te NWs through the X-Ray absorption profiles. At the same time, we performed small and wide angle X-Ray scattering experiments in order to monitor the growth and crystallization of the Te NWs, which we relate to development of the hybrid interface. Understanding the mechanism of polymer/nanoparticle interaction will have broad consequences via assisting in the design and implementation of new hybrid materials with tailored electronic and structural parameters.

Ge dopant enhanced nanoprecipitation and selective phonon scattering in the n-type $\text{Mg}_3\text{Sb}_{1.5}\text{Bi}_{0.5}$ nanocomposite thermoelectric material

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Nanocomposite is an effective approach to improve thermoelectric properties. Here, we report a 40% reduction in the lattice thermal conductivity of $\text{Mg}_3\text{Sb}_{1.5}\text{Bi}_{0.5}$ utilizing a local stress-induced phase separation, yielding an increased thermoelectric figure-of-merit of $ZT=0.6$ at room temperature and 1.5 at 450 °C. High-resolution TEM analysis revealed coherent nanoprecipitates with Bi-rich composition embedded in the lattice and dispersed at grain boundaries, which significantly increases phonon scattering. A size effect relative to the nanoprecipitates was observed, resulting from a balance the alloying disorder scattering and nanoparticle scattering to the phonons. The dopant Ge might open a miscible range between the Mg_3Sb_2 - Mg_3Bi_2 , which could be responsible for the increased nanoprecipitate size.

Topological materials for thermoelectrics

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Since the first-generation three-dimensional topological insulators were discovered in classic thermoelectric systems, the exploration of novel topological materials for advanced thermoelectric energy conversion has attracted increasing attention. The rapid developments in the field of topological materials, from topological (crystalline) insulators, Dirac/Weyl semimetals, to magnetic Weyl semimetals, have offered a variety of exotic electronic structures, for example, topological surface states, linear Dirac/Weyl bands, and large Berry curvature. These topological electronic structures provide a fertile ground to advance different kinds of thermoelectric energy conversion based on the Seebeck effect, magneto-Seebeck effect, Nernst effect, and anomalous Nernst effect. In this talk, we will present a brief introduction of utilizing different topological materials for various thermoelectric energy conversion applications based on their specific topological electronic structures.

Substitutional doping of hybrid organic-inorganic perovskite crystals for thermoelectrics

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Hybrid organic-inorganic perovskites (HOIPs) have generated considerable research interest in the field of optoelectronic devices due to their unique optical and electronic properties. However, there have been significantly fewer reports of the thermoelectric properties of HOIPs. In this presentation, we investigate the thermoelectric properties of bismuth-doped $\text{CH}_3\text{NH}_3\text{PbBr}_3$ single crystals. The high-quality Bi^{3+} -doped single crystals were synthesized by inverse temperature crystallization (ITC) and it was found that the Bi ions substitute onto the lattice of MAPbBr_3 single crystals with very little distortion of the crystal structure. Bi^{3+} doping does not significantly alter the thermal conductivity but dramatically enhance electrical conductivity of MAPbBr_3 single crystals by increasing the charge carrier density by more than three orders of magnitude. We obtained a negative Seebeck coefficient of $-378 \mu\text{VK}^{-1}$ for 15 % ($x = 0.15$) Bi-doped $\text{MAPb}_{1-x}\text{Bi}_x\text{Br}_3$ confirming n-type doping and also calculate ZT. This work highlights routes towards controlled substitutional doping of halide perovskites to optimise them for thermoelectric applications.

Thermoelectric effects in ionic-liquid based ferrofluids

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In a context of energy consumption control, waste heat harvesting has become a huge challenge. There is currently no efficient technology to convert low-grade thermal energy into electricity. Low power densities, high costs and toxic materials limit the use of conventional technologies such as solid-state thermoelectric devices. Alternative devices based on liquid thermoelectrochemical cells have recently shown interesting perspectives [1]. More specifically, due to their remarkable thermoelectric properties, ionic liquids (IL) and IL-based ferrofluids are promising materials. The addition of magnetic nanoparticles in ionic-liquids can indeed increase the thermoelectric coefficient (Seebeck coefficient) and power output [2].

In this work, we will present our latest experimental results of the Seebeck coefficient and power of a thermoelectro-chemical cell containing IL-based ferrofluid and cobalt redox couple. We will discuss how the thermodiffusion of magnetic nanoparticles can increase the Seebeck coefficient in these electrolytes and enhance the power output of thermogalvanic cells. Finally, we will present the behaviour of these ferrofluids as thermally-chargeable supercapacitors.

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Room and high temperature mechanical properties of Mg_2Si , Mg_2Sn and their solid solutions

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Modeling of thermoelectric generators at working temperature requires temperature dependent mechanical properties. In this regard, we present elastic constants for the Mg_2Si - Mg_2Sn material system measured by two different ultrasound techniques at room temperature and up until 623K. Undoped binary Mg_2Si has a Young's modulus of 110GPa, while the value for Mg_2Sn is 78GPa, both agreeing with previous reports. Experimental values for the Young's modulus of the solid solutions exhibit a linear behavior both in dependence of composition and temperature. Using the Poisson ratio, we furthermore, estimated the temperature dependent shear modulus. This allowed us to establish a bilinear equation to predict both elastic moduli as a function of temperature and composition. Interestingly the study of n-type samples of $Mg_2Si_{0.3}Sn_{0.7}$ revealed a reduced Young's modulus ($E=78$ GPa) compared to the undoped sample ($E=86$ GPa), indicating that the mechanical properties depend on the dopant type or level. A study with different dopant levels was used to shed light on the reason behind this discrepancy.

Thermoelectric figure of merit of zinc phosphate glass-reinforced graphite composites

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Zinc phosphate glasses (ZPG) are of interest because of their femto-second response, their chemical durability, and their potential applications in energy materials. The present investigation has been done to enhance the thermoelectric properties of ZPG by adding external guest graphitic particles. In this investigation, Seebeck coefficient was measured as a function of filler volume fraction using a homemade instrument. Electrical and thermal properties of the synthesized zinc phosphate glass-reinforced graphite were also measured respectively by impedance spectroscopy and photothermal radiometry and were reported in a previous work. From these measured values, the calculation of the thermoelectric figure of merit ZT was performed. It is shown that the ZPG/graphite thermoelectric properties are much more improved as compared to the pure ZPG matrix. In addition, the thermoelectric results reveal that the ZPG/graphite properties are dependent on the volume concentration of graphite filler. It is observed that the composite with 5 vol% graphite loading exhibits the best thermoelectric performance at the vicinity of the insulator-semiconductor concentration threshold with a power factor $PF \approx 0.98 \mu\text{W m}^{-1} \text{K}^{-2}$ and a figure of merit $ZT \approx 2.6 \cdot 10^{-4}$.

Effect of processing parameters on structure and microstructure of $\text{Smy}(\text{Fe}_x\text{Ni}_{1-x})_4\text{Sb}_{12}$

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Filled skutterudites $\text{RE}_4\text{M}_4\text{Sb}_{12}$ ($\text{RE} \equiv$ rare earth, $\text{M} \equiv$ transition metal) are studied as thermoelectric materials due to their low thermal and high electrical conductivity. Their structure consists in a bcc cell belonging to the Im-3 space group. M is placed at the center of X6 octahedra; X atoms form around the 2nd site an icosahedral cage, which is of utmost importance, as its filling strongly reduces thermal conductivity by the filler rattling motion. As-cast or even annealed skutterudites are generally highly porous, so they need to be densified to measure thermoelectric properties. In the current work samples were prepared by the conventional melting-quenching-annealing technique followed by spark plasma sintering. The work is focused on the effect of applied pressure on composition, structure and microstructure of three samples ($x=0.50, 0.63$ and 0.80) belonging to the $\text{Smy}(\text{Fe}_x\text{Ni}_{1-x})_4\text{Sb}_{12}$ system. Compositions were sintered at 50, 180 and 400 MPa and subsequently analyzed by optical and electronic microscopy, and X-ray powder diffraction. Diffraction patterns were treated by the Rietveld method. While the cell parameter of Fe80 decreases with increasing the sintering pressure, Fe50 and Fe63 present an increase, in agreement with the concomitant growth of the Sm occupancy factor. The change in the Sm amount also causes an increase in isotropic microstrain, thus entailing that defects introduced by SPS are essentially point defects, and they grow with increasing applied pressure.

Electronic band structure engineering and related thermoelectric properties in rare-earth doped BiCuSeO oxyselenides

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BiCuSeO oxyselenides have been recognised as one of the most promising oxygen-containing thermoelectric materials for energy recovery applications in the medium temperature range. In this study, a series of layered oxyselenides, Bi_{1-x}R_xCuSeO (R = La, Pr or Sm 0 ≤ x ≤ 0.08), was synthesised with a combination of a solid-state reaction and intensive ball milling process, followed by spark plasma sintering. Additionally, the effect of the ball milling on the thermoelectric properties was investigated. Structural analysis performed by surface area measurements and scanning electron microscopy highlights the reduction of the grain size by more than one order of magnitude from 1 – 10 μm to ~400 nm with ball milling. Moreover, the electrical transport properties are noticeably tuned by the ball milling, while the thermal conductivity is almost not affected due to intrinsically low phonon mean free path typical for oxides. Rare-earth for bismuth substitution results in a significant increase of the charge carrier concentration by more than 2 orders of magnitude from 1.1×10¹⁸ to 2.3 – 2.5×10²⁰ cm⁻³ for x = 0 and x = 0.08, respectively. Thus, the electrical resistivity is divided by ~2 at room temperature, and the Seebeck coefficient drops from 270 μV K⁻¹ to 170 μV K⁻¹, while the thermal conductivity is found to be almost unaffected by the doping. The mechanisms behind these changes of thermoelectric properties will be discussed.

Thermoelectric properties of CoSi and of $\text{Co}_{1-x}\text{M}_x\text{Si}$ (M=Fe, Ni) solid solutions

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We study the thermoelectric properties of cobalt monosilicide (CoSi) and its solid solutions with FeSi and NiSi. Recent CoSi band structure calculations revealed a number of differences of the electronic structure from the previous standard two-band semi-metallic model. Particularly, it was shown that the electronic structure features the band-touching nodes with four- and six-fold degeneracy, located at the Γ and R points in the first Brillouin zone, close to the Fermi energy. These band-touching points carry topological charges of ± 4 . This requires modifications of the previously used models for description of CoSi transport properties. The purpose of the study is to obtain experimental data on electronic transport coefficients of CoSi and to analyze the applicability of the simple two-band and the new theoretical models of the electronic structure for interpretation of the experimental results.

We investigate the temperature dependencies of the Seebeck coefficient and the electrical conductivity in a broad temperature range from 100 to 800 K for CoSi and for its solid solutions with FeSi and NiSi. The ab initio calculations of the band structure was carried out using the Quantum Espresso software package. The results of the study showed that the main features of the thermoelectric properties of CoSi and its solid solutions with FeSi and NiSi can be adequately described using the ab initio band structure, taking into account the energy dependence of the relaxation time.

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Preparation and thermoelectric properties of p-type Fe₁₁Ti₃Al₆

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P-type Fe₁₁Ti₃Al₆ was prepared by mechanical alloying followed by cold pressing and thermal annealing. The transport properties including the Seebeck coefficient, electrical resistivity and power factor of the prepared samples were determined at room temperature and the dependence of the transport properties on the annealing temperatures were investigated. It is found that the most suitable condition to prepare the best p-type Fe₁₁Ti₃Al₆ in terms of thermoelectric properties is planetary ball milling for 5 hours and annealing in argon at 700°C, which result in the maximum power factor of $12.1 \times 10^{-5} \text{W/mK}^2$ with the Seebeck coefficient of $31.8 \mu\text{V/K}$ and electrical resistivity of $8.3 \times 10^{-4} \Omega\text{cm}$.

Phonon Anharmonicity and Low Thermal Conductivity of the Type-I Clathrate, $\text{Ba}_{7.81}\text{Ge}_{40.67}\text{Au}_{5.33}$

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The use of complex crystalline systems, such as clathrates, as potential thermoelectric devices has been highlighted over the past few decades due to their high electrical conductivity and low, glass-like lattice thermal conductivity (1-2 W/mK) [1,2]. The community agrees that complexity and anharmonicity both play roles as phonon scattering mechanisms in clathrates, leading to the glass-like behavior, but the proportional weights of these parameters are still under debate. Recent self-consistent phonon (SCP) calculations of the type-I clathrate $\text{Ba}_8\text{Ge}_{30}\text{Ga}_{16}$ [2] point to the importance of the quartic anharmonicity term in describing phonon frequency renormalizations in clathrates. We test the validity of this method on the similar Ge-based clathrate $\text{Ba}_{7.81}\text{Ge}_{40.67}\text{Au}_{5.33}$ and discuss the phonon scattering mechanisms at play in this system. We then propose an equation that relates inelastic neutron scattering measurements to the SCP theoretical calculations using thermodynamic relations, emphasizing the importance of viewing the problem of anharmonicity from both macro and micro lenses. This leads us to find both qualitative and quantitative agreement with the anharmonicity contribution by the SCP method.

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Thermoelectric phenomenology in living organisms. Transport properties in beetles

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Thermoelectric effects provide a link between heat and electrical current fluxes. However, these effects may not be just circumscribed to “inert matter” but to living organism as well. For instance, Ishay et al. showed as the Hymenoptera species, *Vespa Orientalis* may use thermoelectricity in the elytra as an intrinsic biological pump to keep controlled its internal body temperature. Particularly, they measured a Seebeck coefficient of $S=3$ mV/K and $ZT\sim 3.0 \cdot 10^{-3}$.

In this preliminary work, we have investigated the ability of the elytra exoskeleton of a dung beetle species (*Scarabaeus sacer*, Linnaeus, 1758) to produce an electrical potential caused by a temperature gradient i.e. Seebeck effect. Recent works indicate that beetle exoskeleton could serve as a thermoregulator by acting differentially across the light spectrum, preferentially absorbing UV light, as well as suggesting the existence of a sort of internal heat pump based on thermoelectric effects. To explore this question, an experimental set-up was designed and built to measure the electrical transport properties of the exoskeleton of the beetles by using an impedance spectroscopy technique. Moreover, a morphological characterization (perfilometry and electronic microscopy) and compositional (Raman spectroscopy) will be done. Preliminary results will be presented and they will be compared to those obtained in other insects as well as a brief outlook will be given.

Enhanced Electronic Transport by Point Defect Engineering in Ca_2MnO_4 Layered Perovskite

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Thermoelectric oxides are attractive for their natural abundance, non-toxicity, low-cost and chemical and structural stability at elevated temperatures. The $\text{CaO}(\text{CaMnO}_3)_m$ layered perovskites are promising due to their intrinsically low thermal conductivity, which is associated to internal CaO layers residing between adjacent CaMnO_3 sub-cells. This work aims to increase the electrical conductivity of $\text{Ca}_{2-x}\text{R}_x\text{MnO}_4$ ($m=1$) bulk materials ($\text{R} = \text{La}$ or Y and $0.01 \leq x \leq 0.20$) by doping. First-principles calculations indicate that substitution of Y for Ca lowers the electrostatic potential of electrons at the CaO layers compared to La-substitution, predicting increase of electronic transport. We synthesize Ca_2MnO_4 specimens doped with equal amount of either Y or La applying standard solid-state reaction and sintering. The layered structure comprising CaO and CaMnO_3 sub-cells, where the Y-dopant substitutes for Ca-sites, is atomically resolved. In agreement with our computational prediction, the electrical conductivity of the Y-doped materials, measured in the range of 300-1000 K, is about twice as large as that of the La-doped ones. This trend is elucidated in terms of the small polaron hopping model, indicating that Y-doping reduces the conduction activation energy by up to 18 % in the range of 300-750 K compared to La-doping. Our results suggest that energy barriers for electronic transport in oxides may be tailored by point defect engineering.

Reaction sintering and sintering additives for cost-effective production of thermoelectric oxides

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Thermoelectric oxides attract much interest recently. Although their thermoelectric properties are inferior to non-oxides, they exhibit distinct advantages. Thermoelectric oxides are stable in air at higher temperatures, their raw materials are less toxic, and more abundant. To enhance attractiveness of these materials for industrial applications, production costs need to be reduced.

Conventionally, the legs of thermoelectric generators are sintered from green bodies of previously synthesized powder. Reaction-sintering is a fabrication method without a powder synthesis step, as the final phase is formed during the sintering from a raw material mixture. Moreover, the reduction of chemical potential during reaction-sintering is effective as an additional driving force for sintering. We show that reaction-sintering increases the densification of CaMnO_3 (n-type, Sm doped). Consequently, the electrical conductivities improved by about 100 % leading to superior power factors (PF = $230 \mu\text{W}/\text{mK}^2$ for CaMnO_3).

Another approach to reduce the production costs is to lower the sintering temperature by adding sinter additives. The addition of 4 wt% CuO to CaMnO_3 lowers the sinter temperature from 1250 °C to 1050 °C. The achieved power factor PF = $264 \mu\text{W}/\text{mK}^2$ is more than two times higher as reported in literature for the same dopant.

Thermoelectric Properties of Molybdenum Oxides MoO_x from Spark-Plasma Synthesis

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Transition metal oxides are of high interest to the thermoelectric community due to their possible high-temperature applicability, low toxicity and wide range of tunable thermoelectric properties.

Despite the apparent simplicity of the system Mo-O, the binary MoO_x compounds ($2 \leq x \leq 3$) exhibit a wide range of extraordinary physical properties, like the exceptionally low thermal conductivity which we find in Mo₁₈O₅₂ ($x = 2.889$) [1], or the pseudo two-dimensional electrical conductivity of the Mo₄O₁₁ polymorphs ($x = 2.750$). Most of these versatile properties are unknown above room temperature and thus, their applicability for thermoelectrics needs to be studied. Therefore, Spark-Plasma Synthesis (SPS) enables us to prepare gram-sized amounts of single-phase materials suitable for thermoelectric transport measurements over wide temperature ranges ($1.8 \text{ K} \leq T \leq 760 \text{ K}$).

The diversity of transport properties is mainly based on the MoO_x compounds' complex crystal structures which arise from the mixed valence of the Mo cations ranging from +4 to +6. Thus, an understanding of the adaptability of these compounds always requires detailed stereochemical examinations by means of crystal structure determination from X-ray diffraction experiments which we perform.

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Tuning the thermoelectric properties of calcium cobaltite by optimised composition and process

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Calcium cobaltite ($\text{Ca}_3\text{Co}_4\text{O}_9$) is a promising p-type thermoelectric oxide material. Here, we present an approach to optimise the thermoelectric performance of $\text{Ca}_3\text{Co}_4\text{O}_9$ by controlling the chemical composition and fabrication process. $\text{Ca}_{2.7}\text{Bi}_{0.3}\text{Co}_x\text{O}_{9+\delta}$ ($x=3.92, 3.96, 4$) and $\text{Ca}_{3-y}\text{Bi}_y\text{Co}_{3.92}\text{O}_{9+\delta}$ ($y=0.1, 0.2, 0.3$) ceramics were prepared by the spark plasma sintering (SPS). Stoichiometric mixtures of raw materials were combined and calcined at 930 °C for 12 hours, followed by SPS at 750 °C for 5 minutes (pressure of 50 MPa). The samples were subsequently annealed at 750 °C and 930 °C for 12 hours in air.

XRD analysis confirmed formation of the cobaltite misfit phase with minor amounts of secondary phases; SEM-EDS showed the presence of Bi-rich and Co-rich secondary phases in both original and annealed SPS samples. After annealing at 930 °C for 12 hours, the secondary phases were significantly reduced or absent. HRTEM images showed the layers of CoO_2 and rock salt structure stacked along the c axis. By controlling the bismuth substitution, cobalt deficiency and annealing temperatures, the electrical conductivity could be enhanced without degrading Seebeck coefficients and the thermal conductivity was reduced to $1.03 \text{ Wm}^{-1}\text{K}^{-1}$ at 550 °C. As a result, a high ZT value of 0.27 was achieved for $\text{Ca}_{2.7}\text{Bi}_{0.3}\text{Co}_{3.92}\text{O}_{9+\delta}$ ceramics at 550 °C.

Oxide thermoelectrics prepared by laser melting: effects of processing atmosphere

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Traditional thermoelectric materials suffer from two main problems, the toxicity/scarcity of the elements used and their stability at high temperatures or in non-inert atmospheres. Thermoelectric oxides appear to be a promising alternative to traditional materials due to natural abundance of the constituents and high thermal stability. This work focuses on the processing of these materials using the Laser Floating Zone (LFZ) technique. Particular emphasis is given to LFZ processing under various redox atmospheres, allowing unique opportunities for tuning the structural, microstructural and thermoelectric properties. This technique allows the growth of fully dense fibres, as well as the formation of metastable phases and/or promoting different oxidation states by adjusting the growth conditions. Here we report the processing of model manganite- and titanate-based materials including donor-substituted $\text{Ca}(\text{Pr})\text{MnO}_3$ and $\text{Ti}(\text{Ta})\text{O}_2$ systems. XRD/SEM/EDS studies demonstrate some guidelines for tuning the phase composition and microstructure by adjusting the growth rate under different redox conditions. We report high power factor values of $303 \mu\text{Wm}^{-1}\text{K}^{-2}$ at 1120 K for the $\text{Ca}(\text{Pr})\text{MnO}_3$ system and $317 \mu\text{Wm}^{-1}\text{K}^{-2}$ for the $\text{Ti}(\text{Ta})\text{O}_2$ system. The obtained results suggest that LFZ is a suitable technique for processing thermoelectric oxides, if optimized control over growth parameters and re-equilibration conditions is imposed.

Transparent TiO₂:Nb thin films for thermal energy harvesting

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The design of a transparent conducting oxide (TCO) material with thermoelectric properties is a promising technology to produce electrical energy through the harvesting of heat from the environment. TCO applications require coatings with high transparency, combined with useful electrical conductivity. As an alternative to the conventionally used ITO, TiO₂ has been extensively investigated due to its interesting optical and electronic properties and good stability in the adverse environment. A cationic doping of TiO₂ has been documented to improve its electrical conductivity, which will increase the thermoelectric Figure of Merit (ZT). In this project, thin films (~100 nm) of TiO₂ doped with Nb were produced by reactive d.c. magnetron sputtering in high vacuum. Several process parameters were adjusted, such as reactive gas (O₂) partial pressure and deposition time and temperature, which affect the morphology and crystalline structure of the thin films. The goal is to enhance the ZT, by increasing the electrical conductivity and Seebeck coefficient, decreasing the thermal conductivity of the thin films. This relation is challenging and requires very fine tuning of the production parameters. Hence, by modifying the thin film's optical, electric, thermal and thermoelectric properties, enables their suitability as thermal energy harvesters for application in photovoltaic systems, touch displays, amongst other devices, in order to render them more sustainable.

