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ABSTRACT BOOK

POSTER SESSION 2

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ECT'22

Advanced characterization

ID: 04675
Type: Poster
Topic: Advanced characterization

On the Microstructure-Property Relationship of Full-Heusler Fe2VAl Manipulated by Laser Surface Remelting

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Thermoelectric (TE) performance depends not only on the material itself but also on carrier concentration and microstructure. While the influence of the carrier concentration is well known, the influence of the microstructure is still comparatively poorly understood. Hence, the microstructure is often manipulated on a trial-and-error basis.

We present a correlative method of investigating the microstructure and the local TE properties for Fe_2VAl [1,2]. The microstructure was manipulated by laser surface remelting (LSR), showing similarities to a material produced by additive manufacturing methods, such as selective laser melting. Scanning electron microscopy and atom probe tomography were used to bridge the scale from micrometer to nanometer. The local electrical resistivity and thermal conductivity were analyzed by an *in-situ* four-probe technique and scanning thermal microscopy, respectively.

The microstructure within the manipulated region consists of small, elongated grains growing epitaxially from the substrate. A high density of geometrically necessary dislocations in the order of 10^{13} m^{-2} was observed by electron channeling contrast imaging. Segregation of vanadium and nitrogen was found at grain boundaries and dislocations, observed by atom probe tomography. These defects act as scattering centers for electrons and phonons. However, the off-stoichiometric composition within the melt pool of approx. $Fe_2V_{1.1}Al_{0.9}$ can overcome this scattering and decrease the resistivity. At the same time, the thermal conductivity is reduced due to increased phonon scattering at defects.

We conclude that we can manipulate the microstructure and, hence, the properties by using LSR. The combination of detailed microstructural analysis and local measurement of properties offers the possibility of understanding the microstructure-property relationship. This, in turn, opens the door for effective defect/boundary engineering without the need for any time-consuming trial-and-error method.

References:

[1] L. Gomell, et al., Scr. Mater. 193 (2021) 153–157.

[2] L. Gomell, et al., Acta Mater. 223 (2022) 117501.

ID: 04994
Type: Poster
Topic: Advanced characterization

Electrical Contacts Characterization and Computer Simulations of Tetrahedrite Based Devices

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With the crescent need by the industries and cities to become greener and change from fossil energy sources into the renewable ones, the interest in thermoelectric (TE) materials have been increasing every year in the last decades. The absence of gas emissions, moving parts, and the low maintenance requirements, combined with the ability of harvesting waste heat to produce electrical energy, make TE devices highly attractive. However, the current market options are based in toxic and rare elements which make the technology expensive comparatively to its energy conversion efficiency. Therefore, TE materials and devices are currently mainly used in niche markets, and for small scale and specific applications.

To change this tendency, is not just important to search for new, more efficient, and cheaper materials but also to optimize them. Before assembling a new device, it is very important to understand the reactivity between the TE legs and the materials used as electrical contacts. When in contact during long periods and at high temperatures, the formation of interfacial phases between the legs and contacts can ruin the devices performance. Once these problems are solved, it is important to know how to connect the protected legs to the electrodes in order to assure low contact resistances. Still, most of the jointing techniques used in commercial devices are patented and therefore considered industrial secrets.

In this work, the best approaches to assemble/join tetrahedrite based legs to copper contacts are evaluated. To study the best assembling methodologies, several jointing materials and techniques are explored, being the contact resistances measured in a custom-made system. To get a better understanding how the different contact resistances affect the performance of TE devices, simulations using the *COMSOL Multiphysics* software were done considering the contact resistances measured to explain the observed decreased performances of the manufactured modules.

ID: 05020
Type: Poster
Topic: Advanced characterization

Error source analysis of the ‘Combined ThermoElectric Measurement’ (CTEM) apparatus by means of a digital twin

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Simultaneous property measurements can provide a precise characterization of thermoelectric materials. The ‘Combined ThermoElectric Measurement‘ (CTEM) apparatus gives access to temperature dependent data for the Seebeck coefficient, the electric conductivity and the thermal conductivity between room temperature and 600 °C. The measurement procedures are affected by several error sources, which can lead to deviations from reference values for the investigated properties. Starting from a computational model of the measurement system under ideal measurements conditions, potential error sources can be added to the digital twin to investigate their individual influences on the respective results in the real experimental set-up. Here, we report on the actual challenges of the CTEM apparatus and present the performance of the digital twin including specific error sources, such as the radiation impact and coupling of gradient heaters.