Assessing the Limitations of Transparent Conducting Oxides as Thermoelectrics

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Thermoelectrics are materials which can convert heat into electricity and vice versa, which could generate renewable energy and recycle waste heat. Currently, they have low efficiencies, measured as dimensionless figures of merit, ZTs, and are often made from rare or toxic materials such as PbTe and Bi₂Te₃. Transparent conducting oxides (TCOs), which are widely commercialised in touchscreens and photovoltaics, could be rapidly deployed to slow global heating, if they could be made into efficient thermoelectrics, but no systematic study has assessed their potential. Using density functional theory (DFT), we analysed the electronic and thermal properties of the TCOs BaSnO₃, CdO, SnO₂ and ZnO. We demonstrate lattice thermal conductivity (κ_l) is the limiting factor of the ZTs, and that extremely long phonon mean free paths of up to 10 μm are the cause. We further show this makes SnO₂ and ZnO ideal candidates for nanostructuring to suppress thermal transport, backed up by literature experimental results for ZnO; [1] and BaSnO₃ could be an excellent thermoelectric due to its naturally short phonon mean free paths. This demonstrates a thorough ab initio understanding of the κ_l of oxide thermoelectrics is necessary to fully analyse their potential, and to provide guidelines for how to maximise performance.

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Connectivity dependent thermoelectric properties of single thiophene molecule

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Thermoelectric materials can play a key role when converting waste heat into 'use full' electricity, but an organic material with highly efficient thermoelectric properties is yet to be found. These properties are characterised by a thermoelectric dimensionless figure of merit: $ZT=(S^2 GT)/k$. Where T is the temperature [Kelvin], S as the Seebeck coefficient [Volt/Kelvin](thermoelectric power $S=\Delta V/\Delta T$), G the electrical conductance [$1/\Omega$] and k the thermal conductance [Watt/Kelvin] ($k=k_{\text{electron}}+k_{\text{photon}}$). An 'efficient' thermoelectric material would have high-G and high-S and low-k, with the main hurdle of being interdependent.

We present the thermoelectric properties of single thiophene molecule between gold electrodes from two different connection points. I employ density functional theory (DFT) code Siesta to obtain ground state optimised geometry of junctions and corresponding Hamiltonians. I then combine these mean field Hamiltonians with non-equilibrium Green's function method implemented in Gollum code to calculate electron transmission coefficient $T(E)$. From $T(E)$, I compute thermoelectric coefficient S, G, k_e and electronic ZT. Our calculation shows that the thermoelectric properties of single thiophene molecules are connectivity dependent. The Seebeck coefficient is enhanced significantly by changing the connection point to electrodes. This is due to a cross over from constructive to destructive interference.

p-Type to n-Type Transition in Hybrid Ag_xTe/PEDOT:PSS Thermoelectric Materials via Stoichiometric Control During Solution Based Synthesis

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Hybrid materials consisting of inorganic nanostructures embedded in conducting polymer matrices have emerged as promising systems for room temperature thermoelectric applications. They are attractive due to their intrinsic low thermal conductivities, the ability to engineer interfaces for energy filtering effects and phonon scattering, and their ability to take advantage of high-throughput and solution processable manufacturing. Most reported polymer and hybrid materials have been p-type due to difficulties in the n-type doping of conducting polymers along with the nature of the applied nanocrystals, resulting in a strong drive to develop new n-type materials for module development. In this talk I will introduce some of our recent results related to the production of p-type and n-type hybrid Ag_xTe/PEDOT:PSS thermoelectric materials from the same Te/PEDOT:PSS parent structure during aqueous-based synthesis. By varying the stoichiometry of the Ag_xTe nanoparticles in our hybrids, we are able to manipulate the thermoelectric properties. Through this synthetic method we have demonstrated a power factor of 44 $\mu\text{Wm}^{-1}\text{K}^2$ for our highest performing n-type material. In addition, we were also able to realize a 68% improvement in the power factor of our p-type compositions through manipulation of the inorganic nanostructure. This process offers a simple, low-temperature, and cost-effective route towards the production of both efficient n-type and p-type hybrid thermoelectric materials.

In-situ polymerization of polythiophene in a polyurethane matrix for flexible thermoelectric devices

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In recent years the importance of elastic and lightweight thermoelectric materials has increased due to the demand for flexible, stretchable and wearable materials in order to new generation of electronic devices are able to bend and stretch by applying a mechanical deformation. The thermoelectric efficiency of a material increases as the Seebeck coefficient (S) and the electrical conductivity (σ) increase and the thermal conductivity (κ) decreases. Therefore, high electrical conductivity and large Seebeck coefficient are necessary for efficient energy collection, as well as low thermal conductivity. Conductive polymers represent an ideal candidate for flexible thermoelectric applications given their good mechanical and thermoelectric properties. In addition, they are highly compatible with polymeric matrices which can help us reduce thermal conductivity and maximize thermoelectric efficiency.

In this work, thin films of polythiophene have been synthesized in a polyurethane matrix by chemical oxidation using different inorganic salts as oxidizing agent. Polymerization and deposition on a PET substrate is simultaneously performed by applying a heat treatment after spin-coating. The optimization of thermoelectric properties was carried out by determining the maximum percolation curve and varying the monomer:oxidant molar ratio.

Addressing the role of synthesis in affecting PEDOT thermal and electrical conductivity by atomistic simulations

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The use of organic materials, especially intrinsically conducting polymers (CP), for thermoelectric devices is currently encouraged because of their unique mechanical properties (as flexibility and low specific weight, low toxicity, biocompatibility and high relative abundance).

In this perspective, many efforts have been taken in order to optimize CP conversion efficiency by properly tailoring their electrical and thermal conductivity.

One of the main issues is at the moment to clearly address the role of the polymerization conditions on the resulting CP morphological and transport properties.

To this aim we developed a novel computational approach based on a combination of classical molecular dynamics and ab initio Density Functional theory calculations, to generate realistic polymer samples and estimate their corresponding transport properties.

Focusing in particular on PEDOT, we show that different choices of specific reactants used to trigger the polymerization reaction, dramatically influence the corresponding heat transport properties. Such a variations have been then correlated to the corresponding morphological modifications induced by the different reactants.

Finally, a computational approach to estimate the CP carrier transport properties, based on the formalism of Marcus theory, will be presented.

Building intuition on lattice thermal conductivity in half-Heusler materials with machine learning feature selection

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Next generation thermoelectric materials need to have low lattice thermal conductivity for maximizing their efficiency, especially if they are to operate at temperatures where the total thermal conductivity is dominated by heat transfer of the lattice. For finding candidates with a high figure of merit, a large number of different materials can be put through a computational screening method. Because a lot of computational resources are needed for calculating the lattice thermal conductivity, it is costly to calculate the conductivity for all materials entering in the screening process. In this work we analyze easily obtainable material properties of half-Heusler materials, as to discover descriptors linked to the lattice thermal conductivity. The temperature dependent effective potential method in combination with density functional theory calculations is used for calculating the lattice thermal conductivity. A correlation study with materials properties from databases and density functional theory calculations reveal underlying physical mechanisms related to the anharmonicity. The set of different compound descriptors indicating low lattice thermal conductivity is obtained by using machine learning and feature selection methods. In future studies involving screening for new thermoelectric materials the number of costly computations needed can be reduced with the aid of these results.

Thermoelectric properties of TiMSn (M = Ni, Pd, Pt) half-Heusler alloys using hybrid density functional theory: the role of point defects

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Half-Heusler (HH) alloys are thermoelectric (TE) materials that enable direct conversion of waste heat to electricity.[1]

In this work, we investigate three thermoelectric compounds: TiNiSn, TiPdSn and TiPtSn with space group Fm-43 (#216) using hybrid density functional theory and localized Gaussian type orbitals (GTO). We use the CRYSTAL code [2] for all computations. We set benchmarks for TiNiSn by comparing our data to existing literature. Our computations agree well to the established values of Seebeck coefficient (S), power-factor (PF) and thermoelectric figure-of-merit (ZT) for TiNiSn. We extend these calculations to TiPdSn and TiPtSn, for which consistent previous data are limited.

The primary focus, however, is doping the parent material to maximize the thermoelectrics. For this reason, we aim to explain the low band-gap of TiNiSn by modeling defects in the pure system. Our defect model retains the symmetry of the pure system and proves to have a smaller band-gap. The value achieved in this work is 0.23 eV. In addition, the power-factor of the defect TiNiSn is found to be twice than that of the pure TiNiSn. Moreover, the defect model prefers n-type carriers and exhibits a higher power factor.

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Deformation potentials and simulations of thermoelectric properties using first principles: The case of Mg_3Sb_2

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We present a first-principles framework to derive the deformation potential from the electron-phonon coupling matrix elements, which can be further used to investigate the scattering and transport properties of thermoelectric materials within the Boltzmann transport equation. We have chosen the well-studied Si and GaAs as examples of non-polar and polar materials to benchmark our method. We compare the Wannier interpolated electron-phonon matrix elements with that obtained by direct calculation within density functional perturbation theory (DFPT). For the non-polar material, we consider the acoustic deformation potential (ADP) and optical deformation potential (ODP) for intravalley and intervalley transitions. For the polar material, we consider in addition the piezoelectric scattering and polar optical phonon scattering due to the long-range contributions. Then we applied this method to Mg_3Sb_2 to understand the ADP and ODP for holes and electrons, especially for the intervalley transitions in the conduction band. The presented framework can be readily applied to other non-polar and polar materials.

Prediction of giant Seebeck coefficient and thermoelectric power factor in ferroelectric domain walls of GeTe

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Enhancing the efficiency of thermoelectric materials is a very difficult task due to interdependence of electronic transport properties. Here we present an exciting prediction, using first principles calculations, that the Seebeck coefficient and thermoelectric power factor are significantly increased at the ferroelectric domain walls of GeTe. We find that the two-dimensional electron gas confined to domain walls can exhibit large peaks in the local density of states near the Fermi level due to the saddle points in the electronic band structure. Confinement of free charge carriers coupled with the existence of Van Hove singularities leads to an increased energy dependence of the electronic transport properties at the domain walls. This results in a more than twofold increase of the Seebeck coefficient and the thermoelectric power factor in the plane of the domain walls compared to the bulk material. We propose a design of a nano-thermoelectric device that utilizes the exceptional thermoelectric properties of ferroelectric domain walls. Our findings should inspire further investigation of ferroelectric domain walls as efficient thermoelectric materials.

Advanced simulations of thermoelectric coefficients using DFT bandstructures and energy dependent scattering mechanisms

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The predictive performance screening of novel compounds can accelerate the discovery of efficient, cheap, and nontoxic thermoelectric (TE) materials. Large efforts to couple machine-learning techniques and materials databases are currently undertaken, but the adopted computational methods can dramatically affect the outcome. Typically, thermoelectric transport calculations employ the constant relaxation time approximation to reduce computational complexity. However, such simplifications fail to capture the details of bandstructure features and to give accurate results, especially for complex bandstructures. We show that depending on the scattering treatment, different material performance rankings, different optimal doping regimes, and different temperature dependent trends are found. We also give an indication of single relaxation time for half-Heusler materials for different doping concentrations, useful in interpreting data.

We then present a set of new descriptors that we have identified as the most useful and generic: a combination of the number of valleys, the dielectric constant, the conductivity effective mass, and the deformation potential for the dominant electron-phonon process. The proposed descriptors can boost the discovery of new efficient and environment-friendly TE materials in a much more accurate and reliable manner.

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Molecular-scale thermoelectricity for beginners

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If the Seebeck coefficient of single molecules or self-assembled monolayers (SAMs) could be predicted from measurements of their current-voltage (I-V) characteristics alone, then the experimentally more difficult task of creating a set up to measure their thermoelectric properties could be avoided. This talk highlights a novel strategy for predicting an upper bound to the Seebeck coefficient of single molecules or SAMs, from measurements of their I-V characteristics. The prediction begins by making a fit to measured I-V curves using three fitting parameters, denoted a,b,c. This 'abc' theory then predicts a maximum value for the magnitude of the corresponding Seebeck coefficient. Histograms of predicted Seebeck coefficients are compared with histograms of measured Seebeck coefficients of six different SAMs, formed from anthracene-based molecules with different anchor groups and are shown to be in excellent agreement.

Ultra-low thermal conductivity due to geometry dependent specular scattering in nanoporous Si

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Nanostructuring has been shown to substantially decrease the thermal conductivity of semiconducting materials thereby improving their thermoelectric efficiency. Current strategies focus on increasing scattering and reducing the mean-free-path of phonons across the spectrum. Whether coherence effects too can significantly affect thermal transport remains an open-ended question. We identify an unusual anticorrelated specular phonon scattering effect yielding an additional 80% decrease in the thermal conductivity of specific porous geometries. Specular scattering is a necessary requirement for coherence effects, and our simulations suggest that such effects can occur at room temperature. Large-scale equilibrium molecular dynamics (MD) simulations performed for nanoporous Si show the presence of negatively correlated (anticorrelated) heat flux. We further demonstrate with MD how the pore size-to-neck ratio and periodicity can be manipulated to control the strength and duration of the reflections. These results are corroborated by wave-packet simulations which show how heat becomes trapped between pores with narrow necks. The amount of heat trapped between the pores is wave-vector dependent, which could have widespread applications in heat guidance and phonon (frequency) filtering. Finally, we develop a simple analytical ray-tracing model to illustrate how specular scattering can give rise to anticorrelated heat flux, and reproduce the behavior observed in the MD simulations.

From crystalline to amorphous materials: mechanisms for thermal conductivity reduction

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The thermal conductivity is a fundamental physical property that is also important to a number of industrial and technological applications such as thermoelectric devices, heat management in electronic devices and smart windows. In amorphous materials the absence of translational invariance gives rise to complex mechanisms of heat transport different from those in crystalline solids. Several theoretical approaches have been developed to estimate the thermal conductivity of crystals, but the modeling is more complicated for disordered solids.

In this study, we propose to investigate the thermal conductivity of amorphous solids from the harmonic eigenstates and phonons lifetimes inspired by the Kubo and Allen formalism [1-2]. To apply the method, we consider amorphous silica as a prototype. Several representative structures are generated combining classical molecular dynamics and first-principles calculations. Vibrational properties and structure factors are calculated and averaged over the representative structures and are in good agreement with results from the literature. Then the Kubo formula is used to study the thermal conductivity of amorphous silica.

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The influence of deformation on topological properties of CoSi thermoelectric semimetal

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The topology of the electronic structure plays a crucial role in the properties of solids. Some of the well-known thermoelectric materials possess nontrivial band structure topology like Weyl semimetals based on CoSi. This compound has non-centrosymmetric space group (#198), allowing for the existence of linear band crossing (Weyl nodes) with more than 2-fold degeneracy near Γ and R points with corresponding topological charges greater than unity. As mechanical deformation causes the lowering of the crystal symmetry, it may remove the degeneracy and affect the k-space position of nodes and their topological charge. We performed ab initio calculations of the electronic structure of deformed and undeformed CoSi, as well as the calculation of surface states based on the Wannier functions of the same systems. It was shown that the nodes at the Γ and R points with topological charge 4 splits into nodes with smaller charges along with the changes in the slopes of their dispersions. Even splitting into two quadratic Weyl nodes near the Γ point occurs under the deformation in the [111] direction. Based on the symmetry of the CoSi crystal, a kp-Hamiltonian under deformation was constructed with and without the spin-orbit interaction. This analytical model made it possible to analyze the topological properties of the material under the deformations and verify the correspondence of the results of machine calculation to the conclusions obtained based on the symmetry considerations.

α -Bi₂Sn₂O₇: A Potential Room Temperature n-type Oxide Thermoelectric

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Despite growing interest in oxide thermoelectrics, the efficiency of flagship oxide materials remains comparatively low, and most materials only reach the maximum figure of merit, ZT, at very high temperatures. One of the main limiting factors is their large lattice thermal conductivities, which has inspired research into more structurally complex materials. In this study, we apply first-principles modelling to assess the low-temperature polymorph of Bi₂Sn₂O₇ (α -Bi₂Sn₂O₇) as a potential thermoelectric material, due to its complex crystal structure, which should suppress phonon transport, and the presence of Bi p and Sn s states in the conduction band, which should yield high electrical conductivity when donor doped. Lattice-dynamics calculations using third-order perturbation theory predict an ultralow room-temperature lattice thermal conductivity of 0.4 W m⁻¹K⁻¹, the lowest ever predicted for an oxide material, and suggest that nanostructuring to a grain size of 5 nm could further decrease this to 0.28 W m⁻¹K⁻¹. The ultralow lattice thermal conductivity gives α -Bi₂Sn₂O₇ a maximum ZT of 0.36 at 385 K (0.46 with nanostructuring), which is the highest low-temperature value predicted for an oxide thermoelectric. Most importantly, our analysis highlights the relationship between the structural complexity, the chemical nature of the cation, and the short phonon lifetimes, and thus provides guidelines for identifying other novel high-performance oxide thermoelectrics.

Electron-phonon scattering and thermoelectric transport in p-type PbTe from first principles

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We present a first principles model of electron-phonon scattering mechanisms and thermoelectric transport at the L and Sigma valleys in p-type PbTe, accounting for their thermally induced shifts. Our calculated values of all thermoelectric transport parameters at room temperature are in very good agreement with experiments for a wide range of doping concentrations. Scattering due to longitudinal optical phonons is the main scattering mechanism in p-type PbTe, while scattering due to transverse optical modes is the weakest. The L valleys contribute most to thermoelectric transport due to the sizeable energy difference between the L and Sigma valleys at 300 K. We show that both scattering between the L and Σ valleys and additional transport channels of the Sigma valleys are beneficial for the overall thermoelectric performance of p-type PbTe at 300 K. Our findings thus support the idea that materials with high valley degeneracy may be good thermoelectrics.

Gapped metals as thermoelectric materials: a high-throughput screening.Ricci Francesco,¹ Dunn Alexander,^{2,3} Jain Anubhav,² Rignanese Gian-Marco,¹ Hautier Geoffroy¹¹ *Université catholique de Louvain, Belgium*² *Lawrence Berkeley National Laboratory, Energy Technologies Area, CA 94720, USA*³ *Department of Materials Science and Engineering, UC Berkeley, CA 94720, USA*

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The typical strategy to design high performance thermoelectric materials is to dope a semiconducting material until optimal properties are obtained. However, some known thermoelectric materials such as La_3Te_4 , Mo_3Sb_7 , $\text{Yb}_{14}\text{MnSb}_{11}$, and NbCoSb are actually gapped metals, i.e., their band structure displays a gap slightly above or below the band crossed by the Fermi level. This key feature makes these metals comparable to degenerate semiconductors and thus suitable for thermoelectric applications. In this work, we perform a computational high-throughput search for such gapped metals exhibiting attractive thermoelectric properties. Several thousands of metals are found to present this key feature, and about one thousand of them show decent thermoelectric properties as evaluated by a computed zT . We present the different chemistry of gapped metals we discovered such as clathrates, Chevrel phases, or transition metal dichalcogenides and discuss their previous studies as thermoelectric and their potential as new thermoelectric materials.

Optimisation of the Thermoelectric Efficiency of Zirconium Trisulphide Monolayers by Uniaxial and Biaxial Straining

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The goal of this work is to investigate the influence of mechanical deformation on the electronic and thermoelectric properties of ZrS₃ monolayers. We employ density-functional theory (DFT) calculations at the hybrid HSE06 level to evaluate the response of the electronic band gap and mobilities, as well as the thermopower, the electrical conductivity, the phononic and the electronic contributions to the thermal conductivity, and the heat capacity. Our DFT calculations reveal that the band gaps can be increased by up to 17.34 % by strain applied along the y axis by a value of 2.32 eV to be compared with 1.98 eV for the undeformed case. In addition, our calculations predict small changes in the Seebeck coefficient, whereas the electrical conductivity experiences higher variations, with values up 3.40 times higher under a 4% compression. On the other hand, the effects of mechanical deformation on thermal transport are more significant, with a nearly five-fold reduction of the lattice thermal conductivity under a biaxial strain of -4%, which ultimately leads to a doubling of the y-component of the figure of merit.

Design and modelling of integrated devices dedicated to transient Harman measurement of silicon nano-meshes

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In the field of thermoelectric materials, research continues to seek methods to enhance the thermoelectric potential of silicon. Monocrystalline bulk silicon exhibits a relatively low thermoelectric figure of merit in comparison to that of popular thermoelectric materials. However, given the very low consumption of modern integrated circuits, silicon represents an interesting alternative to the conventional materials due to its abundance, non-toxic nature and its compatibility with CMOS technology. Research investigated to enhance zT by increasing the electrical conductivity/thermal conductivity ratio. Therefore, decreasing the thermal conductivity by (i) structure miniaturization such as thin membranes or nanowires , (ii) roughening , (iii) oxidization of the surface, (iv) etching arrays of holes and they achieved relatively low thermal conductivity value. Yet, few experimental measurements of zT were presented. Furthermore, zT was deduced by measuring the three main parameters: thermal conductivity, electrical conductivity and Seebeck coefficient. Non-direct measurement of zT may lead to unacceptable uncertainties in the more than 10% range. In this work, we present a design dedicated to transient Harman measurements and its modelling results for the in plane figure of merit zT of monocrystalline silicon membranes with different thermal conductivity values. We will discuss further implementation of the methodology to silicon nano-meshes.

A computational analysis of heat transfer at the cold side of a TEG

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Due to the wide-spread use of portable devices, power backup solutions with characteristics consistent with mobility, like compactness and safety, are being paid special attention, in recent years.

This work focuses the attention to the optimization of the cold stage of a thermoelectric generator based on a catalytic combustor. Such a system, uses six commercial modules and is capable of an electrical output of 9 W. The TEG is water-cooled through a 3D printed ABS + Aluminum composite heat sink structure. The dissipater, built in ABS, an insulating material, to strongly limit the device weight, represents a critical component of the generator.

The aim of the present work is to improve the TEG performance, by studying the heat transfer mechanisms at the cold side for system. A CFD model has been carried out and validated with experimental data verifying its reliability. The laminar flow regime related to the millimetric scales has been studied; the results for Reynolds number ranging between 800 and 1400 show an enhancement in the thermal performances.

The model has been used to evaluate alternative geometries for the heat sink. An improvement in the thermal gradient profile across the thermoelectric modules was observed in the modelling results suggesting a promising evolution for TEG performance optimization.

Optimization of a simulation for thermoelectric generators and their application in water boiler systems with combustion chamber

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On the path to efficient and sustainable global energy consumption, waste heat recovery plays a vital role. In Austria, 30% of the total end-use energy demand is used for the production of residential heating and hot water. For this purpose, boiler systems with combustion chamber are used and waste heat is generated in the process. This work investigates a possible use of thermoelectric generators (TEG) to recover the waste heat generated in such systems. In this regard, a MATLAB Simulink model based on two Bismuth-Telluride thermoelectric generators is developed. A cascade installation is proposed, with one generator (TEGW) attached to the outer wall of the combustion chamber and a second one (TEGH) installed on the output water circuit, both of them being cooled by the feed water. The calculation model is optimized using experimental methods. The combustion chamber is replicated with the help of a steel plate attached to a cooking plate. The performance of three different Bismuth-Telluride TEGs is investigated, calculating the effective temperature difference on their sides. The losses caused by the improper thermic contact between surfaces are assessed and applied to the model in form of a correction factor. The calculated electrical power output of the system is 9.32 W, with TEGW producing 90.7% of it. Although the output of the proposed configuration is 10% higher than the one of a single module, it is not high enough to justify the additional costs and technical effort.

From basic transport properties to device efficiency: integrated performance prediction based on the Boltzmann transport equation

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For maximized performance the optimization of thermoelectric materials with respect to carrier concentration, chemical composition, etc. is inevitable. Theoretical performance prediction can speed this process dramatically as the synthesis and experimental characterization of all possible combinations is practically impossible. Conventionally, the dimensionless figure of merit (zT) is considered as a measure of performance. However, zT could mislead the search for optimized materials as it is not always a good performance indicator, especially when the TE properties are strongly temperature (T) dependent. To resolve this issue we employed device efficiency as a direct measure of performance by combining a device performance calculation routine (1D, full T dependent) with a physics based material model. A study was conducted on the p-Mg₂Si_{1-x}Sn_x solid solutions for which optimization of carrier concentration (n) and composition (x) is required. Here, a Single Parabolic Band (SPB) model was assumed for the material with acoustic phonon and alloy scattering for the charge carriers. It was found that for $T_{\text{cold}}= 300\text{K}$ and $T_{\text{hot}}= 500\text{K}$, the optimum x in Mg₂Si_{1-x}Sn_x was identified as $x \approx 0.65$ based on zT (at 500K) while from efficiency calculations, it was found to be $x \approx 0.55$. Also, the optimum n differs between the two cases. Our approach provides a way to directly correlate the material physics parameters to device performance.

Interface - transport property correlation in LaNiO_3 - La_2CuO_4 heterostructures: Atomic-scale investigations at the interfaces

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It is well-known that the electrical transport along interfaces[1] and boundaries[2] can be modified by several orders of magnitudes, and various examples such as $\text{LaAlO}_3/\text{SrTiO}_3$ [3] and La_2CuO_4 -based interfaces,[4] were extensively studied. Moreover oxygen stoichiometry and exchange dynamics[5] play an important role as well.

In this study, by means of the atomic-layer-by-layer oxide molecular beam epitaxy technique, we designed oxide heterostructures consisting of tetragonal K_2NiF_4 -type La_2CuO_4 (LCO) and perovskite-type LaNiO_3 (LNO) layers with different thicknesses to assess the heterostructure-thermoelectric property-relationship.

We observed the dependency of transport properties on the individual layer thickness, interface intermixing, and oxygen exchange dynamics in LCO layers that occurs at high temperatures. In particular, as the thickness of the individual layers was reduced, the $\sigma(T)$ decreased and the sign of the $S(T)$ changed revealing the contribution of the individual layers. HR-STEM investigations showed that a substitutional solid solution of $\text{La}_2(\text{CuNi})\text{O}_4$ was formed, when the thickness of the constituent layers was decreased.

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Recent advances in thermoelectric devices architecture

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Thermoelectric generators are solid-state devices that convert a temperature difference into useful electrical power. The thermoelectric energy harvesting technology aims to generate electrical power from thermal energy *via* the Seebeck effect. The thermoelectric performance of devices mainly depends on the type of materials used and their properties. Different strategies were employed to improve material properties. However, most of the thermoelectric devices use conventional fabrication method and device design that sometimes leads to complicated system integration, which limits their application. This study aims to report the recent implementation in thermoelectric devices architecture and progress in emerging fabrication method.

Microwave-hydrothermal synthesis and thermoelectric characterization of nanostructured $\text{Sn}_{1-\delta}\text{S}$

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Microwave-hydrothermal synthesis is a fast and effective method to synthesized tin sulphide with a reasonably high thermoelectric performance. This one-pot solution approach generates a high concentration of Sn vacancies, randomly distributed in the structure, yielding a composition of $\text{Sn}_{0.87}\text{S}$, as determined by neutron powder diffraction. The synthesized powder was sintered by Spark Plasma Sintering (SPS). Thermoelectric properties were determined in the compacted pellet of the material, achieving a relatively high figure of merit ZT of 0.76 at 523 K. This is the result of the remarkably high Seebeck coefficient (682 $\mu\text{V}/\text{K}$), low thermal conductivity (0.57 $\text{W}/\text{m}\cdot\text{K}$) and relatively low electrical resistivity ($5.6 \times 10^{-4} \Omega \text{ m}$) at 523 K. Furthermore, the reasonably high carrier density ($2.5 \times 10^{18} \text{ cm}^{-3}$ at room temperature) and good mobility (13 $\text{cm}^2/\text{V}\cdot\text{s}$ at room temperature) found for the microwave-synthesized sample and the influence of its Sn vacancies still open the possibility to improve the thermoelectric performance through chemical doping or band-gap engineering.

Titanium-doped zinc aluminum oxide with enhanced thermoelectric performance

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ZnO is a promising thermoelectric material for high-temperature applications; however, its thermoelectric performance is limited by strong coupling between the electrical and thermal transport properties. In this study, we introduce second- and third-phases into ZnO-matrix to enhance the power factor (PF) by charge carrier energy filtering. We show that increasing the TiO_2 content leads to a significant increase of the Seebeck coefficient of ZnAlO. The spatial distribution of aluminum (Al) and titanium (Ti)-rich phases in ZnO was studied by high-resolution scanning electron microscopy and transmission electron microscopy. Analysis of energy dispersive X-ray spectroscopy maps shows the presence of three phases: ZnO, $ZnAl_2O_4$, and Zn_2TiO_4 . The Al-rich precipitates reside on the surface of ZnO, and the intermediate Ti-rich phase resides in the ZnO grains. Such microstructural features are not frequently observed in oxide materials. Furthermore, co-doping with Ti^{4+} and Al^{3+} has improved the electrical conductivity of ZnO. In the present study, all materials exhibited linearity of $K_{lattice}$ with T^{-1} at high temperatures, it follows an intrinsic Umklapp scattering at high temperatures. While the deviation from the linearity represents that the extrinsic phonon scattering is initiated due to the point defects and second-phases. This yields a figure of merit of ~ 0.1 at $800^\circ C$ in ZnAlTiO matrix which is 10 times higher than the ZnAlO.

Investigating chromium nitride thin films for prospective thermoelectric applications: CrN, Cr₂N and (Cr, V)N

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Rock-salt cubic chromium nitride is unique among transition metal nitrides due to its semiconducting properties. Furthermore, a secondary interstitial compound of chromium nitride, hexagonal Cr₂N, also exists which shows metallic properties. CrN is shown to have a relatively high Seebeck coefficient and low thermal conductivity which could lead to prospective thermoelectric applications. Additional doping and alloying could further enhance these properties. In this study, sub-stoichiometric CrN and (Cr, V)N thin films were deposited by dc-reactive magnetron sputtering. $\theta - 2\theta$ X-ray diffraction shows CrN (111) preferential orientation growth. Thermoelectric measurements of pure CrN show a low electrical resistivity between 1.2 and $1.5 \times 10^{-3} \Omega \text{ cm}$ and high Seebeck coefficient and power factor values which range between $370 - 430 \mu\text{V/K}$ and $9.1 - 15.4 \times 10^{-3} \text{ W/mK}^2$ respectively. Energy dispersive spectroscopy measurements show that alloying these films with small amounts (less than 5%) of vanadium results in cubic (Cr, V)N thin film with a reduced electrical resistivity averaged around $0.8 \times 10^{-3} \Omega\text{cm}$, Seebeck coefficient value of $270 \mu\text{V/K}$ and a power-factor of $9.1 \times 10^{-3} \text{ W/mK}^2$.

Thermoelectric composite ceramics based on anisotropic oxides

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There are various relevant material classes in terms of thermoelectrics, each having its own advantages. As one promising thermoelectric material class, oxide-based ceramics benefit from an excellent chemical stability in air even at high temperatures. Regarding oxides, the $\text{Ca}_3\text{Co}_4\text{O}_9$ (CCO) is well-known for its high power factor combined with a low thermal conductivity. To enhance the thermoelectric properties of CCO, we investigated the influence of individually adding perovskite-related oxides such as the mixed ionic-electronic conductor $\text{La}_2\text{NiO}_{4+\delta}$ or the large bandgap semiconductor $\text{Na}_2\text{Ca}_2\text{Nb}_4\text{O}_{13}$ to obtain sintered composite ceramics. All three oxides are characterized by layered structures and therefore anisotropic transport properties. To benefit from a preferred orientation in a textured green body gained by uniaxially pressing, the added oxides were synthesized as large anisotropic plate-like crystals in the size of several microns. The demanded crystal shapes were obtained by using molten-flux syntheses for the added oxides.[1] Extensive analyses of the composite ceramics were performed, which showed the influence of the added phases on the thermoelectric properties and enabled the identification of reaction products between CCO and the added phases. As a result, multiphase composite ceramics with enhanced thermoelectric properties were obtained.

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Chemical Substitutions in Tetrahedrites for thermoelectric applications

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The current thermoelectric materials with commercial applications have as constituents expensive and/or toxic elements, such as the Bi, Pb and Te, putting the problem of their future employment in a broad scale. A potential alternative to solve this problem is the use of a mineral called tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$), which is composed of earth-abundant elements with lower toxicity, and displays good electrical and thermal properties that lead to a zT of 0,6 at 700K. This value is still too low when compared with current commercial thermoelectric materials (with $zT > 1,0$), but, as it has been shown by several studies, it can be increased by substitutions. The focus of the present work is the investigation of the effect of two simultaneous isovalent substitutions in tetrahedrite properties, following the $\text{Cu}_{12-x}\text{M}_x\text{Sb}_4\text{S}_{13-y}\text{Se}_y$ composition, where $M = \text{Ni}, \text{Co}$ or Cr . The samples were prepared by casting at 1193 K for 1 hour, followed by slow cooling, and annealing at 723 K for 7 days. At the present stage, all X-ray diffractograms showed that the samples have tetrahedrite as the main phase, with a small presence of other phases. The materials are now queued for thermoelectric properties measurements.

Synthesis and characterization of thermoelectric Co_2XSn ($X = \text{Zr, Hf}$) Heusler alloys

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We present here the results of an experimental investigation on the synthesis, structure, microstructure, mechanical, electrical conductivity, and Seebeck coefficient of Co_2XSn ($X = \text{Zr, Hf}$) alloys. Both in Co_2ZrSn and Co_2HfSn alloys, the main constituent is a full Heusler-type compound that coexists with small amounts of secondary phases. Rather high Vickers hardness (around 900 HV) and an indentation fracture toughness typical of ceramics (around $2 \text{ MPa}\cdot\text{m}^{1/2}$) were found for both the alloys. The electronic transport properties of the two alloys were measured for the first time. The temperature dependence of both the Seebeck coefficient and the electrical conductivity of the two alloys shows a change in correspondence of the Curie temperature; in particular, the Seebeck coefficient reaches a constant plateau, while the electrical conductivities show a transition from metallic to semiconductor behaviour. Almost constant values of the power factor have been obtained above the Curie temperature, which is promising for an efficient exploitation of thermal gradients of several hundreds of degree in waste heat harvesting applications. On the basis of results from this work and from the literature, it is eventually possible to discuss the effect of the substitution of the X element on the electronic transport properties in the series Co_2XSn ($X = \text{Ti, Zr, Hf}$).

TaCoSn: synthesis and characterization of a new *n*-type half-Heusler compounds

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Half Heusler alloys are ternary intermetallic compounds. TaCoSn is a new composition which has been predicted to be stable through ab-initio calculations, but has been experimentally verified only once by solid-liquid reaction. Currently, there have been no experimental data reported on thermoelectric properties of TaCoSn despite its theoretically predicted high thermoelectric performance.

In this work, the synthesis of TaCoSn by melting and mechanical alloying was studied. Pure elements could not be successfully alloyed by arc melting because of the large difference between their melting points. Thus, binary phases, such as Ta₂Co and CoSn₂, were obtained instead of the expected ternary phase.

As milling proceeds, crystallographic reflections disappear leaving place to a broad halo, suggesting the progressive amorphization of the powders. The presence of an exothermic peak around 753 K in the differential thermal analysis indicates the crystallization of the amorphous phase into a crystalline phase with half Heusler structure. After crystallization, an endothermic peak around 875°C appears probably because of decomposition of the half Heusler phase.

Bulk samples for thermoelectric measurements were sintered by Spark Plasma Sintering (SPS), at different temperature (973, 1100 and 1223 K). The effect of sintering processes and the starting powders on microstructural, structural, mechanical and thermoelectric properties is evaluated.

Thermoelectric properties of half-Heusler superlattices and SrTiO₃ thin films

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Thermoelectric materials possess a huge potential at industrial levels due to the fact they can be actuators for cooling or warming, as well as for energy harvesting to convert the waste heat into electricity.

In the present work we study the thermoelectric properties of TiNiSn-HfNiSn half Heusler superlattices and SrTiO₃ thin films. A systematic and dramatic decrease of the cross-plane κ has been measured by the 3ω technique. The transition between coherent-incoherent (wave-particle) transport was observed as a minimum in k as a function of period thickness, p . This minimum comes from the competition between the phonons diffusively scattered by each interface and the band-folded phonons. These findings open a novel approach for the manipulation of the thermal conductivity based in the control of coherent phonons in SLs. On the other hand, we report on the thermoelectric properties of Nb-doped SrTiO₃ epitaxial thin films with respect to different parameters such as: film thickness varying from 30 to 200nm, substrate and Niobium content (2-15 mol%). A maximum power factor of $8.9 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$ and $2.7 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$ and thermoelectric figure of merit of 0.49 and 0.18 were measured at room temperature in a 50 nm thick film grown on lanthanum aluminate and lanthanum strontium aluminate, respectively. The overall enhancement of thermoelectric properties suggests SrTi_{1-x}Nb_xO₃ is a very promising n -type candidate for room to high temperature applications.

Connectivity dependent thermoelectric properties of single thiophene molecule

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Thermoelectric materials can play a key role when converting waste heat into 'use full' electricity, but an organic material with highly efficient thermoelectric properties is yet to be found. These properties are characterised by a thermoelectric dimensionless figure of merit: $ZT = (S^2 GT)/k$. Where T is the temperature [Kelvin], S as the Seebeck coefficient [Volt/Kelvin] (thermoelectric power $S = \Delta V/\Delta T$), G the electrical conductance [$1/\Omega$] and k the thermal conductance [Watt/Kelvin] ($k = k_{\text{electron}} + k_{\text{photon}}$). An 'efficient' thermoelectric material would have high- G and high- S and low- k , with the main hurdle of being interdependent.

In this poster, I will present the thermoelectric properties of single thiophene molecule between gold electrodes from two different connection points. I employ density functional theory (DFT) code Siesta to obtain ground state optimised geometry of junctions and corresponding Hamiltonians. I then combine these mean field Hamiltonians with non-equilibrium Green's function method implemented in Gollum code to calculate electron transmission coefficient $T(E)$. From $T(E)$, I compute thermoelectric coefficient S , G , k_e and electronic ZT . Our calculation shows that the thermoelectric properties of single thiophene molecules are connectivity dependent. The Seebeck coefficient is enhanced significantly by changing the connection point to electrodes. This is due to a cross over from constructive to destructive interference.

Thermoelectric Properties of Sub-stoichiometric Electron Beam Patterned Bismuth Sulphide

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Direct patterning of thermoelectric metal chalcogenides can be challenging and is normally constrained to certain geometries and sizes. Here we report the synthesis, characterization, and direct writing of sub-10 nm wide bismuth sulfide (Bi_2S_3) using a single source, spin coatable, and electron beam sensitive bismuth (III) ethylxanthate precursor. In order to increase the intrinsically low carrier concentration of pristine Bi_2S_3 , we developed a self-doping methodology in which sulfur vacancies are manipulated by tuning the temperature during vacuum annealing, to produce an electron-rich thermoelectric material. We report a room temperature electrical conductivity of 6 S m^{-1} and a Seebeck coefficient of $-21.41 \mu\text{V K}^{-1}$ for a directly patterned, sub-stoichiometric Bi_2S_3 thin film. We expect that our demonstration of directly-writable thermoelectric films, with further optimization of structure and morphology can be useful for on-chip applications.

Influence of various fabrication methods on structural and thermoelectric properties of In-filled CoSb₃ skutterudites

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The different fabrication methods can have a significant impact on the structural and, as a result, on the functional properties of materials. In this work bulk samples with nominal composition of InCoSb₃ were fabricated by means of two techniques: 1) induction melting followed by spark plasma sintering; 2) induction melting and melt spinning quenching followed by spark plasma sintering. X-ray diffraction and energy-dispersive X-ray analysis confirms the formation of single-phase CoSb₃ skutterudites with a negligible amount of InSb secondary phase. Typically, the presence of InSb precipitates leads to a dramatic decrease of the lattice thermal conductivity. Moreover, melt spinning leads to a so-called nanostructured microstructure and thus to the reduction of the lattice thermal conductivity 55% along with the enhancement of the power factor by 25%. The combined improvement in the transport properties results in a high value of $zT \sim 1.1$ at 575 K. More details about influence of methods and the existence of InSb precipitates on thermoelectric properties will be presented.

Enhanced thermoelectric performance of $\text{Zn}_{1-x}\text{Al}_x\text{O}$ fabricated by chemical co-precipitation

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Due to its low cost, high thermal stability and high Seebeck coefficient, ZnO-based ceramics are of great interest for research as promising high-temperature and environmentally friendly thermoelectric (TE) materials. However, high thermal conductivity and low electrical conductivity hinder the widespread utilisation of ZnO as TE material.

In this work, $\text{Zn}_{1-x}\text{Al}_x\text{O}$ powder ($x = 0 - 0.06$) was obtained by chemical co-precipitation of crystalline hydrates solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ mixing with NaOH solution. This method is simple, reproducible and allows one to carry out precise doping at the molecular level and to obtain Al-doped ZnO nanopowder at room temperature. To fabricate dense bulk samples, all the obtained powders were consolidated by spark plasma sintering.

The total thermal conductivity of the obtained pellets sharply reduces upon Al doping level due to increased point defect scattering, and reaches $\sim 4.7 \text{ W m}^{-1} \text{ K}^{-1}$ at 1100 K for $x = 0.04$ which is 20% less than that for $x = 0$. The electrical conductivity of the optimally doped sample $\text{Zn}_{0.96}\text{Al}_{0.04}\text{O}$ is almost two orders of magnitude higher than those for undoped ZnO, which is attributed to the charge carrier optimization. On the other hand the absolute values of the Seebeck coefficient are divided by 2. All the above contributions cause the $zT = 0.5$ at 1100 K for $\text{Zn}_{0.96}\text{Al}_{0.04}\text{O}$.

Cost-effective synthesis of *n*-type Si-SiGe composite with $zT \sim 1$

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In an effort to drive SiGe-based alloys another step closer to widespread application, Si-SiGe composite was fabricated by high-energy ball milling followed by spark plasma sintering. Solid solution of $\text{Si}_{75}\text{Ge}_{25}$ was obtained within 40 minutes (700 rpm and powder-to-balls mass ratio of 1:40) and then mixed with coarse crystalline Si in the stoichiometric ratio of $\text{Si}_{100-x}(\text{Si}_{75}\text{Ge}_{25})_x$ ($x = 15 - 35$) and ball milled again for 6 hours at 300 rpm. Finally, the resultant samples were densified using the spark plasma sintering technique at 1400 K under Ar atmosphere for 5 min under uniaxial pressure of 50 MPa.

X-ray diffraction and scanning electron microscopy highlights the formation of composite material with Si as matrix and inclusions of heavily doped SiGe. Upon x increase the thermal conductivity decreases by $\sim 40\%$ along with the electrical transport properties remains almost constant in the whole temperature range.

A maximum zT of ~ 1 at 1100 K is achieved for the sample with nominal composition of $\text{Si}_{75}(\text{Si}_{75}\text{Ge}_{25})_{25}$, which is comparable to those of the state-of-the-art *n*-type $\text{Si}_{80}\text{Ge}_{20}$. Furthermore, such composites exhibit almost one order of magnitude higher $zT_{\text{max}}/C_{\text{m}}$ ratio (where C_{m} is the material cost), mainly due to much lower concentration of Ge. The details on the structural and transport properties will be discussed.

3D Model and Geometrical Optimizing of a New Thermopile Configuration Based on $\text{Cu}_{55}\text{Ni}_{45}$ and $\text{Ni}_{90}\text{Cr}_{10}$ Thermocouples for Planar Membrane-Based Micro-Thermoelectric Generators

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The results presented in this study are focused on modeling and optimizing of a novel planar thermopile configuration which integrate low-cost and eco-friendly thermoelectric (TE) materials based on Constantan ($\text{Cu}_{55}\text{Ni}_{45}$) and chromel ($\text{Ni}_{90}\text{Cr}_{10}$) thermocouples (TCs). The two TE materials are arranged thermally in parallel on top of each other and they are isolated by a thin SiO_2 layer in the way to be connected electrically in series. This configuration allows us to optimize the TC area density and to double their number compared to a classical planar thermopile. The original embedding increases significantly the performance of our planar micro thermoelectric generators (μTEGs) which are made by using this new thermopile configuration and that we have realized by CMOS-compatible silicon technology. The numerical simulation has been made by a 3D-finite element modeling using COMSOL Multiphysics software. The first results show that for 1W input heat injected in a standard 30 mm^2 surface module and with a fixed strip width of $200\text{ }\mu\text{m}$, the output power density can exceed 1 mW/cm^2 with an efficiency factor of $0,12\text{ }\mu\text{W cm}^{-2}\text{ K}^{-2}$ for μTEGs configurations with 2 and 3 membranes. The optimal thicknesses of the TE materials are evaluated to be $3\text{ }\mu\text{m}$ and $6\text{ }\mu\text{m}$ respectively for 2 and 3 membranes based μTEGs . For thinner TE material films, between 0.4 and $1\text{ }\mu\text{m}$ thick, the μTEG with 4 membranes presents the best results with an output power up to $800\text{ }\mu\text{W/cm}^2$ and an efficiency factor of $0.09\text{ }\mu\text{W cm}^{-2}\text{ K}^{-2}$.