Co-doped $FeSi_2$ with its well-studied transport properties is a thermoelectric reference material for measurements of the Seebeck coefficient and currently being used to study the CTEM apparatus to validate its measurements procedures and experimental set-up. As a consequence of present disturbing effects, the results of the thermoelectric properties deviate from referenced values. Due to the fact, that the different error sources occur simultaneously, it is very difficult to identify individual error sources experimentally and to find possible corrections for the analysis. A digital twin of the CTEM apparatus was developed on the base of a network simulation using Modelica^{TM} environment. Here, we concentrate on assumed error sources, which have been implemented separately and in a combined manner, which allowed for identification of relevant error sources by matching numerically determined measurement results to those from real experiments. This enabled for the specification of correction procedures for the experimental set-up, which can be added to the analysis in order to reduce the impact of measurement errors.

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Topic: Advanced characterization

Characterization of Thermoelectric Generator Modules: Analytical Study on Heat Flow Determination under Transient Temperature Conditions.

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Thermoelectric generator modules (TEM) are in common use as power sources for spacecrafts. Moreover, industries develop them for recuperation of waste heat in automobiles and stationary applications. A challenge that remains to date is the precise determination of power output, heat flow, and efficiency due to the absence of guidelines and standards. Most research has concentrated on steady state characterization approaches at stabilized temperature conditions, which lead to long measurement durations. On the other hand, determination of TEM properties under transient thermal conditions is limited mainly to approaches with a Peltier-induced change of TEM boundary temperatures by variation of the electric load current. Here we present first investigations on a method for determining temperature fields under transient boundary conditions (temperature and electric current flow) in single thermoelectric (TE) legs. This case has been simulated using a network model under ideal conditions using OpenModelica (OM). The model prediction of temperature fields in a TE-Leg is validated against the analytic solution of the governing partial differential equation. Overall this work represents the first in a series of steps into a new characterization technique for TEMs under transient measurement conditions. Future work will involve simulations of more complex measurement configurations, as well as investigations into resulting deviations between the PDE and OM. Moreover, the solutions to the corresponding PDE for said configurations will allow for derivation of measurement functions for TEM properties of interest.

ID: 05052
Type: Poster
Topic: Advanced characterization

Figure of Merit and Thermal Conductivity – Characterization of Thermoelectric Materials by the Powerful Combination of Light/Laser Flash Analyzer (LFA) and Seebeck Analyzer (SBA)

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1) NETZSCH Analyzing & Testing

The maximum efficiency of a thermoelectric device is described in terms of its figure of merit ZT. In order to achieve the required high value a high electrical conductivity ?, a high Seebeck coefficient S and a low thermal conductivity ? are required.

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Selected application examples demonstrate the high capability of the combination of both, SBA and LFA in a wide temperature range.

ID: 05077
Type: Indiferrent
Topic: Advanced characterization

Measurement device for measuring the electrical conductivity, the Hall constant and the Seebeck coefficient up to 800 °C.

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The determination of electrical transport properties like the electrical conductivity, the charge carrier density, the charge carrier mobility, and the Seebeck coefficient is of increasing importance in material characterization for high temperature applications. Currently, several, often costly measurement devices are required for this, especially when intended for high-temperature application.

In our contribution, we report on the current state of development of a measurement device that allows the combined measurement of the above-mentioned parameters up to a maximum operating temperature of 800 °C. The measurement device moreover avoids to use expensive furnaces and electromagnets, making it a cost-effective alternative.

The main component of the new measurement system is the sample holder, which is based on a 635 µm thick alumina substrate. A screen-printed platinum heating structure on the bottom side of the Al_2O_3 sample holder was designed by FEM-simulations 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 gradient within the sample area. Thermal imaging validated a homogenous temperature distribution for Hall-measurements as well as a temperature difference for Seebeck-measurements. On the top side, four moveable electrodes allow measurements of any geometry according to van der Pauw's method. Two additional thermocouples were placed between the sample and the electrodes to determine the contact point temperature and the occurring thermoelectric voltage. Measurements of known materials confirm the functionality of the measurement device.

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Type: Poster
Topic: Advanced characterization

Systematic study of Ag2(SeTeS)1 chalcogenides for wearable thermoelectrics

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Wearable renewable energy generators are an attractive alternative to battery-based systems and can generate power up to a few Watts for portable electronic equipment. Although the most inorganic semiconductor materials are brittle at room temperature (RT) the $Ag_2(SeTeS)_1$ chalcogenides show exceptional plastic deformability and high thermoelectric performance making them suitable materials for wearable thermoelectrics. In this study, we investigate ternary and quaternary $Ag_2(SeTeS)_1$ solid solutions with Se/Te doping closer to Ag_2S end.