Stacking faults in AgSbTe₂ thermoelectric alloys

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Efficient thermoelectric materials require low thermal conductivity. Planar defects can scatter phonons effectively, especially as their spacing approaches the mean free paths of phonons. We find such high density of stacking faults at the grain boundaries of AgSbTe₂ thermoelectric alloys.

Here we introduce electron contrast channelling imaging (ECCI) to investigate the distribution of stacking faults.[1] From their atomic arrangement resolved by scanning transmission electron microscopy (STEM), an unusually long translation vector is identified. Such stacking faults are stabilised by the depletion of Ag in their vicinity, as investigated by atom probe tomography (APT). We use the Debye-Callaway model to evaluate the impact of stacking faults on the lattice thermal conductivity.

References

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FEM simulation of CoSb₃ densification within SPS

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Finite elements model has been developed for SPS process simulation. The material under the study was CoSb₃. The model considered thermal, electric, and mechanical phenomena. The main goal of the work was to simulate the displacement curve. Material has been considered as nonlinear, the densification mechanism was described through the creep model. The material model was Garofalo (hyperbolic sine). Strain exponent, creep rate coefficient and creep activation energy have been calculated as the result of porosity change rate function. The simulated and experimental displacement curves were fitted due to the reference stress value adjustment.

Flexible Thermoelectric Devices: from Printing Methods to Microlithography

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Flexible micro and nanogenerators for thermal energy harvesting emerged in the last decade as alternative power sources on the field of IoT, namely wireless sensors powering and avoiding issues related to battery lifetime and reliability. These nanogenerators constitute a business opportunity for the next industry generation, the so-called Industry 4.0. The main strategies developed until the now, are depositing high-performance thermoelectric (TE) materials on the top of flexible substrates or using organic polymeric materials to produce efficient composites, such as by producing films using inks/pastes composed of an inorganic material and a polymeric matrix as a binder to attach onto the flexible substrate. This presentation extends the knowledge on the production of optimized TE generators (TEG) using 2 different microfabrication methodologies, by printing and microlithography processes:

1. On flexible printing methodology, optimized $\text{Bi}_2\text{Te}_3/\text{PVA}$ TE composite was used for TE applications. A full study to obtain the best ratio between the inorganic and organic materials, allied with the percolation study, was performed to achieve a higher power factor.
2. By lithography processes, Bi_2Te_3 and Sb_2Te_3 legs were produced by Ion Beam Sputtering deposition. Herein, several thermal treatments were performed in the polyimide substrate (between 200 and 325°C).

Finally, a comparison of the different planar devices produced by different methodologies will be presented and discussed.

Electrochemically Exfoliated Graphene Oxide for Thermoelectric Applications

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In this study, thermoelectric properties of electrochemically exfoliated graphene oxide (EGO) were measured. The synthesis process for EGO samples consisted on the sequential process of electrochemical intercalation of perchlorate anions and MeCN in (HOPG) graphite, the expansion of the graphite using microwaves to evaporate the trapped acetonitrile, followed by electrochemical exfoliation in DMF and deposition on Nylon membrane to obtain a free standing film. These films were later electrochemically reduced yielding rEGO. The thermoelectric properties were measured for EGO films with thickness of $14 \pm 1 \mu\text{m}$, prior and post reduction treatment. The electrical conductivity was measured using a four point probe and measured at room temperature to be $10 \pm 1 \text{ Scm}^{-1}$ and $225 \pm 10 \text{ Scm}^{-1}$, for the EGO and rEGO respectively. The Seebeck coefficient was measured between 80K - 400K allowing us to identify the mode of transport, whilst measurements at room temperature resulted in Seebeck coefficients of $32 \pm 2 \mu\text{VK}^{-1}$, for both films. Therefore, power factors at room temperature were calculated as $1 \pm 0.1 \mu\text{Wm}^{-1}\text{K}^{-2}$ and $22 \pm 3 \mu\text{Wm}^{-1}\text{K}^{-2}$, for the EGO and rEGO respectively. The power factor was seemed to increase after reduction due to the increase of electrical conductivity while maintaining an adequate Seebeck coefficient. A further study showed a further increase the power factor to $48 \pm 10 \mu\text{Wm}^{-1}\text{K}^{-2}$ due to a subtle change in morphology, caused by using a different pore size filter.

Flow Velocity and Direction Sensor concept based on thermoelectric couples

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A flow velocity and direction sensor based on thermoelectric couples was modeled and simulated in COMSOL multiphysics software. The sensor consists of eight thermocouples composed of *n*-type bismuth telluride (Bi_2Te_3) and *p*-type antimony telluride (Sb_2Te_3), strategically placed around a central aluminum heater. In order to evaluate the direction of the water, trigonometric and sigmoidal calculations between the voltage output of the four interior thermocouples were able to predict the angle of the direction of the flow, with an error less than 5 degrees for a water flow velocity ranging from 0.001 to 1 m/s. For the water flow velocity evaluation, an electric current pulse was applied at the heater, and a linear relationship between the flow velocity and the time between the peak output of the two rows of thermocouples was achieved for water flow velocities ranging from 0.01 m/s to 1 m/s.

Thermoelectric Effect in Metal Dental Restorations

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This will be a composite poster comprising three separate posters previously presented at ICT2017 in Pasadena, ICT2018 in Caen, and ECT2019 in Limassol. The common theme of the posters is to highlight the fact that the thermoelectric behavior of metallic dental materials and restorations should be known. For example, dental amalgams are inhomogeneous mixtures of dissimilar metals. We should therefore expect their thermoelectric behavior to be more significant than any pure metal or any true alloy. Experimental investigations should therefore have been carried out in order to determine whether any electrical or electromagnetic effect arising from the thermoelectric behavior of metal dental restorations is large enough to dissipate electrical energy through the nerves in people's heads. However, it appears that when considered separately, thermoelectric scientists have been able to find sufficient excuse for ignoring calls made in each of the posters for such investigations to be carried out. The author feels that by presenting all three posters together the argument is made much more powerfully, and anyone with any real understanding of the thermoelectric effect, coupled with a genuine ability to think scientifically, will recognise that our apparent ignorance of the thermoelectric properties of metal dental materials cannot be justified.

Correlation of electronic and thermoelectric properties of transition metal dichalcogenides with strain and layer thickness

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Transition metal dichalcogenides (TMDs) offer a huge flexibility in tuning electronic properties. Their electronic structure changes dramatically from bulk to few monolayer samples. Using first-principles calculations performed within density functional theory and B1-WC hybrid functional, we studied the thickness and epitaxial in-plane strain dependences of the electronic and thermoelectric (TE) properties for TMD bulk and thin films, which form in 2H (MoS₂, MoSe₂, MoTe₂, WS₂, WSe₂, WTe₂) and 1T (SnS₂, SnSe₂, HfS₂, HfSe₂, HfTe₂, ZrS₂, ZrSe₂) structures. The thickness and in-plane strain change significantly electronic properties near the forbidden band gaps. We understand at atomic level these changes in terms of the interplay between in-plane σ and π bonding through sp^2 hybridization and the strong metal-chalcogen bonding inside atomic layers. Thickness and in-plane strain are effective ways to tune electronic band structures in order to increase the degeneracy of carrier pockets and optimize TE properties of TMDs. The correlation of electronic and TE properties with the bonding information for different pairs of atoms and their orbital contribution will be discussed.

Optimization of a H₂ self-powered sensor based on TE Si fabric

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Self-powered sensors running on small differences of temperature are considered promising candidates to cover the increasing demand of sustainable and maintenance-free wireless sensor networks for the Internet of Things (IoT).

A cost-effective self-powered hydrogen thermoelectric sensor is presented here for battery-less IoT nodes. The device is based on low density paper-like fabrics made of functionalized thermoelectric Si nanotubes able to harvest energy from the heat released by exothermic reactions, such as the hydrogen catalytic oxidation. This gives an accurate value of the reacting gas concentration without any external power requirement.

This self-powered sensor can autonomously measure concentrations as low as 250 ppm of hydrogen in air while generating power densities up to 0.5 $\mu\text{W}/\text{cm}^2$ for 3% H₂ at room temperature that can be eventually used to store or send the reading.

Analytical study of tunable device parameters predict that there is a wide margin of performance improvement. Varying fabric TE and catalyst layer thickness, doping level, device area and fabric density allow to tune the sensor output accordingly to the point of operation.

The aforementioned features, added to the cost-effective, reproducible and scalable synthesis route, its adaptability to any desirable shape, and the abundancy, non-toxicity and integrability of silicon, makes the proposed device very attractive for future implementation of self-powered wireless sensors nodes.

Zero contact resistance integrated p-doped Si NWs

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Nano structuration allows increasing thermoelectric figure of merit $ZT = S^2\sigma T/k$ by decreasing k . Silicon nanowires (Si NWs) with diameters in the order of ~ 100 nm present a significantly reduced k and can be currently obtained with controlled morphology, crystallinity and doping.

Typically, TE characterization of Si-based nanostructures, so far, have not demonstrated an efficient micro-device integration scheme, easily up-scalable and free from contact/parallel resistances. Apart from this non-representative TE characterization approach, another source of error in previous approaches arises when determining ZT from different samples.

In this work, boron doped $\langle 111 \rangle$ Si NWs with rough surface were grown and monolithically integrated in micro-fabricated test devices by means of the bottom-up CVD-VLS growth. The electrical (σ) and thermal (k) conductivities of were measured in the very same single nanowire by using self-heating method. Thermal conductivities as low as 15 W/Km were obtained thanks to nanostructuration. We demonstrate as well how both electrical and thermal contact resistances have been suppressed thanks to the monolithically integration of the NWs into the microdevice.

Finally, complementary Seebeck measurements of similar integrated NWs into specific devices were used to compute the Seebeck coefficient. This way, full characterization (ZT) of the nanostructure is achieved in a wide range of temperatures, with values ranging from 0.02 at 300 K to 0.2 at 620 K.

Thermoelectric properties of intermetallic compounds based on $Y(Ni_xCo_{1-x})_2$

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The results of electrical resistivity and Seebeck coefficient measurements of YCo_2 compound and $Y(Ni_xCo_{1-x})_2$ alloys, where $(0 \leq x \leq 0.2)$, are presented. The measurements were carried out at a temperatures of 100–800 K. YCo_2 is an exchange-enhanced paramagnet, where scattering of the charge carriers with itinerant spin fluctuations give essential contribution to the electronic and thermal transport. We study here the effect of substitution in cobalt sublattice by nickel on thermoelectric properties of $Y(Ni_xCo_{1-x})_2$ alloys. The substitution of cobalt for nickel leads to a modification of electronic structure in a vicinity of Fermi energy due to increasing population of the 3d band, and to appearance of additional scattering of the charge carriers on static disorder in cobalt sublattice. With increasing Ni-content, both, the electrical resistivity and the Seebeck absolute value increase. We discuss the experimental results with rigid-band structure approximation taking into account scattering of the charge carriers on magnetic fluctuations and on the static disorder.

Effective Thermal Conductivity of $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ - $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ Oxide composite: Role of Particle Size and Interface Thermal Resistance

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Reduced thermal conductivity (k) plays a vital role in the performance of thermoelectric materials. In this study, we present a novel approach to reduce the k in thermoelectric composite materials using acoustic impedance mismatch (AIM) and the Debye model. Also, the correlation between interface thermal resistance (R_{int}) and particle size of the dispersed phase on the k of the composite is discussed using Bruggeman's asymmetrical model. In particular, the k of an oxide composite which consists of a natural superlattice Aurivillius phase ($\text{SrBi}_4\text{Ti}_4\text{O}_{15}$) as a matrix and perovskite ($\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$) as a dispersed phase over a wide temperature range from 298 K-773 K is investigated. The k of the composites as a function of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (particle size $\sim 3\mu\text{m}$) volume fraction increases at each temperature indicating the negligible effect of R_{int} on k of the composite when the particle size of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is greater than Kapitza radius (a_K) ~ 500 nm. However, a significant reduction in the k of composite, even lower than the k of the matrix when the particle size of LSMO is smaller than the a_K is observed, depicting that R_{int} dominates for particle size lower than a_K due to increased surface to volume ratio. The obtained results have the potential to provide new directions for engineering composite thermoelectric systems with desired thermal conductivity and promising in the field of energy harvesting.

Investigation of the thermoelectric performances of nanostructured β -FeSi₂

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Iron disilicide can be an outstanding candidate for thermoelectric application if one achieves to improve its thermoelectric performances. After doping by Co or Al, leading to n-type or p-type extrinsic semi-conductor (respectively) its figures of merit reach 0.4 (843 K) and 0.2 (850 K) respectively. However, the thermoelectric performances of the pure β -FeSi₂ are limited by its rather high thermal conductivity, about 20 W/m K at RT and 5.5 W/m K at 900 K.

We report here the effect of nanostructuration on the thermoelectric properties and the thermal conductivity of dense pellets obtained by spark plasma sintering. It is well known that this technique limits the grain coarsening and permits to maintain the nanostructuration while sintering.

A decrease in the thermal conductivity, by a factor 3 at 323 K, was observed between bulk and nanostructured samples. This is explained by the phonon scattering at the interfaces. Although the ZT of pure β -FeSi₂ is still low, this study shows that the nanostructuration is an important route to investigate on doped alloys.

Thermoelectric properties of the non-textured and textured Bi_{1.9}Gd_{0.1}Te₃ compounds prepared by cold isostatic pressuring and spark plasma sintering

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Features in thermoelectric properties of non-textured and textured Bi_{1.9}Gd_{0.1}Te₃ compounds are analysed. Cold isostatic pressuring was applied to prepare non-textured samples, whereas textured samples were fabricated via spark plasma sintering. The same starting powder was used for both preparation methods. Texturing [001] axis coincided with direction of spark plasma sintering pressuring. Thermoelectric properties of non-textured sample are isotropic that is due to random grains orientation. Strong anisotropy in electrical resistivity and thermal conductivity, measured in directions parallel and perpendicular to direction of spark plasma sintering pressuring was found for textured sample. Texturing is partially recovering anisotropy inherent to single-crystalline bismuth telluride via redistributing anisotropic contributions from crystal a-b plane and c-axis into thermoelectric properties. Electrical resistivity decreases and thermal conductivity increases for parallel measuring orientation as compared to these properties for perpendicular measuring orientation. Highest thermoelectric figure-of-merit (~0.75 at ~420 K) was observed for textured sample for perpendicular measuring orientation.

High-efficient segmented PbTe-based thermoelectric module for energy applications

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In this study, we performed the design and modeling of the thermoelectric (TE) module consisted of n- and p-type segmented PbTe-based materials for the medium temperature range. The strategy of the advanced electronic structure engineering was applied to each section of the TE n- and p-legs for the fabrication of the high-performance generator module. The soul of this strategy is to keep the chemical potential in optimal in terms of energy conversion position over the entire temperature range. Using the computer simulation by finite elements methods we estimated that the maximum efficiency of such developed segmented PbTe-based module reached the value of ~15.0% for the temperature gradient of $\Delta T = 525$ °C ($T_h = 550$ °C, $T_c = 25$ °C) which is among the best state-of-the-art values reported to date. The design and construction of such a unique segmented module can significantly support the further implementation of the TE technologies for energy harvesting needs.

Influence of hydrogen content in 4340 steel on the mechanical properties and thermoelectric effect

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The issue of hydrogen presence in metals is a topic of great importance in materials science. Hydrogen even in very low concentrations can cause so-called hydrogen embrittlement. In particular, no rapid and non-destructive diagnostic methods have been developed so far to predict the phenomena associated with the interaction of hydrogen in metals. The presence of hydrogen dissolved in metal significantly changes the electronic properties of metal (e.g. Seebeck coefficient, work function) and mechanical properties. The main motivation of this research was to find a rapid and non-destructive method of determining the hydrogen content in the sample. The data obtained in this study indicates the correlation between the amount of hydrogen in investigated materials and the value of Seebeck coefficient measured on the surface. Presented findings obtained for uncoated steel are an introduction for further analysis of this correlation in steels coated with Zn/Ni or Cr layers produced by electrochemical methods.

Enhanced thermoelectric performance in Bi-Sb-Te/Sb₂O₃ nanocomposite systems

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Engineering of thermoelectric materials through hybridization with nanoparticles has been proved effective to boost their thermoelectric efficiency by providing the means to decouple thermal and electrical transport phenomena. Here, we report the synthesis of p-type Bi_{0.5}Sb_{1.5}Te₃/X wt.% Sb₂O₃ (X=0, 1, 2, 4, 6) nanocomposites, in which the Sb₂O₃ nanoparticles are dispersed mainly at the grain boundaries of the Bi_{0.5}Sb_{1.5}Te₃ matrix. It is shown that incorporation of up to 4 wt.% Sb₂O₃ into the matrix results in simultaneous enhancement of the Seebeck coefficient (by filtering of low energy charge carriers) and decline of thermal conductivity (mainly by charge carrier scattering at the interfaces), both of which contribute to improving the thermoelectric figure of merit to a maximum of 1.5 at 350 K. Moreover, the nanocomposites with 2, 4, and 6 wt.% Sb₂O₃ demonstrate ZT>1.0 up to 450 K, making them commercially appealing for thermoelectric applications at a wide temperature range. Furthermore, it is shown that Bi_{0.5}Sb_{1.5}Te₃/4 wt.% Sb₂O₃ samples exhibit excellent thermal and chemical stability in ambient atmosphere and 300–475 K temperature range over a 24-month period. [1]

References

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Pencil Traces on Paper to Fabricate a Thermoelectric Generator

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Graphite pencil traces on regular Xerox paper are successfully employed to constitute a thermoelectric generator. Graphite traces act as both p-type and n-type thermoelectric legs with the help of polyethylenimine polymer, allowing fabrication of graphite based thermoelectric generator. The fabrication method is quite simple and straightforward, and also requires no conducting paste to make electrical connections between the thermoelectric legs. A test module having 5-pairs of p-n legs was fabricated on a piece of paper that produced a voltage of 9.2 mV generating an output power of 1.75 nW at ~60 K temperature difference. Present work demonstrates that a common pencil art on a paper can work as a cheap, flexible, and environmentally friendly thermoelectric generator.

Thermoelectric properties of n-type half-Heusler NbCoSn by heavy-element Pt substitution

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The favorable electronic structure of half-Heusler alloys with a valence electron count of 18 promote them as good thermoelectric materials. Theoretical reports described a high electrical power factor in the NbCoSn half-Heusler alloy, which has not been investigated in-depth experimentally. Heavy-element Pt-substituted NbCoSn alloys were synthesized and characterized, carrying out structural analysis and thermal transport measurements. This substitution optimizes the carrier concentration, improving the electrical power factor, and simultaneously reducing the lattice thermal conductivity due to the enhanced mass fluctuation scattering of phonons. Increased grain size due to annealing of the samples further increases carrier mobility, which is ascribed to the decreased grain boundary scattering. The reduced lattice thermal conductivity along with a maximum power factor of $\sim 3.4 \text{ mWm}^{-1}\text{K}^{-2}$, yields a figure of merit zT of ~ 0.6 at 773 K for the post-annealed $\text{NbCo}_{0.95}\text{Pt}_{0.05}\text{Sn}$, an increase of 100% compared to the undoped NbCoSn. This work highlights the important roles of the doping element and micro-structure on the thermoelectric properties of half-Heusler compounds.

Ca₃Co₄O₉ films with enhanced thermoelectric properties from Ca(OH)₂/Co₃O₄ multilayers with adjusted component fractions

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Nanoporous Ca₃Co₄O₉ thin films have been synthesized by annealing the as deposited multi-layered Ca(OH)₂/Co₃O₄ films growth on mica substrates. The effect of initial phase distribution of Ca(OH)₂ and Co₃O₄ on formation of nanoporous Ca₃Co₄O₉ thin films are investigated by designed a series of experiments. The Ca(OH)₂ (001) layers in the as deposited multi-layered Ca(OH)₂/Co₃O₄ films are beneficial for the formation of nanoporous Ca₃Co₄O₉ thin films after annealing. Otherwise, the layers of Co₃O₄ rather than CoO in as deposited multi-layered CaO/Co₃O₄ films appears necessary for the formation of Ca(OH)₂. The obtained nanoporous Ca₃Co₄O₉ thin film exhibits high porosity, high electrical conductivity and high power factor at room temperature. The power factor and electrical conductivity are around 1.65 μW cm⁻¹ K⁻² and 90 S/cm, respectively.

Modelling the process of functional materials synthesis in reaction crucibles

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The reaction crucible method is one of the experimental methods of combinatorial analysis, with the help of which equilibrium phase diagrams are constructed. In contrast to the diffusion pair method inside a reaction crucible made of a chemical element with the highest melting point, one or two components can be in a liquid state during annealing, which significantly accelerates the formation of intermediate phases.

The main disadvantage of this technique is the problem of "disappeared" phases. This problem is explained by the kinetics of the formation of a new phase and the interaction between the equilibrium phases in the diffusion zone, which is characterized by gradients of component concentrations.

The aim of this study is to develop a modified method of reaction crucibles using electric current to solve the problem of disappeared phases in this method of combinatorial analysis.

In order to do so a Comsol Multiphysics model was created. A thermal, mechanical, electrical and chemical modules were used in order to accurately simulate the process.

The model demonstrates the synthesis process and grants an opportunity to observe various parameters at any time point. This data may be helpful for sample's properties evaluation.

Development of a mathematical model of the automotive thermoelectric generator system operation taking into account the negative impact on engine power and the specific driving cycles

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It is considered for combustion engines to have nearly 60-70% of fuel energy to be dissipated to the environment by the exhaust gases. Automotive thermoelectric generator (ATEG) application is proved to be a solution for increasing vehicle fuel economy by exhaust gas waste heat recovery. To optimize ATEG design, various parameters have to be tested. For this purpose, a mathematical model of the ATEG system operation has been developed. This model is used to calculate ATEG output characteristics and to estimate overall vehicle efficiency improvement taking into account the specific driving cycles and the negative influence of hydraulic resistance of the generator by its presence in the vehicle exhaust system on the internal combustion engine. The model is based on the nonlinear equations of thermal flows balance and power balance implemented in MATLAB software by means of quadratic residual optimization methods. A simulation was performed using VAZ-21126 engine, which demonstrated that up to 400 W of electric power can be obtained using ATEG. The simulation results are compared with data obtained from laboratory experiments. We discuss error bars and the accuracy of the simulation results for our own developed thermoelectric car system.

Thermoelectric properties of nonmetallic filled β -manganese phases: a new family of compounds with extremely low lattice thermal conductivity

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Structural, thermal and transport properties of non-metallic filled β -manganese phases with the chemical composition $A\text{Tr}_6\text{Te}_{10}$ (A: Pb^{2+} , Sn^{2+} ; Tr: In^{3+} , Ga^{3+}) were analyzed. It was observed, that the ternary compounds crystallize in a disordered rhombohedral R32 structure at high temperatures and they undergo a polymorphic phase transition into ordered trigonal P3221 structure at low temperatures. Measurement of heat transport properties revealed that all studied samples with non-metallic filled β -manganese structure have extremely low values of thermal conductivity κ (below $0.6 \text{ Wm}^{-1}\text{K}^{-1}$) over the entire temperature range, being one of the requirements for promising thermoelectric material. Measurements of electronic transport properties show that $\text{PbGa}_6\text{Te}_{10}$ and $\text{SnGa}_6\text{Te}_{10}$ have large positive values of the Seebeck coefficient ($100\text{-}650 \mu\text{VK}^{-1}$) over the entire measured temperature range. However, the electrical conductivity results low. Consequently, further detailed study of the crystal structure is required for understanding and optimization of transport properties towards high performance on energy conversion.

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Combining phonon accuracy with high transferability in machine-learned interatomic potentials

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Vibrational properties play a crucial role for the application of thermoelectric materials. [1] Good thermoelectric properties are typically connected with low thermal conductivity. Computing thermal conductivity and other phonon properties with density functional theory is very slow. Therefore, this approach cannot be used for high-throughput computations and is typically circumvented. [2,3] In this poster, we explore how machine-learned interatomic potentials can be used to calculate phonons and thermal conductivities and thereby aim at an accelerated calculation of these properties. [4] We arrive at excellent agreement with reference data of density functional theory (agreement of phonon frequencies within 0.1-0.2 THz). We also show that this can be combined with excellent quality of the potential for amorphous materials.

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Simulation of the convection behavior in a liquid-based thermoelectric generator

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Energy harvesting using thermoelectric generators (TEG) based on ionic liquids (IL) has shown great potential in recent years. Previous studies indicate that IL as active substances in TEGs have the capability to reduce the thermal conductivity, thus causing a high temperature gradient and increasing cell voltage compared to solid-state materials. However, sufficient electrical current extraction turns out to be a challenge. For IL-based TEGs ion interactions of IL with the electrode-interfaces are considered to play a crucial role in generating high generator voltages. In order to better understand the physical conditions and thus to support the design of an optimal TEG cell, finite element analysis (FEA) is used to simulate the thermal and hydrodynamic behavior. To verify the simulation, measurements are carried out to determine the flow velocity and convection behavior using 2D particle image velocimetry (PIV) in a dimensionally variable TEG cell using different media. Water, which has well-known properties, is used to verify the simulated model, followed by simulation and measurement with the ionic liquid ethylammonium nitrate (EAN). Further investigations were performed with different temperature gradients, different cell volumes, and additional IL-types. In a future approach, the thermoelectric behavior as well as the attachment-model is to be integrated into the simulation to allow an estimation of the generated electrical power.

Solvothermal synthesis route and electronic properties of a new Cu-rich tetrahedrite ($\text{Cu}_{12+x}\text{Sb}_4\text{S}_{13}$)

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The aim of the research was the development of a single-step synthesis method of the new $\text{Cu}_{12+x}\text{Sb}_4\text{S}_{13}$ phase with tetrahedrite structure under solvothermal conditions, using 1-(2-aminoethyl) piperazine serving both as a solvent and reagent. The physical properties of the new Cu-rich tetrahedrite phase are not well investigated; therefore, electronic structure calculations of this phase were performed.

We have observed that the stoichiometric tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) is created even after 6 hours of synthesis. However, extending the synthesis time led to the transformation of this phase into tetrahedrite with excessive Cu content. A new phase, almost pure $\text{Cu}_{12+x}\text{Sb}_4\text{S}_{13}$ ($x \sim 2$), has a larger cell parameter than $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ and can be obtained after 10 days.

The influence of the Cu excess in $\text{Cu}_{12+x}\text{Sb}_4\text{S}_{13}$ on electronic properties was studied using electronic structure calculations by the KKR-CPA method accounting for the presence of Cu vacancy defects and chemical disorder on three inequivalent Cu sites. The problems of co-existence of two tetrahedrite phases with different stoichiometry and different occupancies of Cu sites as well as the tendency of tetrahedrite structure to release Cu atoms were addressed to total energy analysis. The determined impact of increasing Cu content on the character of electronic bands in the vicinity of the Fermi energy was discussed in the context of potential thermoelectric properties.

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Measuring Thermo-mechanical stresses in Thermoelectric leg

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Sustaining longevity of the thermoelectric modules remain a challenge. Many companies are trying to explore new stable materials and methodologies to improve structural designs in order to construct reliable modules for harsh atmospheres. Currently, due to successful experiments, thermoelectric modules are being utilized in different space missions and industrial premises. Unsegmented thermoelectric modules are simple to operate but their applications are limited due to low conversion efficiencies. Whereas, segmented thermoelectric modules got significant amount of advantage over unsegmented thermoelectric modules, materially and performance wise, but structural reliability, from medium to high temperature (up to 1000 °C and more) is still unresolved challenge. Segmented modules encounter high stress due to increase in operating temperature. Difference in coefficient of thermal expansion between different materials and changing temperature produces different types of stresses within structure. Consequently, these stresses create deformation (bending, deflection) and cracks at thermoelectric legs. In this paper a comprehensive mathematical model for Thermoelectric modules is discussed. The experimental and numerical simulation results, driven from thermo-mechanical stresses, are presented. Finite element simulation is used to demonstrate the influence of thermo-mechanical stresses on each thermoelectric material and module's legs.

PbTe nanopowder prepared using the Pulsed Plasma in Liquid technique

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Thermoelectric nanomaterials are gaining interest due to their unique properties related to phonon scattering and energy filtering phenomena, however, their preparation is usually done by costly and non-scalable processes e.g. high-energy ball milling. Pulsed Plasma in Liquid (PPL) is a novel, low-cost, and easily scalable, top-down method for the preparation of nanopowders of conductive materials. The PPL setup consists of two electrodes made of precursor materials submerged in a dielectric liquid. When the electric field between the electrodes is strong enough, a spark is induced that leads to partial evaporation of the electrode materials (creation of plasma) followed by rapid quenching in the surrounding liquid that prevents grain growth.

In this work, for the first time, the PPL method was applied to prepare the PbTe nanopowder. SEM and EDX analyses confirmed the desired elemental composition of PbTe with slight random deviations from stoichiometry. Powder XRD analysis revealed single phased materials with patterns matching that of PbTe (s.g. Fm-3m). TEM observation of the finest grains revealed amorphous clusters of Pb and Te atoms. Grain sizes varied from below 20 nm in the finest amorphous fraction, up to few tens of nm in the highly crystalline fraction. The applied method can be successfully used for the preparation of the other nano-sized thermoelectric materials.

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The impact of microstructure and interface thermal resistance on thermal conductivity in PbTe-CoSb₃ bulk polycrystalline composite

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Using effective media theory (EMT), we present the impact of particle size and interface thermal resistance (R_{int}) on total thermal conductivity (κ) of a composite. Understanding these relationships will allow us to control the heat transport phenomena in composite thermoelectric materials. Systematic experimental and theoretical research was conducted on a series of polycrystalline composite $(1-x)\text{Pb}_{0.99}\text{Sb}_{0.01}\text{Te}/(x)\text{CoSb}_{2.94}\text{Te}_{0.06}$ materials with different particle sizes. The structural (XRD) and microstructural analysis (SEM/EDS) was performed to confirm the chemical and phase composition. The acoustic impedance difference (ΔZ) between the PbTe and CoSb₃ phases was determined. The R_{int} was estimated using the Acoustic Impedance Mismatch (AIM) model and the Debye model as well as it was measured by Laser Flash Analysis (LFA) method over the temperature range from 50°C to 400°C. Based on several variants of the Bruggeman model, it was found that ΔZ and R_{int} are relatively small due to little differences in sound velocities in both phases. Determined Kapitza radius is rather small (~100nm), therefore, any noticeable reduction in κ will be obtained for particles smaller than this size. Our approach concerning the selection of the components with different elastic properties and particle size smaller than the Kapitza radius leads to a new direction in the engineering of composite thermoelectric materials with designed thermal properties.

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Thermal and electrical properties of Al₂O₃ layers prepared by anodic oxidation

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The research was focused on thermal and electrical properties of thin oxide layer (Al₂O₃) for potential application in electronics as a dielectric surface. The substrate to produce oxide layers were plates from the commercial aluminium alloy EN AW – 1050 A with an aluminium content of min. 99.5%. It has good mechanical properties, high thermal conductivity and is perfect for anodizing. The alloy was subjected to pre-treatment on a grinding and polishing machine. Then chemically purified in aqueous solutions of hydroxide and nitric acid at elevated temperature. Anodizing tests were carried out in sulfuric acid in two series, the first at constant current density and variable time, and the second at constant time and variable current density. Voltage changes during anodizing were measured. The last step of the process was sealing the coatings. Samples with different ceramic layer thicknesses were tested for thermal conductivity using LFA method. The electrical properties like breakdown voltage resistance (min. 30V - max. 100V) were also measured. The microstructure of the surface and cross-section of the alumina layer formed under experimental conditions was observed by scanning electron microscopy. As a result, produced layers on aluminium alloy have high thermal conductivity similar to thermal conductivity of the tested alloy and breakdown voltage resistance at 100V was obtained. The Al₂O₃ coatings observed on SEM are homogeneous and their pores are evenly distributed.

Concepts for achieving thermal control in thermoelectric generators under variable heat sources

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The development of new efficient non-toxic and affordable thermoelectric materials rises the possibility of developing viable Thermoelectric Generators (TEGs) for cost-sensitive applications such as automotive ones. However, TEGs are very sensible to the thermal level. They are both temperature limited and have poor output if their hot side temperature is not high enough.

Several concepts to achieve thermal control which have been explored by the authors using heat exchangers (HXs) with phase change in automotive exhaust applications are presented. These applications typically suffer from highly variable thermal sources during driving. One option is to absorb all the heat from the heat source exclusively by vaporization and then deliver it by condensation at a specific boiling temperature to the TEGs using thermosiphons (TSs) or heat pipes (HPs). Another option is to embed these devices into the exhaust HX and use them just to facilitate the spreading of the heat from the overheated regions of the HX to its cooler regions. This heat spreading is also done at controlled phase change temperature, so that heat spreading will only happen in situations where overheating would otherwise occur. This way it seems possible to maximize heat absorption and optimize thermal level along a broad range of operating conditions without overheating concerns. This, along with the use of affordable materials, might enable viable automotive TEGs.

US Program

Selective Laser Melting of $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ and Resulting Nano- and Micro-structures

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Thermoelectric modules are often overlooked due to their inefficiency compared to other energy-conversion technologies. Previous research shows that controlling the material structure with different manufacturing techniques (hot pressing, spark plasma sintering, and melt spinning) can optimize the material properties and improve efficiency. In this work, we investigated a new manufacturing approach, selective laser melting, and the nano- and micro-structures induced in $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ from the novel processing mechanism. Microscopy results showed the grain morphology in the laser melted bulk samples had a high aspect ratio, and grains were oriented in the build direction. Scanning and transmission electron microscopy images revealed amorphous and rectangular features at grain boundaries and within grains of the material. Energy dispersive spectroscopy results showed bismuth, oxygen, and tellurium rich areas, which suggested the formation of oxides and phase separation zones during the repeated rapid melting and solidification that occurs in selective laser melting. Seebeck coefficient measurements showed a shift in material behavior from n- to p-type, likely from the formation of sparse bismuth oxide inclusions. Because selective laser melting is an additive manufacturing technique (colloquially known as 3D printing), this work informs the impact of emerging manufacturing processes on the structure and properties of bismuth telluride and similar semiconductor materials.

Native Defects in CuInTe_2

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Chalcopyrite diamond-like semiconductors are promising p-type thermoelectric materials as a result of the native defects. In this talk, we focus on the defects in off-stoichiometric CuInTe_2 along with the high temperature thermoelectric properties. Calculations indicate that electronic properties are controlled by the three dominant defects V_{Cu} , Cu_{In} , and In_{Cu} . To validate these calculations, intentionally off-stoichiometric samples were produced by melt synthesis followed by a hot-pressing procedure. Collectively, the off-stoichiometric samples show a range of carrier concentrations that span five orders of magnitude. Both copper rich and copper deficient samples are found to have high hole carrier concentrations as a result of the CuIn anti-site defects and copper vacancies respectively. However, indium rich samples show very low hole carrier concentrations nearing 10^{15} cm^{-3} as a result of In_{Cu} defects. The high temperature Seebeck coefficients suggest that at such low carrier concentrations, bipolar conduction may be occurring. Mobility of the off-stoichiometric samples suggests that copper vacancies act as strongly scattering point-defect sites while the other native defects scatter less strongly. Such vacancy scattering extends to the thermal conductivity where a reduction in κL contributes to a higher zT value. Understanding and controlling the native defects in CuInTe_2 provides a route towards n-type dopability as well as optimization of the p-type material.

Discordant nature of Cd in PbSe: off-centering and core-shell nanoscale CdSe precipitates lead to high thermoelectric performance

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This work demonstrates a synergistic combination of mechanisms in p-type PbSe brought about by the addition of CdSe to achieve the enhancement in the power factor and concomitant reduction in thermal conductivity, eventually yielding a record average $zT_{\text{ave}} \sim 0.83$ across 400-923 K. This significant advance is realized by all-scale microstructure construction via Cd alloying. We find that the behavior of the Cd atoms in the octahedral rock salt sites is discordant and results in an off-center displacement and distortion. Such off-centered Cd in the PbSe matrix creates 1) L-sigma electronic energy band convergence, 2) flattened L band, both contributing to higher Seebeck coefficients, and 3) enhanced phonon scattering which leads to lower thermal conductivity. Above the solubility limit (>6% CdSe), we also observe endotaxial CdSe nano-precipitates with core-shell architecture formed in PbSe, whose size, distribution and structure gradually change with Cd content. The nano-precipitates exhibit zinc blende crystal structure and tetrahedral shape with significant local strain, but are covered with a thin wurtzite layer along the precipitate/matrix interface, creating a core-shell structure embedded in PbSe. This newly discovered architecture causes further reduction in lattice thermal conductivity. Moreover, potassium is found to be an effective p-type dopant in PbSe-CdSe system, leading to enhanced power factor, a maximum zT of ~ 1.4 at 923 K for $\text{Pb}_{0.98}\text{K}_{0.02}\text{Se}$ - 6% CdSe.

Aikinite: a promising sulfide for thermoelectric applications

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Large-scale production of thermoelectrics devices requires the design of novel materials that exhibit high performance, are low cost, environmentally sound, and earth-abundant. In this context sulfide minerals are a promising family. Here, we discuss the electronic and vibrational properties of aikinite. $XCuBiY_3$ (with $X = Pb$ and $Y = S$) crystallizes in an orthorhombic cell where Cu has a distorted tetrahedral coordination, S has octahedral coordination, while Pb is bonded to eight S in an approximate octahedral environment. The material is a semiconductor with a gap of 0.5 eV. The bands reveal large effective masses at Γ -Z direction in both the valence and conduction bands. The phonon spectrum exhibits optical phonons below 50 cm^{-1} which may lead to a low lattice thermal conductivity. We performed chemical substitutions to optimize the performance and limit the toxicity ($X = Sn$, $Y = Sn, Se, Te$). Electronic and thermal transport results are computed using the PAOFLOW package integrated in AFLOW π high-throughput framework. Our results show that these minerals are promising candidates in thermoelectric applications.

Temperature-dependent bond strength and sound velocity in $(\text{GeTe})_m\text{Sb}_2\text{Te}_3$ alloys

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$(\text{GeTe})_m\text{Sb}_2\text{Te}_3$ alloys have been previously shown to be excellent thermoelectric material with the figure of merit >2 when fully optimized. The $(\text{GeTe})_m\text{Sb}_2\text{Te}_3$ superlattice can be visualized as m layers of GeTe inserted into the center of each Sb_2Te_3 slab, which expands the initial unit cell of Sb_2Te_3 to include long-range ordered 3D blocks with vacancies between the blocks. The $(\text{GeTe})_m\text{Sb}_2\text{Te}_3$ superlattice exhibits a phase transition from rhombohedral ($R3m$) to cubic rock salt ($Fm-3m$) at high temperatures, similar to GeTe. This reversible phase transition is accompanied by abrupt changes in electrical and optical properties, enabling applications in phase-change memory devices. However, even though the structural and thermal properties of these materials have been studied in some depth, the effect of the phase transition on bond strength and phonon transport properties has not been studied. In this study, we combine high temperature X-ray diffraction and high-temperature resonant ultrasound spectroscopy to measure the lattice parameters, elastic moduli, and sound velocity in $(\text{GeTe})_m\text{Sb}_2\text{Te}_3$. We find that the elastic moduli and speed of sound increase gradually with increasing temperature up to the phase transition, then exhibit a final sharp increase upon transforming to the rock salt structure after which the elastic moduli begin to decrease. Our results suggest that with increasing temperature, the ordered vacancy layers diffuse gradually into the surrounding distorted rock salt matrix, increasing the interlayer bond strength, thus leading to the anomalous temperature-dependence of the thermal conductivity.

Enhancement of Thermoelectric Performance for n-type PbTe-xGeTe

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Thermoelectric materials can convert waste heat directly into electricity without gas emissions and hazardous moving parts, which provide a future for waste heat harvesting. The efficiency of the thermoelectric module is directly decided by the average figure of merit, zT_{avg} . PbTe thermoelectric material has the outstanding medium-temperature thermoelectric performance. The p-type PbTe-based thermoelectric materials have achieved high zT value above 2 by incorporating nanostructures and band convergence. However, n-type PbTe shows inferior performance than p-type counterpart in thermoelectric efficiency. Here, the significant progress was made in raising the thermoelectric performance of n-type PbTe using Ga-doping and GeTe-alloying. This strategy can introduce two midgap states between the conduction and valence bands. These midgap states lead to the increased density of states effective mass and the enhanced Seebeck coefficient. Moreover, the discordant Ge atoms in the PbTe matrix and introduced Ga_2Te_3 nanoscale precipitates cause intense phonon scattering and significantly reducing the thermal conductivity. As a result, a peak zT_{max} of ~ 1.47 at 673 K and the record high zT_{avg} of ~ 1.27 from 400-773 K for n-type PbTe were obtained for $\text{Pb}_{0.98}\text{Ga}_{0.02}\text{Te}-5\%\text{GeTe}$ sample.

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Analysis of the Method of Four Coefficients

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To date, the thermoelectrics community relies on a three-coefficient SPB model with the presumption of acoustic phonon scattering. This assumption does not capture the overall energy dependence on relaxation time as scattering mechanism in a material changes. To probe these changes we focus on utilizing a fourth measurement of electronic transport, the Nernst coefficient. The Nernst Effect, in conjunction with the three traditional transport measurements (Seebeck, Hall, and conductivity) can be used to directly calculate the Fermi level, effective mass, scattering parameter, and relaxation time. This method, known colloquially as the method of four-coefficients, is currently under-utilized due to the difficulty of Nernst measurements. Plagued by low signals and unclear analytic limits, outlining where the Nernst effect is highest is critical to the success of this four-coefficient approach. Here we focus on the analysis of the method of four coefficients and the pitfalls therein. We investigate this approach via analytically and numerically over a range of realistic material parameters. We begin with foundational mathematics and ultimately demonstrate the correlation between four electronic, measurable coefficients to four underlying material parameters. As such, we are able to demonstrate regions of theoretical high Nernst values and how error propagates through this analysis.

Spin-thermoelectric Properties Characterization by Electron Spin Resonance (ESR)

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Spin-based thermoelectric materials have shown prospect to enhance the thermopower and thermoelectric figure-of-merit from properties like magnon/paramagnon-electron drag and spin entropy. Magnetic semiconductors, therefore, are being considered to boost the thermoelectric performance of the materials. Here, one major roadblock is to characterize the spin-thermoelectric effects versus temperature and magnetic field. Accurate measurement techniques are often based on inelastic neutron scattering (INS), different types of magnetometers, and magnetic resonance. Among these, magnetic resonance provides some unique advantages like versatile sample type, wide temperature range, broad frequency spectrum, and high sensitivity. Besides, magnetic resonance measurement can provide critical information like magnetic phase, phase transition temperature, g-values for magnetic ions, and spin-lattice relaxation time. To demonstrate the versatility and capabilities of the magnetic resonance measurement, especially ESR, we probed spin-lattice relaxation time of the undoped and differently doped MnTe using ESR. MnTe is an antiferromagnetic semiconductor with significant magnon- and paramagnon-electron drag thermopower. Magnon and paramagnon lifetimes are essential parameters that determine the drag thermopower and are related to the spin-lattice relaxation time. Magnon and paramagnon lifetimes obtained from ESR for MnTe showed a good agreement with those determined from INS measurement.

Full Experimental Seebeck Tensor Characterization for (p × n)-Type Transverse Thermoelectrics

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In (p × n)-type transverse thermoelectric materials, highly anisotropic ambipolar conduction leads to an off-diagonal Seebeck coefficient, generating a voltage drop perpendicular to an applied temperature gradient. However, most standard experiments only measure longitudinal Seebeck coefficients along specific directions, which is insufficient to fully characterize transverse thermoelectric properties. Here, we present an all-in-one setup for measuring the full Seebeck tensor. By sandwiching a rectangularly shaped sample between two anodized aluminum blocks, homogeneous temperature gradients can be applied successively along all 3 orthogonal directions and measured by built-in thermocouples, with longitudinal and transverse Seebeck voltages measured with strategically placed contacts. A pre-characterized isotropic PbTe sample is measured for calibration. The diagonal Seebeck coefficients agree with the calibration value to within 10%, and four of the six off-diagonal terms are correctly zero to within 3% of the diagonal value. The two other off-diagonal coefficients, however, are off by ~50% due to relatively large contact offset (~0.5mm) comparing with the small sample thickness (~1mm), which can be overcome in a newer design by more precise placement of the contacts. This method allows full characterization of all components of the complete anisotropic Seebeck tensor in transverse thermoelectrics for the first time.

Evaluating Mobilities of Both Carriers from a Single Bulk Sample Using Photo-Seebeck Effect

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When a semiconductor is under photoexcitation, the voltage response to a temperature gradient is the photo-Seebeck effect. In this work, we study this effect, focusing on the contribution from transport of photo-excited carriers. We demonstrate that by combining photo-Seebeck with photoconductivity measurements, one can determine the ratio between electron and hole mobilities, and hence both of them when one is known. This is found for the case of defect-free samples, where no detail on the absorbance, carrier lifetime or recombination is necessary. Our method does not require chemical doping, which could introduce defects and is often not feasible. It applies to both thin film and bulk samples. We further suggest that for semiconductors with significant influence from defects, photo-Seebeck measurements can be combined with another photo-transport property, such that one could probe the defect influences on each type of carriers: the mobility reduction due to scattering, or carrier density reduction due to trapping. This framework integrates the information from photoexcitation and thermal gradients to provide a general method to determine fundamental electronic properties of materials.

Creep behavior of thermoelectric materials

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Since the 1960's, NASA has implemented Radioisotope Thermoelectric Generators (RTGs) to supply energy for many of its satellites and space probes. Similar generators for industrial and automotive waste heat recovery have been proposed and many new thermoelectric generator materials have been investigated. Nonetheless, mechanical integrity for the full operational life of the thermoelectric modules, which can extend to decades, has not been given much consideration in such applications. Among many contributors, clamping forces, vibrational stresses, and thermally-induced mismatch stresses may combine to give stress levels high enough to deform the thermoelectric module by creep, thus diminishing its useful lifetime. To date, few thermoelectric materials have been tested for creep, including Bi_2Te_3 , PbTe , $\text{Mg}_{1.96}\text{Al}_{0.04}\text{Si}_{0.97}\text{Bi}_{0.03}$, and TAGS-85. In the present talk, we show the case of the compressive creep deformation behavior of two thermoelectric materials; half-Heusler n-type $\text{Hf}_{0.3}\text{Zr}_{0.7}\text{NiSn}_{0.98}\text{Sb}_{0.02}$ and n-type Skutterudite ($\text{Yb}_{0.3}\text{CoSb}_3$) alloys, at 500-705 °C. When subjected to uniaxial compressive stresses at 600 °C, the n-type half-Heusler alloy $\text{Hf}_{0.3}\text{Zr}_{0.7}\text{NiSn}_{0.98}\text{Sb}_{0.02}$ exhibits Newtonian flow, consistent with diffusional creep of its fine-grain (1-7 μm) microstructure achieved via spark-plasma sintering of powders. In addition to its promising thermoelectric performance at high temperatures, this alloy sustains very high compressive stresses at 600 °C (from 21 to 359 MPa, for ~ 23 days) without macroscopic failure. On the other side, the n-type Skutterudite (Yb-CoSb_3) alloy showed modest creep resistance, in between that of low-temperature thermoelectrics (Bi_2Te_3 , PbTe) and high temperature ones (half-Heuslers and Mg_2Si -based)

Determination of the thermoelectric figure of merit using the Peltier cooling effect

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The maximum temperature depression, ΔT_{\max} , that can be obtained using the Peltier effect is simply related to the figure of merit, zT , of a thermocouple and can, in principle, be used to determine that quantity. However, for good thermoelectric materials, with zT of the order of unity or greater, this temperature depression, ΔT_{\max} , can be very large and it is difficult to assign the measurement to a particular temperature. This is less of a problem if the thermocouple consists of a semiconductor and a metal since zT and ΔT_{\max} are then much smaller. We have been developing a procedure for the measurement of the dimensionless figure of merit of a semiconductor using semiconductor-metal thermocouples in which the relative form factors of the two branches are optimized. We also show that there are attractive features in the measurement of ΔT_{\max} when the ratio of the form factors for the two branches is very far from being optimized. Our experiments on couples consisting of a bismuth telluride alloy and constantan show that radiation losses are significant at ordinary temperatures.

Extended anharmonic collapse of phonon dispersions in SnS

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The lattice dynamics and high-temperature structural transition in thermoelectric SnS were investigated via inelastic neutron scattering, high-resolution Raman spectroscopy and anharmonic first-principles simulations. We uncover a spectacular, extreme softening and reconstruction of an entire manifold of low-energy acoustic and optic branches across a structural transition, reflecting strong directionality in bonding strength and anharmonicity. Further, our results solve a prior controversy by revealing the soft-mode mechanism of the phase transition that impacts thermal transport and thermoelectric efficiency. Our simulations of anharmonic phonon renormalization go beyond low-order perturbation theory and capture these striking effects, showing that the large phonon shifts directly affect the thermal conductivity by altering both the phonon scattering phase space and the group velocities. These results provide a new level of microscopic understanding of phase stability and thermal transport in technologically important materials, providing further insights on ways to control phonon propagation in thermoelectrics.

Anharmonicity in binary chalcogenides through Raman spectroscopy

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Anharmonicity addresses interactions between two or more lattice vibrations (or phonons) which describe physical properties of crystalline materials, such as heat capacity, lattice heat conduction, and temperature dependence of phonon frequencies. Here, we present a combined temperature dependent polarized Raman and heat-capacity study of single crystalline SnSe which is a binary chalcogenide that exhibits strong anharmonicity. Through detailed analyses, we determined the contribution of the quasi-harmonic volume expansion, and anharmonic phonon-phonon interaction (which includes the three- and four-phonon processes) to the temperature dependent Raman frequency shifts. We found that the contribution of the three-phonon process was dominant in SnSe that is extensively studied for its thermal transport properties with high zT , unlike the four-phonon process which is dominant in GeTe attributed to its large phonon band gap (which limits the number of decay channels available for three-phonon process). Consistent with our Raman analyses, the study of our temperature-dependent heat-capacity and lattice thermal conductivity also revealed the presence of strong anharmonicity in both SnSe and GeTe. Thus, Raman spectroscopy provides useful information about phonon interactions, highlighting the importance of phonon engineering approaches to improving thermoelectric performance.

The dependence of mechanical and thermal properties on dislocation strain and intrinsic defects in PbTe

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Modern reports on heavily-doped, p-type PbTe materials reach the zTs necessary for improved space power generation or waste heat recovery, largely thanks to lattice softening from high dislocation densities. However, unexplained brittle behavior at high electronic doping levels occurs in p-type PbTe, but not in n-type PbTe. This distinctively asymmetric trend restricts our community's best-performing materials for practical use. Our mechanical and elastic property measurements on single crystal and polycrystalline PbTe contradict previously suggested explanations for embrittlement, such as bond stiffening from PbTe's Σ band. We also show certain dopants break the previously established mechanical trend. Strain measurements through neutron powder diffraction show that ball milling can double the amount of strain in undoped PbTe beyond unstrained samples. Introducing extrinsic p-type dopants increases the strain by another factor of two and better maintains strain at high temperatures. We propose that increased dislocation strain, which reduces thermal conductivity, is also linked to embrittlement. Our results suggest a crucial dependence of strain on extrinsic dopant and intrinsic defect character. Introducing dislocation strain thus appears to be beneficial for thermal properties and detrimental mechanically. This study seeks to explore the link between these properties and offers routes to tune them through phase boundary mapping and intrinsic defect engineering.

Microstructural Evolution in Thermoelectric Materials

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Typically, thermoelectric materials are measured and thermally cycled for relatively short periods of time. As a result, some of the long-term effects due to high temperature exposure may be overlooked. This talk will discuss the findings of our recent study on $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_{3+x}$ (BST) compounds in which we document the volume expansion of the sample during high temperature annealing. Additionally, this volume expansion resulted in porosity, which yielded in an improvement in thermoelectric performance parallel to the pressing direction of our hot-pressed samples. In this study, comprehensive materials characterization was used in conjunction with Effective Medium Theory (EMT) to develop an explanation for the improved thermoelectric performance in our porous BST samples. In particular, we used high resolution electron microscopy to identify stepping in individual twin boundaries, in combination with Electron Backscattered Diffraction (EBSD) to prove that there was a statistical increase in the twin boundary percentage during annealing. Furthermore, we were able to identify and rule out the influence of other microstructures whose presence and morphology remained consistent throughout annealing. In summary, we show the importance of annealing samples to ensure thermal stability during operation, as well as highlight the changes in twin boundary structure and population with the hopes of encouraging future work in the area of twin boundary engineering in BST compounds.

Microscopic Mechanisms of Glass-Like Lattice Thermal Transport in Cubic $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ Tetrahedrites

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Materials based on cubic tetrahedrites ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) are useful thermoelectrics with unusual thermal and electrical transport properties, such as very low and nearly temperature-independent lattice thermal conductivity (κ_L). We explain the microscopic origin of the glass-like κ_L in $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ by explicitly treating anharmonicity up to quartic terms for both phonon energies and phonon scattering rates. We show that the strongly unstable phonon modes associated with trigonally coordinated Cu atoms are anharmonically stabilized above approximately 100 K and continue hardening with increasing temperature, in accord with experimental data. This temperature induced hardening effect reduces scattering of heat carrying acoustic modes by reducing the available phase space for three-phonon processes, thereby balancing the conventional $\sim T$ increase in scattering due to phonon population and yielding nearly temperature-independent κ_L . Furthermore, we find that very strong phonon broadening lead to a qualitative breakdown of the conventional phonon-gas model and modify the dominant heat transport mechanism from the particle-like phonon wave packet propagation to incoherent tunneling described by off-diagonal terms in the heat-flux operator, which are typically prevailing in glasses and disordered crystals. Our work paves the way to a deeper understanding of glass-like thermal conductivity in complex crystals with strong anharmonicity.

When Band Convergence is Not Beneficial for Thermoelectrics

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Band convergence, or alignment of band pockets, is widely known to benefit thermoelectric performance. Generally speaking, convergence of multiple band pockets increases carrier concentration for given Fermi level, which increases conductivity for the same Seebeck coefficient. However, this is based on the assumption that there is no significant alteration in electron scattering behaviors due to the convergence. With explicit treatment of electron-phonon scattering, we show that this benefit depends on the manner in which the bands converge and the mechanism of interband/intervalley scattering. Critically, multi-band convergence at a single k-point is much less beneficial (if not altogether harmful) than multi-pocket convergence at distant k-points. In the former case, one band increases while the other band decreases in interband scattering as they converge, and the increasingly disparate pocket lifetimes and mobilities lowers the Seebeck coefficient and render power factor enhancement inaccessible. In the latter case, convergence of pockets better preserves their scattering behaviors, thereby successfully leading to improved power factor. We establish and validate these guidelines by performing state-of-the-art first-principles calculations on $\text{CaMg}_2\text{Sb}_2\text{-CaZn}_2\text{Sb}_2$ Zintl alloy and Full-Heusler Sr_2SbAu .

Transition from crystal-like to amorphous-like heat conduction in structurally-complex crystals

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The physics of heat conduction puts practical limits on many technological fields such as energy production, storage, and conversion, as well as high-power and high-frequency electronics. Heat conduction in simple, defect-free crystals is generally well understood and seems to be well described by the phonon-gas model (PGM), where phonon wave-packets are viewed as heat carrying particles which propagate their mean free path before being scattered. It is widely appreciated that the PGM does not describe the full vibrational spectrum in amorphous materials, since this picture likely breaks down at higher frequencies. In this work, in an attempt to bridge our understanding between crystal-like (described by the PGM) and amorphous-like heat conduction, we study structurally-complex crystalline $\text{Yb}_{14}(\text{Mn,Mg})\text{Sb}_{11}$ experimentally using inelastic neutron scattering and computationally using a two-channel lattice dynamical approach. One channel is the commonly considered PGM, and the second we call the diffuson-channel since it is mathematically the same mechanism through which diffusons were defined. Our results show that the diffuson-channel dominates in $\text{Yb}_{14}\text{MnSb}_{11}$ above 300 K, which is a champion thermoelectric material above 800 K. We demonstrate a method for the rational design of amorphous-like heat conduction by considering the energetic proximity phonon modes and modifying them through chemical means.

A chemical understanding of grain boundary dominated charge transport in thermoelectric materials

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Many emerging thermoelectric materials feature irregular electrical conductivity with semiconducting behavior below 500 K and metallic transport at higher temperatures. Because suppression of the low-temperature electrical conductivity degrades the thermoelectric performance on the cold side, establishing the origin of the low-temperature scattering and developing strategies to mitigate its effect are important issues. Here, we address these questions in the promising thermoelectric alloys of PbQ and NaSbQ_2 ($Q = \text{S, Se, Te}$). We show the expected metallic conduction is recovered by reducing the density of grain boundaries (GBs) giving robust evidence the charge carrier scattering originates at the GBs. We moreover demonstrate that the GB scattering is strongest in the sulfide PbS-NaSbS_2 materials and weakest in the tellurides PbTe-NaSbTe_2 . We use density functional theory and a simple charge transport model to show the prominence of grain boundary scattering in each family is explained by the different dielectric permittivities and respective strength of charge carrier screening in each material and also show how this can be intuitively predicted with simple chemical principles that consider the polarizability of the host atoms in each compound. We finally suggest weak dielectric screening explains why many other emerging thermoelectrics also have strong GB scattering and discuss the implications for engineering proper microstructure in ionic thermoelectric materials.

Thermal Resistance at a Twist Interface: Dislocation Grid and Misorientation Phonon Scattering

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Grain boundary/ interface engineering in thermoelectric materials is viewed as a route to scatter phonons and reduce the thermal conductivity of a material. The primary models to describe phonon scattering at an interface, the acoustic mismatch model and diffuse mismatch model, only consider the bulk properties of the material on either side of the interface, but not the structure that can exist at the interface itself. At the nanoscale, low-energy grain boundaries are composed of arrays of dislocations which produce periodic strain fields. Here, we discuss the scattering effects of a twist interface, which can be decomposed into two interpenetrating sets of screw dislocations, forming a dislocation grid. Strain scattering theory is used to capture the thermal resistance due to the dislocation grid, while a reformulation of the acoustic mismatch model is used to capture the scattering effects of the solid rotation at the twist interface. The thermal boundary resistance predictions from the model capture experimental trends and are close in magnitude to molecular dynamics results. Additionally, a comparison to previous results for tilt boundaries shows that for a similar misorientation angle, twist boundaries provide a higher phonon scattering effect.

Understanding Defects from a Chemical Perspective

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The formation and properties of point defects in materials are influenced by the local chemical environment of the defect. Much of the properties of point defects are of importance from a chemical perspective due to their close ties to the macroscopic electrical and thermal properties of the material. In this talk, we discuss the defect chemistry of Mg_2Si , a promising thermoelectric candidate for which the defect-host chemical interactions are not well-understood. Using first-principles calculations, we observe a large dopability window in Mg_2Si , with self-compensation likely induced by the donor Mg interstitial defect. The likelihood of defect formation is presented from a molecular orbital perspective, in which the filling of antibonding states correlates with higher defect formation energies.

Inherent anharmonicity of harmonic solids

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Since the groundbreaking realization that atomic vibrations account for most of the capacity of a solid to store heat, so-called “lattice dynamics” has given rise to foundational theories of the thermal behaviors of materials. The frequencies and polarizations of these vibrations (i.e. phonons) are governed by the complex bonding between atoms, which is physically represented by a spring-mass model that can account for interactions (spring forces) between the atoms (masses). The lowest order “harmonic” approximation only considers linear forces between atoms and is thought incapable of explaining phenomena like thermal expansion and thermal conductivity, which are attributed to non-linear (anharmonic) interactions. It is tacitly assumed that the harmonic and anharmonic properties are entirely independent – even though no real material is found with very little anharmonicity. Here we show that harmonic vibrational pressure relates thermodynamically to thermal expansion and thus the Grüneisen parameter γ , a metric of anharmonicity. We derive a model of thermal expansion in solids where this vibrational or phonon pressure is balanced by the elastic pressure due to strain in the material (analogous to an elastic balloon membrane balancing the pressure of a gas). This model captures the magnitude and temperature dependence of thermal expansion in real solids and provides an estimation of γ that is comparable to values obtained using quantum mechanical methods. Furthermore, chemical intuition that γ should trend with bond type and atomic coordination, is physically justified using a simplified analytical model. Our results indicate that harmonic and anharmonic interactions in solids are inherently linked. We anticipate that this model of phonon pressure can be used as a starting point for more sophisticated analysis and may be useful in understanding other complicated material phenomena such as thermal transport in complex materials. Furthermore, this study provides a pathway for high-throughput screening of anharmonicity for computational materials design.

GPU-Accelerated Ray-Tracing Methods for Determining Radiation View Factors in Multi-junction Thermoelectric Generators

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A robust computational framework is developed to numerically resolve the radiation view factors, (F_{ij}), within three-dimensional geometries, and, in particular, thermoelectric generators (TEGs). The proposed methodology utilizes a graphics processing unit (GPU)-accelerated ray-tracing algorithm to capitalize on the parallel nature of the view factor formulation. Rapid TEG geometry definition is accomplished via use of stereolithography (STL) files. To maintain geometric compatibility, the shadow effect, resulting from interference with the TEG's interconnectors and thermoelectric legs, is accounted for via the Möller-Trumbore (MT) ray-triangle intersection algorithm with back-face culling enabled. Additionally, if a non-planar geometry is specified, a self-intersection algorithm, in combination with the MT algorithm, is utilized. The effect of interconnector thickness, thermoelectric leg height to width ratios, TEG packing density, and number of junctions on F_{ij} is explored for various TEG configurations. Validation is performed against numerous analytical values, in addition to a point-in-polygon (PiP) algorithm for single-junction TEGs. Results indicate that for a constant packing density, F_{ij} decreases asymptotically for an increasing distance across the TEG's hot- and cold-sides. For an increasing packing density, F_{ij} decreases. In a multi-junction device, F_{ij} increases as junction number increases, ultimately plateauing for constant design parameters.

Best Practices for Finite Volume Modeling of Thermoelectric Generators

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The paramount metric for any numeric model's validity is how well it balances energy. A comprehensive study of factors that determine a model's ability to balance energy has been completed in ANSYS CFX due to the level of customization available and expediency. The performance of the CFX model was benchmarked against ANSYS Thermal Electric to ensure the results were valid. It was found that agreement of material property fits to experimental data, capturing all thermoelectric phenomena and the resolution of current and thermal gradients all significantly impact a model's ability to balance energy. To illustrate the first point, a material property sensitivity study was performed on both analytic and numeric models for five different sets of thermoelectric materials. To investigate when it can be appropriate to neglect certain heat source terms, a Thermoelectric Effects study was performed, comparing models that neglected the bridgman effect, the bridgman and thomson effects and a complete model that included all thermoelectric effects. Finally, a minimal mesh element size study was performed on the numeric model for all materials and the results were used to quantify a metric relating minimal mesh element size per current density produced in the system to the degree of energy balance the model is able to achieve.

Mg₃Bi₂-xSbx-based device with a high thermoelectric energy conversion efficiency

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Low-grade waste heat harvesting by thermoelectric energy conversion can contribute to sustainable energy utility. However, the large-scale thermoelectric application is partially hindered by the unsatisfied performance near room temperature and the relatively high cost of the thermoelectric devices. Herein, we fabricate a low-cost n-type Mg₃Bi₂-based compound with a peak zT of 1.24 at 573 K. A unicouple constructed by the n-type Mg_{3.2}Bi_{1.29}Sb_{0.7}Te_{0.01} and the p-type Bi_{0.2}Sb_{1.8}Te₃ exhibits a record-high efficiency of ~8.9% under a temperature difference of 270 K at the hot-side temperature of 573 K. These findings demonstrate the Mg₃Bi₂-based thermoelectric materials are highly promising for low-grade waste heat recovery.

All-Inorganic Halide Perovskites as Potential Thermoelectric Materials: Dynamic Cation off-Centering Induces Ultralow Thermal Conductivity

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Halide perovskites are anticipated to impact next generation high performance solar cells because of their extraordinary charge transport and optoelectronic properties. However, their thermal transport behavior has received limited attention. In this work, we studied the thermal transport and thermoelectric properties of the $\text{CsSnBr}_{3-x}\text{I}_x$ perovskites. We find a strong correlation between lattice dynamics and an ultralow thermal conductivity for series $\text{CsSnBr}_{3-x}\text{I}_x$ reaching $0.32 \text{ Wm}^{-1}\text{K}^{-1}$ at 550 K. The $\text{CsSnBr}_{3-x}\text{I}_x$ also possess a decent Seebeck coefficient and controllable electrical transport properties. The crystallography data and theoretical calculations suggest the Cs atom deviates from its ideal cuboctahedral geometry imposed by the perovskite cage and behaves as a heavy atom rattling oscillator. This off-center tendency of Cs, together with the distortion of SnX_6 ($X = \text{Br}$ or I) octahedra, produces a highly dynamic and disordered structure in $\text{CsSnBr}_{3-x}\text{I}_x$, which gives rise to a very low Debye temperature and phonon velocity. Moreover, the low temperature heat capacity data suggests strong coupling between the low frequency optical phonons and heat carrying acoustical phonons. This induces strong phonon resonance scattering that induces the ultralow lattice thermal conductivity of $\text{CsSnBr}_{3-x}\text{I}_x$.

3D Extruded Composite Thermoelectric Threads for Flexible Energy Harvesting

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Whereas the rigid nature of standard thermoelectrics limits their use, flexible thermoelectric platforms can find much broader applications, for example, in low-power, wearable energy harvesting for internet-of-things applications. Here we realize continuous, flexible thermoelectric threads via a rapid extrusion of 3D-printable composite inks (bismuth telluride n- or p-type micrograins within a non-conducting polymer as a binder) followed by compression through a roller-pair, and we demonstrate their applications in flexible, low-power energy harvesting. The thermoelectric power factors of these threads are enhanced up to 7 orders-of-magnitude after lateral compression, principally due to improved conductivity resulting from reduced void volume fraction and partial alignment of thermoelectric micrograins. This dependence is quantified using a conductivity and Seebeck vise for pressure-controlled studies. The resulting grain-to-grain conductivity is well explained with a modified percolation theory to model a pressure-dependent conductivity. Flexible thermoelectric modules are demonstrated to utilize thermal gradients either parallel or transverse to the thread direction.

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The relation between materials zT and thermoelectric cooler performance

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Thermoelectric coolers (TEC) are devices based on thermoelectric effect. They offer unique advantages including on-spot, precise temperature control and all-solid-state operation. In this work, relationship between coefficient of performance (COP) and materials figure of merit zT is discussed and we show that material zT is the material property metric for device performance including cooling power. Meanwhile, individual properties especially Seebeck coefficient as well as device design may also affect device performances. We use the concept of relative current density u and compatibility factor s to analyze how materials properties affects COP of device. We discuss how material properties translate to optimum leg performance, and how the latter is related to optimum couple performance with another leg. To ensure best couple COP, the cross sections of legs must be optimized. We also estimated the room of improvement assuming zT is not improved but individual properties can be tuned. We found that when two legs of a TEC couple have similar zT , the individual properties have little influence on couple performance within the range of realistic properties. However, when the two legs have different zT s, temperature dependence of Seebeck coefficient has notable influence on the couple performance. Lastly, we confirm that no improvement should be expected with more complicated leg designs beyond a constant cross section.

3D ink-extrusion additive manufacturing of Bi_2Te_3 thermoelectrics

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3D ink extrusion is an emerging multistep AM technique that combines material shaping by extrusion with thermal treatments to obtain geometrically complex objects. Recent process developments allow to process pure metals, complex alloys, brittle thermoelectrics and composites which are challenging for beam-based AM. Additionally, using 3D ink printed oxide precursors followed by co-reduction and sintering in H_2 allows to obtain the desired alloys and intermetallics in situ instead of relying on pre-alloyed powders. Intermetallics and especially thermoelectrics remain challenging for AM due to their inherent brittleness, required stoichiometric control and use of elements with high vapor pressures. I will discuss recent progress towards AM of Bi_2Te_3 -based thermoelectrics using 3D ink extrusion and sintering. The initial ink can be loaded with pre-alloyed Bi_2Te_3 powders, that are then directly sintered, or with blends of $\text{Bi}_2\text{O}_3 + 3\text{TeO}_2$, that are co-reduced and reacted to form Bi_2Te_3 in situ during thermal treatment in a reducing H_2 atmosphere. In situ synchrotron X-ray diffraction elucidates the complex co-reduction of Bi_2O_3 and TeO_2 requiring precise process control to obtain the desired Bi_2Te_3 phase with useful thermoelectric performance. The presented 3D ink extrusion approach is a cost effective and versatile alternative to beam-based AM and foreseen to significantly widen the range of 3D printable materials, especially for high temperature capable composites and intermetallic compounds.

The Integrated Thermoelectric Device - Waste Heat Recovery from Diesel-Powered Public Transit Buses

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An integrated thermoelectric device (iTED) is a restructured thermoelectric generator that incorporates the hot-side heat exchanger into the hot-side interconnector, augmenting device electrical and thermal performance. A fully-coupled thermal-fluid-electric analytic model was constructed to evaluate the performance of all permissible pin-fin iTED design configurations over all operating ranges of a Cummins ISL-powered transit bus. Thermal-fluid characteristics of the fluid domain were based upon experimentally-derived correlations for flow over a rod bundle, whereas the thermal-electric characteristics of the solid domains were based upon the thermoelectric general energy equation and a thermal resistance network. The two domains are coupled through an iterative algorithm. The analytic model was validated by a fully-coupled thermal-fluid-electric numeric model developed in both ANSYS Fluent and ANSYS CFX. Discretization and model form uncertainty were quantified for the numeric models. Through the implementation of the iTED, a multi-kilowatt generator was developed and shown to exhibit high net power output and device thermal conversion efficiency through its inherent ability to capture large quantities of waste heat. Performance of the iTED was then compared to that of a conventional thermoelectric device and shown to substantially increase all performance metrics.

Van der Waals heterostructure based solid-state thermionic cooler.

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The miniaturization of electronic devices leads to a rapid increase in heat power densities. Management of the large heat power densities in nanoscale devices is a major scientific and engineering challenge. In microelectronics and nanoelectronics, the self-heating effects significantly reduce both transistor efficiency and lifetime, and in very large-scale integrated circuit (VLSI), the heat generation and thermal management becoming one of the bottlenecks to further improve clock speed and make smaller feature sizes. Solid-state thermionic (SSTI) coolers embedded with devices are among the only viable options to solve some of these problems. The same SSTI devices with the same design can also be used as heat to electrical power generators for applications such as wearable electronics. In this work, we study thermionic cooling across gold-graphene-WSe₂-graphene-gold structures computationally and experimentally. Graphene and WSe₂ layers were stacked, followed by the deposition of gold contacts. The I-V curve of the structure suggests near-ohmic contact. A hybrid technique that combines thermoreflectance and cooling curve measurements are used to extract the device zT . The measured Seebeck coefficient, thermal and electrical conductance, and zT values at room temperatures are in agreement with the theoretical predictions using first-principles calculations combined with real-space Green's function formalism.

Thermo-mechanical investigation of annular thermoelectric generator

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Thermoelectric generators (TEGs) have been extensively researched for power generation in applications such as automotive, industrial waste and PV. Although flat TEG modules have been the focus of research efforts, most of heat sources are cylindrical and tubular heat exchangers are implemented. Therefore, it is of interest to investigate a TEG geometry that can easily be integrated with the heat source such as annular TEGs. Large temperature gradients across the TEG leg results in a significant thermal stress that affects the module's reliability. Unlike flat TEGs, annular TEGs experience higher thermal stresses due to the geometry nature of the annular shape. In this work, coupled thermoelectric/thermal stresses finite element model is constructed using ANSYS Workbench. The model simulates the annular shaped legs, copper conductors connecting between the P and N legs and the solder that welds the legs to the copper conductor. The heat exchangers on the hot and the cold sides across the annular TEG are modeled as thermal boundary conditions to mimic the behavior of the module in a real waste heat recovery system. The aim of this study is to investigate both the thermoelectric performance and the thermal stresses under different thermal and electrical loads to find the optimum annular leg geometry parameters such as diameter ratio and leg thickness. The model will show the location of the maximum thermal stresses in which the cracks and the module failure will occur.

An efficient approach for calculating thermoelectric transport properties

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Accurate prediction of thermoelectric transport properties has so far proved challenging due to the difficulty of computing electron lifetimes. Existing approaches are either accurate but extremely computationally demanding, or low cost and highly unreliable. We introduce a new framework for calculating the electronic transport properties of solid-state materials from first-principles. With performance close to that of state-of-the-art methods at a fraction of the computational cost, the technique is both accurate and amenable to high-throughput calculations.

Designing chemical analogs to PbTe with intrinsic high band degeneracy and low lattice thermal conductivity

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High-efficiency thermoelectric materials require simultaneously high power factors and low thermal conductivities. Aligning band extrema to achieve high band degeneracy, as realized in PbTe, is one of the most efficient approaches to enhance power factor. However, this approach usually relies on band structure engineering, e.g., via chemical doping or strain. By employing first-principles methods with explicit computation of phonon and carrier lifetimes, here we show two full-Heusler compounds Li_2TlBi and Li_2InBi have exceptionally high power factors and low lattice thermal conductivities at room temperature. The expanded rock-salt sublattice of these compounds shifts the valence band maximum to the middle of the Σ line, increasing the band degeneracy by a factor of three. Meanwhile, resonant bonding in the PbTe-like sublattice and soft Tl–Bi (In–Bi) bonding interaction is responsible for intrinsic low lattice thermal conductivities. Our results present an alternative strategy of designing new thermoelectric materials.

Lattice instabilities and phonon thermal transport : A case study for TlBr

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Materials with simple crystal structure usually exhibit substantial lattice thermal conductivity due to a lack of strong phonon-phonon scattering channels. Here by a combination of experimental measurements, and first principles calculations, we show that TlBr, a very simple system with CsCl-structure exhibits surprisingly strong anharmonic scattering resulting in an extremely low room temperature lattice thermal conductivity of ~ 0.5 W/mK. Moreover at low temperature we find a high lattice thermal conductivity of 155 W/mK. This extreme range of conductivity behavior results from lattice-instability-related anharmonicity, effective only at temperatures above ~ 30 K. Tuning these instabilities by pressure, strain may yield a pathway to ultralow thermal conductivity via intrinsic phonon resistance in similar materials.

Computational predictions on ternary selenides and tellurides diamond-like semiconductors: establishing the boundaries of achievable dopability.

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While recent developments in computational prediction have shown good progress for thermoelectric materials discovery, prediction of dopability in complex materials remains a challenge. For optimal thermoelectric performance, both the carrier type and carrier concentration must be carefully controlled. Traditionally, (i) demonstrations of targeted control over these quantities, and (ii) links between experimentally-measured carrier concentrations and first-principles predictions both remain rare in the literature. In this work, we show our recent efforts to establish the range of dopability achievable in ternary selenides and tellurides diamond-like semiconductors (DLS) using first-principles simulations, and compare the predicted range to what has been reported in experiments. DLS have long been of interest in the thermoelectrics community, but a systematic analysis of their dopability and a demonstration of carrier concentration control is still lacking. Besides, the majority of DLS semiconductors are reported to be p-type, with very sparse reports of n-type materials, which has been hampering the advance of thermoelectric modules based on these materials. We predict that n-type conductivity can be achieved in some DLS semiconductors under proper growth conditions, by (i) control over intrinsic defects concentration, which can be done via a direct link between predicted optimal growth environment and phase boundary mapping, and (ii) extrinsic dopants. Also, we propose effective n-type dopants for one particular material (AgInTe_2), which is the focus of ongoing experimental work.

Modeling Transport in (p x n)-Type Transverse Thermoelectrics: Partial Gap Activation Model

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As an alternative to conventional thermoelectric materials, (p x n)-type transverse thermoelectrics are intrinsic bulk single crystals with orthogonal p- and n-type Seebeck behavior that can yield transverse thermoelectric performance within a single-leg structure, and possible microscale cooling applications with minimum fabrication complexity. We introduce a partial gap activation (PGA) model to explain why activation energies for conduction along p- and n-type directions are different. Expanding the model beyond the naïve Arrhenius law to account for the full Fermi-Dirac distribution, this model is able to consistently explain experimentally measured resistivity, Seebeck, and Hall effect as a function of temperature. The model assumes that mobility is limited by acoustic phonon scattering in the high temperature limit, thereby introducing only two fit parameters in the model, the electron and hole deformation potentials. Using density functional theory (DFT) to calculate the anisotropic band masses, the model can deduce the temperature dependent energy gap and Fermi energy of (p x n)-type transverse thermoelectric candidate materials directly from experimental Seebeck and resistivity. The model is demonstrated with ReSi_{1.75}, and the temperature dependent variation in energy gap from the PGA model is in excellent agreement with DFT calculations.

Experimental Validation of High Thermoelectric Performance in RECuZnP_2 Predicted by High-Throughput DFT Calculations

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Thermoelectric materials can convert waste energy back to useful electricity and hence, contribute to the generation of clean energy. However, thermoelectric materials are currently limited by high cost and low efficiencies. The search for high-efficient thermoelectric materials is hindered by the interrelated electrical and thermal transport properties. High-throughput screenings based on density functional theory (DFT) can accelerate the search and discover novel high-performance thermoelectric candidates. In a recent screening of more than 20,000 disordered inorganic compounds, enhanced electronic properties were observed for various RECuZnP_2 compounds. The thermoelectric transport properties were measured for three different RECuZnP_2 compounds indicating high thermoelectric efficiencies. Advanced DFT calculations (i.e., AMSET and compressive sensing lattice dynamics) were performed confirming the high thermoelectric performance. These methods can compute the scattering rates of electrons and phonons (even with strong anharmonicity) and provide unique insights of the underlying physics in thermoelectric compounds.

Computational Discovery of an Enormous Class of Stable Quaternary Chalcogenides with Very Low Lattice Thermal Conductivity

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The development of efficient thermal energy management devices such as thermoelectrics, barrier coatings, and thermal data storage disks relies on compounds which possess low lattice thermal conductivity (κ_l). Here, we present an enormous class of thermodynamically stable quaternary chalcogenides $AMM'Q_3$ (A=Alkali, alkaline earth, post transition metals; M,M'=transition metals, lanthanides; Q= chalcogens) that possess intrinsically low κ_l using high-throughput DFT calculations. Leveraging the computed energetics of hundreds of thousands of multi-nary compounds in the Open Quantum Materials Database (OQMD), we discovered a large number (nearly 1000) of thermodynamically stable chalcogenides through successive screening based on the calculations on multiple crystallographic prototypes of the experimentally known $AMM'Q_3$ compounds. We validate the low- κ_l in this family of compounds by calculating the lattice thermal conductivity taking several representative compounds using the highly accurate anharmonic lattice dynamics methods. Our predictions suggest new experimental research opportunities in the synthesis and characterization of these stable, low- κ_l compounds.

Understanding the origins of high valley degeneracy in PbTe using the tight-binding approximation

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PbTe is one of the highest-performing known thermoelectric materials. Much of its promising thermoelectric performance can be attributed to high valley degeneracy due to having a valence band minimum (VBM) and conduction band maximum (CBM) at the L point in the first Brillouin zone. The existence of the VBM at L has been explained by the mixing of Pb-s states with the Te-p states that make up the valence band edge. However, the dominance of Te-p states presence of Pb-p states near the VBM suggest that the Pb-s orbitals may not be as crucial as previously thought. The tight-binding (TB) model, or Linear Combination of Atomic Orbitals (LCAO) serves as a computationally inexpensive method to gain qualitative insights into chemical trends in electronic structures of materials. In this study, we use a TB model including nearest and next-nearest neighbors to understand the extent to which various atomic orbital interactions contribute to having a VBM at L versus Γ . Based on the dominant interactions at play, a crystal orbital picture is developed that explains the shape of the valence band dispersion between L and Γ . Furthermore, we show that it is possible to obtain a VBM at L even if the Pb-s states are removed, contradicting the idea that the filled Pb-s lone pairs are solely responsible for the high valley degeneracy, and suggesting that the Pb-p states are at least as important in determining the position of the VBM in PbTe and the other lead chalcogenides.

Doping by Design: Finding New n-type Dopable Zintl Phases for Thermoelectrics

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Doping remains a bottleneck in discovering novel materials for functional applications. The current computational approach to materials discovery is to identify candidates by predict the functional properties of a pool of known materials, and hope that the candidates can be appropriately doped. What if we could "design" new materials that have the desired functional and doping properties? In this work, we propose a chemical replacements in structure prototype (CRISP) approach as a route to realize doping by design. Within CRISP, we first identify a promising prototype structure that exhibits high functional performance and desired doping. Next, logical chemical replacements in the prototype are used to generate new plausible compounds. We hypothesize that the doping characteristics and high performance of the prototype structure are translated to the new compounds created by chemical replacements. The plausible compounds are then computationally assessed for their stability, performance, and dopability. It has been predicted that Zintl phases, if doped n-type, will exhibit high thermoelectric performance; however, n-type Zintl phases are a rarity. We utilize the CRISP approach to discover 7 new, previously unreported ABX_4 Zintl phases in the $KGaSb_4$ prototype structure. Using detailed first-principles defect calculations, we confirm the n-type dopability of these newly predicted phases, validating the approach as a route to discover new compounds with desired doping.

Synthesis, crystal structure, and transport properties of two polymorphs of $\text{Ba}_8\text{Cu}_{16}\text{As}_{30}$ clathrate

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Clathrates are widely known for their diverse chemical compositions as well as their low thermal conductivity originating from the crystal structure. These attributes allow for substantial tuning of compositions to optimize thermoelectric performance. The anionic clathrate framework forms large cages which are filled with the cationic guest atoms to form a charge balanced compound. Until recently, two ternary type I clathrates with group XI transition metal and a pnictogen have been reported. These two clathrates, $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$ and $\text{Ba}_8\text{Au}_{16}\text{P}_{30}$, both exhibit ordering of Cu (or Au) and P in the framework. This ordering changes the unit cell symmetry from the typical type I clathrate Pm-3n space group to a superstructural Pbcn space group with 4 times volume increase. Recently, a single crystal of $\text{Ba}_8\text{Cu}_{16}\text{As}_{30}$ was reported with no superstructural ordering. In this study, the report of $\text{Ba}_8\text{Cu}_{16}\text{As}_{30}$ with no superstructural ordering is confirmed in addition to the discovery of a polymorph with an ordered Cu/As framework. A detailed investigation of $\text{Ba}_8\text{Cu}_{16}\text{As}_{30}$ including in-situ high resolution synchrotron powder X-ray diffraction, single crystal X-ray diffraction, and selected area electron diffraction revealed the polymorphic nature of type I clathrate $\text{Ba}_8\text{Cu}_{16}\text{As}_{30}$. The transport properties of $\text{Ba}_8\text{Cu}_{16}\text{As}_{30}$ are superior to those of the phosphide analogue due to enhanced thermopower.

Intermediate-Level Doping Strategy to Simultaneously Optimize Power Factor and Phonon Thermal Conductivity for Improving Thermoelectric Figure-of-Merit

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The conventional doping strategy for thermoelectric materials generally focuses on a shallow donor/acceptor model with the energy level close to the band edge as for electronic devices. However, thermoelectric devices operate over a large temperature difference, and the optimal carrier concentrations increases with increasing temperature. A shallow level cannot meet the requirement over a large temperature range. Here, an innovative strategy of introducing an intermediate level is proposed. Such an intermediate level introduces more carriers with increasing temperature, consistent with the trend of increasing optimal doping concentration with temperature, enabling larger power factor over a broader temperature range. Furthermore, the intermediate level typically requires more impurities, leading to increased phonon scattering. This strategy allows simultaneous optimization of carrier concentration over a wide temperature range and suppression of thermal conductivity via stronger point-defect phonon scattering. Experimental results from heavily-doped ZrCoSb employing shallow, intermediate, and deep levels successfully corroborate this strategy, where simultaneously improved power factor and zT are obtained by introducing an intermediate level. Our work indicates that the performance of known thermoelectric materials should be re-evaluated by introducing an intermediate level to unleash their full potential.

Axis-Dependent Conduction Polarity in Re_4Si_7 Single Crystals

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Most electronic materials typically exhibit a single type of conduction polarity, either electrons or holes, along their principle axes. Layered materials have different bonding and band curvatures within the layer and orthogonal to it, and therefore can exhibit different conduction polarities along these axes. Here we establish that Re_4Si_7 , a narrow band gap semiconductor, is one such material, and has the largest conduction anisotropy in any material to date. A single crystal of Re_4Si_7 was grown and the temperature-dependent conduction properties have been characterized across different crystallographic orientations. We characterize the direction dependent thermopower, and electronic and thermal conductivity, and find that Re_4Si_7 simultaneously exhibits p-type conduction in-plane and n-type conduction cross-plane. We establish the origin of this effect occurs via a multi-carrier mechanism. Finally, considering that most modern device technology requires integrating materials with p-type and n-type regions for functionality, the large axis-dependent conduction anisotropy in Re_4Si_7 makes it a promising platform to explore new device concepts. Indeed, through constructing proof-of-concept transverse thermoelectric devices we show that a single crystal of Re_4Si_7 can efficiently convert an off-diagonal heat gradient into electricity.

Thermoelectric Transport of Semiconductor Full-Heusler VFe_2Al

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The full-Heusler VFe_2Al has emerged as an important thermoelectric material in its thin film and bulk phases. VFe_2Al is attractive for use as a thermoelectric materials because of it contains only low-cost, non-toxic and earth abundant elements. While VFe_2Al has often been described as a semimetal in over two decades of research, here we show the electronic and thermal properties of VFe_2Al can be explained by considering VFe_2Al as a valence precise semiconductor like many other thermoelectric materials but with a very small band gap ($E_g = 0.03 \pm 0.01$ eV). Using a two-band model for electrical transport and point-defect scattering model for thermal transport we analyze the thermoelectric properties of bulk full-Heusler VFe_2Al . We demonstrate that a semiconductor transport model can explain the compilation of data from a variety of n and p-type VFe_2Al compositions assuming a small band-gap between 0.02 eV and 0.04 eV. In this small E_g semiconductor understanding, the model suggests that nominally undoped VFe_2Al samples appear metallic because of intrinsic defects of the order of $\sim 10^{20}$ defects/cm⁻³. We rationalize the observed trends in weighted mobilities (μ_w) with dopant atoms from a molecular orbital understanding of the electronic structure. The electrical and thermal models developed allow us to predict the zT versus carrier concentration curve for this material, which maps well to reported experimental investigations.

Anomalously low thermal conductivity in novel Sb-based clathrates obtained by rapid mechanosynthesis

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Semiconducting clathrates based on pnictogen atoms (As, P, Sb) are promising thermoelectric materials due to their uniquely complex crystal structures, and resultant low thermal conductivity. Here, we report on finding novel compounds $K_{58}Zn_{128+x}Sb_{200-x}$ and $K_8Zn_{18-y}Cu_ySb_{28}$. The samples were produced by fast route of mechanical milling and reactive hot pressing. The $K_{58}Zn_{128+x}Sb_{200-x}$ clathrate attains novel structure type: space group I23 (no. 197), $a = 22.4701 \text{ \AA}$, 386 atoms per unit cell. Potassium atoms are enclosed in Zn-Sb framework, which forms pentagonal dodecahedra (5^{12}) and hexakaidecahedra ($5^{12}, 6^4$) reminiscent to those of type-II clathrate, yet some of the smaller 5^{12} cages are strongly distorted. $K_8Zn_{18-y}Cu_ySb_{28}$ crystallizes in type-I clathrate structure: space group Pm-3n (no. 223), $a = 11.5921 \text{ \AA}$, $Z = 1$. Both compound are intrinsic conductors with energy gap of approximately 350 meV established by analysis of electrical resistivity. Seebeck coefficient reached high values, up to 470 $\mu\text{V/K}$ at 500 K for $K_{58}Zn_{128+x}Sb_{200-x}$. Thermal conductivity of the newly discovered phases is anomalously low, down to c.a. $0.4 \text{ WK}^{-1} \text{ m}^{-1}$ in 300-500 K range for $K_{58}Zn_{128+x}Sb_{200-x}$. Narrow band gap and small thermal conductivity combined with low price of constituent elements make these newly discovered compounds ideal candidates for thermoelectric materials, as soon as the carrier concentration is tailored towards degenerate semiconductor behavior.

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Thermal chiral anomaly in the magnetic-field induced ideal Weyl phase of $\text{Bi}_{1-x}\text{Sb}_x$ topological insulators

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The chiral anomaly in Weyl semimetals has been predicted theoretically to produce negative longitudinal magneto-resistivity. This has been observed experimentally in several Weyl systems and deemed the transport signature of Weyl semimetals. However, such experiments can be contaminated by extrinsic effects originated from distorted pathways of the electric current in a magnetic field [1]. Thermal conductivity measurements involve no charge transport thus avoid extrinsic effects that plague electrical measurements. Here, we unambiguously demonstrate the thermal analog of the chiral anomaly in topological insulator bismuth-antimony alloys ($\text{Bi}_{89}\text{Sb}_{11}$ and $\text{Bi}_{85}\text{Sb}_{15}$) driven into an ideal Weyl semimetal state by a Zeeman field, with the chemical potential pinned at the Weyl points, and in which the Fermi surface has no trivial pockets. The experimental signature is a large enhancement of the thermal conductivity in an applied magnetic field parallel to the thermal gradient that follows the Wiedemann-Franz law above 60 K. The effect is absent in setups where the magnetic field is not oriented along the axes that produce Weyl semimetal state, and in the ordinary semimetal $\text{Bi}_{95}\text{Sb}_5$.

[1] Vu et al., arXiv:1906.02248 (2019).

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Electronic and Vibrational Properties of Colusites and Tetrahedrites

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Among sulfides there are several efficient, environmentally friendly, and cost effective thermoelectric materials. The structural and chemical complexity of materials such as colusites and tetrahedrites is an asset to achieve low thermal conductivities and large power factors but the delicate interplay of many degrees of freedom hinders, at times, important aspects of the search. Using first principles calculations, we will discuss conceptual cornerstones in colusites and tetrahedrites. Our theoretical investigations are part of experimental collaborations that stimulated and verified our results. We will discuss important structural features tetrahedrites and the interplay between disorder and chemical substitution in colusites.

Ca₁₄AlBi₁₁—a new Zintl phase from earth-abundant elements with a great potential for thermoelectric energy conversion

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The salt-like nature of Zintl pnictides is responsible for the high-temperature stability and excellent thermoelectric performance at high temperatures. The family of compounds, which adopts the Ca₁₄AlSb₁₁-structure type is well-known for its excellent thermoelectric properties in the high-temperature region (800-1200 K). We present the Zintl phase Ca₁₄AlBi₁₁, which has been synthesized and structurally characterized for the first time. Ca₁₄AlBi₁₁ is the first aluminobismuthide among the “14–1–11” family whose structure is unequivocally established. Despite the electronic structure calculations indicate this compound as a small-gap semiconductor, the resistivity measurements show temperature dependence akin to those of heavily doped semiconductors or the bad metals with the value of $\rho_{300} = 1.05 \text{ m}\Omega\cdot\text{cm}$. Specimens of Ca₁₄AlBi₁₁ also exhibit excellent thermopower, with high-temperature values of the Seebeck coefficient approaching 200 $\mu\text{V}/\text{K}$. These values are comparable with the best p-type Zintl thermoelectric materials and are among the best within the known isostructural bismuthides. Ca₁₄AlBi₁₁ represents a new platform for the development of novel, low-cost thermoelectric materials with good transport properties and enhanced thermal stability. This phase is amenable to doping by rare-earth elements, which opens up many opportunities for tuning charge-carrier concentration and optimizing the transport properties in this class of materials.

Structure, Transport Properties, and Optimization of $\text{Yb}_{21}\text{Mn}_4\text{Sb}_{18}$

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Our group has recently reported on a new Zintl phase $\text{Yb}_{21}\text{Mn}_4\text{Sb}_{18}$ with favourable thermoelectric properties in the mid-to-high temperature range ($zT \approx 0.8$ at 800 K). The efficiency of this material comes mainly from its large Seebeck coefficient ($\sim 290 \mu\text{V K}^{-1}$) and extremely low thermal conductivity ($\sim 0.4 \text{ W m}^{-1} \text{ K}^{-1}$). DFT calculations show that the large density of states near the Fermi level are contributed mostly by the Mn and Sb atoms that participate in the $[\text{Mn}_4\text{Sb}_{10}]^{22-}$ motif of the structure which give rise to the large Seebeck coefficient. The structure of this complex system was analyzed through synchrotron powder X-ray diffraction, single crystal X-ray diffraction and PDF studies which revealed inherent structural disorder that contribute to the low thermal conductivity of the system. We are currently investigating the optimization this material through substitutional doping on the various sites. The structure and property relations of our on-going doping studies will be presented.

Exceptionally high electronic mobility in defect-rich $\text{Eu}_2\text{ZnSb}_{2-x}\text{Bi}_x$ alloys

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The Zintl compound, Eu_2ZnSb_2 , has been shown to have exceptionally low lattice thermal conductivity and high electronic mobility resulting in a promising thermoelectric figure of merit, $zT \sim 1$ at 823 K. The built-in disorder of the structure and its proven potential for high thermoelectric efficiency warrants further exploration into this family of materials. Here we investigate the thermoelectric properties of the isostructural compound, Eu_2ZnBi_2 and the corresponding solid solution $\text{Eu}_2\text{ZnSb}_{2-x}\text{Bi}_x$ series ($x = 0, 0.25, 1, 2$). We show that Eu_2ZnBi_2 is a heavily doped small band gap semiconductor or semimetal subject to intrinsic defects with a carrier concentration on the order of $10^{20} \text{ h}^+ / \text{cm}^3$. Interestingly, the Bi analogue exhibits a factor of two increase in the mobility despite its larger carrier concentration, which is accounted for by the two-fold decrease in m DOS. The greatest mystery in this material system is demonstrated by the increase in mobility as Bi is alloyed into the Eu_2ZnSb_2 structure despite the continued decrease to lattice thermal conductivity. This dichotomy suggests a complex relationship between scattering of electrons and phonons which is to our benefit in designing higher zT materials. In fact, the single parabolic band model predicts a factor of three or more increase in zT for Bi-rich compositions suggesting a means to engineer higher performing thermoelectric materials than the original reported $zT \sim 1$.

Structure, Magnetic Properties, and Enhanced Thermoelectric Figure of Merit in the Quinary Phase $\text{Yb}_{13-x}\text{Ca}_x\text{BaMgSb}_{11}$ ($x = 1 - 6$).

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In this work we aim to improve on $\text{Yb}_{14}\text{MgSb}_{11}$ by substituting Ca and Ba into the Yb sites ($\text{Yb}_{13-x}\text{Ca}_x\text{BaMgSb}_{11}$ ($x = 1, 2, 3, 4, 5$)). The stark mass differences between Ca, Ba, and Yb will cause a decrease in κ_{tot} due to alloy scattering. $\text{Ba}_{14}\text{MnSb}_{11}$ and $\text{Ca}_{14}\text{MgSb}_{11}$ have semiconductor-like resistivities and wider bandgaps than $\text{Yb}_{14}\text{MgSb}_{11}$. Incorporating Ba and Ca should expand the band gap of $\text{Yb}_{14}\text{MgSb}_{11}$ which will reduce the bipolar conduction seen in $\text{Yb}_{14}\text{MgSb}_{11}$ that leads to reduced thermoelectric performance at the highest temperatures. PXRD shows mostly pure phase samples and EMPA shows the sample compositions are close to the nominal composition. Speed of sound measurements indicate the lattice stiffens increases as a function of Ca from $x = 1 - 3$ where the stiffening plateaus then grows again at $x = 6$. Despite the stiffening lattice, κ_{tot} decreases until $x = 3, 4$ at which point it increases slightly. Seebeck and resistivity are only slightly affected by Ca incorporation leading to a zT of 1.45 at 1273 K in the $x = 4$ sample. Additionally, single crystals of composition $\text{Yb}_{9.7(2)}\text{Ca}_{3.85(5)}\text{Ba}_{0.29(4)}\text{Mg}_{1.13(3)}\text{Sb}_{11.0(1)}$ are grown from Sn flux synthesis to determine cation site preferences. The structure is solved, and magnetic measurements reveal that about 1 Yb^{3+} is present in the structure.

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The Effect of Multi-Band Transport on Thermal Conductivity in $\text{Yb}_{14}\text{MgSb}_{11}$

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The lattice thermal conductivity of a material above its Debye temperature should either decrease with increasing temperatures, as in a crystal, or remain independent of temperature, as in a glass. However, multiple literature reports of the $\text{Yb}_{14}\text{MgSb}_{11}$ crystal indicate its lattice thermal conductivity increases with increasing temperature well above its Debye temperature. Herein we study the thermal conductivity and electrical transport of the $\text{Yb}_{14}\text{MgSb}_{11}$ solid solution and show this increase in lattice thermal conductivity can be attributed to an electronic effect arising from multi-band transport. We go on to show the effect multi-band transport has on thermal conductivity is pervasive in literature but is often misattributed to the thermal conductivity arising from phonon transport.

Single Crystal and Annealing Study on n-type $\text{Mg}_3(\text{Sb,Bi})_2$

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There has been significant interest in Mg_3Sb_2 and related compounds since the recent demonstration of high zT in the n-type thermoelectric $\text{Mg}_3(\text{Sb,Bi})_2$ Alloys. It is known that there is a significant electrical insulation at near temperature in this system, which is suspected to be due to the grain boundary resistance. While researchers recognize the potential improvement by removing grain boundaries, it is challenging to synthesize single crystal n-type material because of the lack of understanding in the defect energy. In this presentation, I will talk about how we can synthesize the single crystal n-type Mg_3Sb_2 along with the saturation annealing technique. Single crystals show 2 times higher electrical performance compared to the polycrystalline. This leads to a multi-fold improvement in the thermoelectric performance zT at room temperature compared to polycrystalline samples.

Systematic over-estimation of lattice thermal conductivity in materials with electrically-resistive grain boundaries

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Reducing the thermal conductivity κ of a material via nano-structuring to create small grain sizes is one of the most common strategies to improve thermoelectric materials. In such polycrystalline materials heat carrying phonons are scattered at the grain boundaries, which directly improves the thermoelectric quality factor and ultimately the figure-of-merit zT . In some cases, however, such as in Mg_3Sb_2 , SnSe , and Mg_2Si an opposite trend is found where higher lattice thermal conductivity reported in small grain polycrystalline material than in large grain or single crystal materials. This unphysical result indicates a problem with the conventional use of the Wiedemann-Franz law. Here, we trace this problematic finding to the electrical resistance at the grain boundaries, which leads to an overestimation of the lattice thermal conductivity κ_L . In materials with significant grain boundary electrical resistance, the estimated electronic contribution to the thermal conductivity $L\sigma T$ is low because the measured electrical conductivity σ is low. However within the grain electrons may still be transporting more heat than the total conductivity suggests, leading to an overestimation of κ_L if the conventional $\kappa_L = \kappa - L\sigma T$ is used with the measured values of κ and σ . The overestimation of κ_L in small-grain samples is shown to be pervasive across a broad range of thermoelectric materials and a correction is necessary to properly understand and predict their charge and heat transport.

N-type $\text{Mg}_3\text{Sb}_{2-x}\text{Bi}_x$ with Improved Thermal Stability for Thermoelectric Power Generation

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Recently, the n-type $\text{Mg}_3\text{Sb}_{2-x}\text{Bi}_x$ alloys with high thermoelectric performance were reported. This material holds great potential for applications in waste heat recovery due to the high average zT in the temperature range between 300 and 773 K. However, systematic studies in the thermal stability of the $\text{Mg}_3\text{Sb}_{2-x}\text{Bi}_x$ alloys are still lacking, and the possible degradation in the thermoelectric performance could greatly limit the practical applications. Here, we studied the thermal stability of the $\text{Mg}_3\text{Sb}_{2-x}\text{Bi}_x$ alloys via the in-situ measurement of the electronic thermoelectric properties at different temperatures and also microstructural and composition characterizations. Our results showed that $\text{Mg}_3\text{Sb}_{2-x}\text{Bi}_x$ alloys were unstable when the temperature was above 673 K due to the significant Mg loss. By coating $\text{Mg}_3\text{Sb}_{2-x}\text{Bi}_x$ alloys, the Mg loss can be effectively suppressed and thus greatly improved the thermal stability. Additionally, the energy conversion efficiency measurement validated the high thermoelectric performance of the $\text{Mg}_3\text{Sb}_{2-x}\text{Bi}_x$ alloys and further confirmed the improved thermal stability for the boron nitride coated sample. Therefore, our study provides an effective strategy for improving the thermal stability of $\text{Mg}_3\text{Sb}_{2-x}\text{Bi}_x$ alloys, thus promoting them as a promising candidate for thermoelectric power generation.

Origin of unexpectedly low thermal conductivity in AMg_2X_2 ($A = Mg, Ca, Yb$, $X = Sb, Bi$)

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Thermoelectric materials enable direct conversion of waste heat into electrical energy. The conversion efficiency is inversely proportional to the thermal conductivity, which is generally dominated by phonons in semiconductors. Zintl compounds AMg_2X_2 constitute a class of new thermoelectric compounds with excellent thermoelectric performance in n-type $Mg_3(Sb,Bi)_2$ alloys, with zT values up to 1.6 reported so far. Mg_3Sb_2 exhibits very low lattice thermal conductivity (~ 1 - 1.5 W/mK at 300 K), comparable with PbTe and Bi_2Te_3 , despite a much lighter average ionic mass. We report on neutron scattering and first-principles studies of the lattice dynamics of AMg_2X_2 . Inelastic neutron scattering measurements provided the temperature dependence of the phonon density of states (DOS). Extra peaks were found at low frequency in Mg_3Sb_2 and Mg_3Bi_2 compared to $CaMg_2X_2$ or $YbMg_2X_2$, possibly originating from softer low-frequency TA phonon branches. Considerably stronger softening with temperature is also observed in Mg_2X_2 than in $CaMg_2X_2$ or $YbMg_2X_2$. These anharmonic effects were examined with first-principles simulations, including ab initio molecular dynamics. We present our analysis of the thermal conductivity based on INS measurements and simulations.

Spin Seebeck effect in Vanadium Tetracyanoethylene

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Vanadium tetracyanoethylene ($V(TCNE)_x$, $x \sim 2$) is an organic based ferrimagnetic coordination compound, with extremely low Gilbert damping which is comparable to yttrium iron garnet. Due to its non-crystalline nature, it is interesting to investigate how spin waves propagate in the material. One possible way is through thermally driven spin pumping, namely spin Seebeck effect (SSE). Here, we present a systematic study on the temperature and thickness dependence of SSE in $V(TCNE)_x$. The thin films (thickness on the order of 100 nm) are grown via chemical vapor deposition on a platinum layer on sapphire substrate. By applying a temperature gradient perpendicular to the $V(TCNE)_x/Pt$, a large SSE signal is collected. Further analysis on the temperature and thickness dependence helps us understand the length scales of the propagation of spin waves.

Spin-Seebeck and anomalous Nernst effects in MnBi and Bi/MnBi composites

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The spin-Seebeck effect (SSE) is an advective transport process in a bilayer composed of a ferromagnet (FM) and a non-magnetic material (NM) with strong spin-orbit coupling. In a temperature gradient, the flux of magnons in the FM transfer spin angular momentum to the electrons in the NM, which, by the ISHE contributes an SSE voltage. In contrast, the intrinsic anomalous Nernst (ANE) conductivity in homogeneous FMs is understood as a non-advective process because of the temperature gradient on electrons. These two effects can be combined to produce an enhanced transverse voltage in composite materials, like Ni/Pt [1]. Here, we synthesized composites of aligned MnBi needles in a Bi matrix. In this geometry, we expected an additional SSE contribution from the magnons in MnBi to the Nernst effect in the Bi; however, the contribution subtracted from the overall effect.

[1] S. Boona et al., Nat. Comm. 7 (2016)

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Thermoelectric Transport Measurement of Supported Holey Silicon Thin Films across a Broad Temperature Range

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Silicon thin films are compatible with the semiconductor industry and possess a relatively large thermoelectric power factor, indicating their potential as good thermoelectric devices. However, the high thermal conductivity of silicon yields a low thermoelectric figure of merit, zT , which is not desirable for thermoelectric applications. By patterning the silicon thin films with periodic nano-sized holes spaced closer than the phonon mean free path, their thermal conductivity can be greatly suppressed while their electronic properties are roughly maintained. Here, we present a hybrid approach based on thermoreflectance imaging technique and heat spreader method for the in-plane thermal conductivity measurement of the supported holey silicon thin films, which we refer to as heat diffusion imaging method. The thermal conductivity is extracted from the temperature distribution profile measured on the film on the substrate. The measurements do not require film suspension or multiple thermometer deposition. By coupling the thermoreflectance imaging system with a cryostat, we were able to conduct measurements from 40 K to 400 K. A silicon thin film sample without the holes was measured as a validation for our method. Finally, thermoelectric properties of the holey silicon films under studying were measured, and a zT of 0.09 at room temperature and an estimated zT of 0.29 at 650 K are reported.

Thermoelectric Properties of Minerals with the Mawsonite Structure

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Synthetic copper sulfides have emerged as promising non-toxic and low-cost materials for thermoelectric power generation in low-grade waste heat recovery systems. Similarly to tetrahedrite and colusite, mawsonite ($\text{Cu}_6\text{Fe}_2\text{SnS}_8$) exhibits a modified corner-sharing Cu-S tetrahedral network which usually leads to p-type character and low thermal conductivity. We explore the applicative potential of mawsonite by combining a theoretical analysis of electronic, transport and vibrational properties, including the effect of isovalent substitutions of Fe, Sn and S [1]. Our findings highlight the role of the weakly bonded copper component in achieving a very low thermal conductivity. We also demonstrate that the Cu-S bond builds a 2D conductive network where the contribution from other elements is negligible. Magnetic calculations point to an anti-ferromagnetic ground state substantially affected by the covalency of the bonds within the conductive plane.

[1] I. Siloi et al., ACS Applied Energy Materials 2 (11), 8068-8078 (2019)

Effect of Coulombic Interactions and Dopant Distribution on Charge Transport Dynamics in Polymer Thermoelectrics

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Organic semiconductors hold tremendous potential to address the demand for cheap and sustainable thermoelectric materials. However, they need to be electrochemically doped to improve their electrical conductivity which introduces complexities in the electronic structure because of poor screening of dopant-polymer interactions. We investigate the effect of dopant-polymer Coulombic interactions and the physical distribution of dopants on both the density-of-states and Seebeck vs. conductivity trade-off curve. Our charge transport model is based on electron hopping between localized sites with a modified Gaussian disorder model to account for the impact of dopant size and clustering on the energies. We iteratively solve the non-linear Pauli's master equation to compute time-averaged occupational probabilities of the sites from which relevant transport quantities are calculated. We find that poor screening of dopant-polymer interactions increases the energetic disorder which closely follows the Coulomb interaction energy with the nearest dopant. The broadened DOS causes a larger difference in energies between neighboring localized sites which reduces carrier hopping rate and thus the electron mobility. Also, deep Coulombic traps cause an additional tail in the otherwise Gaussian DOS which is further enhanced with clustering of dopant molecules. We fit experimentally determined iodine-doped P3HT and PDPP4T to our simulations and find that the changing size and shape of the heavy-tailed DOS distribution brought on by doping dictates the slope of the Seebeck vs. conductivity plots. We conclude that reducing the dopant-carrier Coulomb interactions and minimizing dopant clustering can have a beneficial impact on conductivity and thermoelectric power factor of Organic semiconductors.

Morphological effects on intrinsically conductive polymers

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Intrinsically conductive polymers have made large advancements through optimization of chemical structure and method of polymerization, increasing conductivities up as high as 10^3 S cm^{-1} . Thin film conductive organic polymers have further seen increased attention due in part to their intrinsically low thermal conductivities ($0.2\text{-}0.6 \text{ Wm}^{-1}\text{K}^{-1}$). This can be seen with the state-of-the-art conductive polymer poly(3,4-ethylenedioxythiophene) PEDOT, which has been reported to have a zT as high as 0.42. Interestingly, while the overall electronic structure of PEDOT may not change, differences in polymerization methods and counterion selection have both shown drastic differences in final electrical properties and morphology. The underlying role of polymerization methods and counterion selection is therefore investigated in order to explore how the conductive polymers underlying charge transport properties are affected. Through this work we present findings that suggest morphology plays a significant role in enhancing thermoelectric properties.

Altering Spin Concentrations in Self-Doped Small Molecules

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N-type doping methods in organic systems typically combine small ionizable species with a semiconductor scaffold in solution before casting the pair into films. How dopants distribute within the cast semiconductor is unpredictable. The distribution of dopants, which vary from small to very large in their relative sizes, may affect semiconductor continuity, grain boundaries, morphology and packing of the semiconductor, electronic state distribution near the Fermi-energy, and yield topological variations in the electronic structure. Direct comparisons between different doping concentrations can therefore be rather nebulous, making the selection of the proper dopant for a given organic semiconductor highly convoluted. These challenges may be mitigated using self-dopants, where the electron source is covalently attached to the semiconductor. We have investigated the effects of steric hinderance, counterions, and dopant/semiconductor proximity on the efficiency of self-doping in a variety of perylene diimides. We believe our findings offer design considerations for the fabrication of effective self-dopants in n-type organic semiconductors.

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Investigating thermoelectric transport at the hard-soft interface of hybrid Te-PEDOT:PSS nanowires

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Organic-inorganic hybrid materials offer great promise as solution-printable thermoelectric materials to realize robust, flexible devices that can directly convert heat to electricity (or vice versa). These materials however have struggled to surpass the performance of their rigid inorganic counter parts due to a lack of control and insight into structure-function relationships and the heterogeneity of bulk, polycrystalline, thin films reported thus far. Herein we perform a systematic study of a model hybrid system comprising individual core/shell nanowires of Te-PEDOT:PSS. We show that as the nanowire diameter is reduced, both higher electrical conductivity and lower thermal conductivity are measured, while the Seebeck coefficient remains nearly constant - this collectively results in a figure of merit, zT , of 0.18 at room temperature for a 42 nm diameter nanowire. The origin of the decoupling of transport parameters lies in the fact that electrical transport occurs through the organic shell, while thermal transport is driven by the inorganic core. This study establishes design principles for high performing thermoelectrics to leverage the unique interactions in hybrid nanowires.

Development of n-type $\text{Mg}_3\text{Sb}_2\text{-Mg}_3\text{Bi}_2$ alloys

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There has been significant interest in $\text{Mg}_3(\text{Sb,Bi})_2$ since the recent demonstration of high zT in the n-type materials. In this study, we demonstrate that the $\text{Mg}_3\text{Sb}_2\text{-Mg}_3\text{Bi}_2$ alloy can be a promising material for low- mid temperature range. The main mechanisms of this improvement are optimization of the band structure and microstructure. The understanding of these mechanisms is crucial to the cooling and wasted heat recovery applications of $\text{Mg}_3\text{Sb}_2\text{-Mg}_3\text{Bi}_2$ alloy. Considering the limited number of state-of-art n-type thermoelectric materials for the low-grade heat recovery and cooling technology, the further development of $\text{Mg}_3\text{Sb}_2\text{-Mg}_3\text{Bi}_2$ alloys is a significant step towards the commercial application of thermoelectric materials.

Anisotropic thermoelectric properties of Mg_3Sb_2 studied by first principles calculations

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Towards high thermoelectric (TE) figure of merit zT , high crystal lattice symmetry and thus high band degeneracy and multiple pocketed Fermi surface are favored. On the other hand, quite some state-of-the-art TE materials adopt low crystal lattice symmetry: Bi_2Te_3 (R-3m, space group #166), GeTe (R-3m, #166), SnSe (Pnma, #62) to name a few. In this vein, Te-doped n-type Mg_3Sb_2 with $zT \sim 1.6$ at 720 K is getting increasing attention. Given a low lattice symmetry (trigonal lattice, P-3m1, #164), the TE properties including zT of Mg_3Sb_2 -based compounds are anisotropic. To date, experimental study of Mg_3Sb_2 -based compounds is mainly on the polycrystalline samples, a few data sets taken on the single crystalline samples exhibit a large discrepancy. To clarify the intrinsic TE properties of Mg_3Sb_2 , here we conducted first principles calculations and solved semi-classical transport equations with electron-phonon coupling properly taken into account. For p-type Mg_3Sb_2 , the electrical conductivity is found to be strongly anisotropic while the Seebeck coefficient and thermal conductivity are less anisotropic. For n-type Mg_3Sb_2 , the electrical and thermal transport properties are practically isotropic. Our calculated zT values agree well with the experimental data of both n-type and p-type Mg_3Sb_2 .