A series of samples was prepared by rapid casting: $Ag_2S_{1-x}Se_x$, $Ag_2S_{1-x}Te_x$ and $Ag_2S_{0.5}Te_{0.5-x}Se_x$ (x = 0.1, 0.2, 0.3, 0.4) in to form of Ø = 3 mm, 12 mm long homogeneous ingots. Significantly high ZT = 0.47 at RT was observed for $Ag2S_{0.7}Se_{0.3}$ (so far measured by Harman method).

$Ag_2(S/Se)_1$ and $Ag_2(Se/Te)_1$ ternary systems crystalize in an orthorhombic or monoclinic structure, depending on the detailed S/Se, Se/Te atomic ratio. Addition of Te into these systems is introducing favorable cubic phase, as well observed in $Ag_2(S/Te)_1$ ternary middle region. Well known monoclinic – cubic phase transformation of $Ag_2(S/Se)_1$ [1] is pulled down to lower temperatures (even under RT) where it stabilizes with rising Te concentration. Highly disordered Ag atoms stay present in the cubic phase mimicking amorphous structure examined by diffraction.

In this contribution we present a systematic study of $Ag_2(SeTeS)_1$ chalcogenides. Temperature induced structural phase transformations are examined by differential scanning calorimetry and synchrotron in situ diffraction. Inelastic neutron scattering investigations shed light on the compounds' phonon properties showing a phonon renormalization and broadening with addition of Se/Te to Ag_2S and temperature treatment. The results are backed up by density functional theory and molecular dynamics calculations. We present data from thermoelectric characterizations carried out from RT up to 200°C.

[1] Bontschewa-Mladenowa, Z. and Zaneva, K. (1977), Untersuchung des Systems Ag2Se-Ag2S. Z. anorg. allg. Chem., 437: 253-262. https://doi.org/10.1002/zaac.19774370137

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Topic: Advanced characterization

Extracting thermal diffusivity of thermoelectric materials using micro four-point probe

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Thermoelectric energy conversion is a viable means of harvesting energy to help achieve a low carbon economy. For this purpose, metrological characterization of state-of-the-art thermoelectric materials needs to be developed. Here, we developed a new micro four-point probe (M4PP) technique for direct characterization of the thermal diffusivity for bulk thermoelectric materials, non-destructive and without extensive sample measurement preparation. M4PP's are routinely used in the semiconductor industry for electrical characterization of electro-magnetic properties. In addition to conventional electrical conductivity measurements using the M4PP, we have recently demonstrated the ability to measure the Seebeck coefficient of bulk semiconductors and thermoelectric materials. In the current work, we extend the capability of M4PP metrology to extract thermal diffusivity, a parameter which is vital for determining the performance of thermoelectric materials.

Measurements are performed by passing an alternating current between two electrodes, generating a modulated temperature gradient in the sample via Joule heating. As a consequence of the Seebeck effect, a second harmonic voltage signal is generated and measured with the lock-in technique. The phase delay of the second harmonic signal is directly proportional to the thermal diffusivity of the sample and depends on the electrode separation and the measurement frequency. Thus, we investigate and compare two separate approaches to extract the thermal diffusivity, using variable electrode pitch and variable frequency, respectively. As benchmark materials, we demonstrate the validity of our measurement on Bi_2Te_3 and skutterudite thermoelectric samples. The proposed method allows to characterize the thermal diffusivity of thermoelectric materials in a few seconds and further helps in accelerating the development of energy-efficient materials.

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Type: Poster
Topic: Advanced characterization

Lattice dynamics and anharmonicity of thermoelectric BiCuSeO

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Very recently, new classes of thermoelectric materials with very low thermal conductivity (less than 1W/m.K at room temperature and above) and mainly composed of chalcogen and pnictogen atoms have been developed. It was proposed that the increase of the anharmonicity due to the electron lone pair of the pnictogen atoms was the reason behind this low thermal conductivity. However, direct spectroscopic proof confirming this scenario is still lacking, hence the importance of spectroscopic studies of the lattice dynamics. Among these materials, BiCuSeO has large ZT up to 1.5 for doped samples at 900K because notably of its very low thermal conductivity. Recent work has also confirmed the presence of electron lone pair of the 6s states of bismuth in this compound. Other interesting points are the very simple tetragonal crystal structure of BiCuSeO and its close crystallographic proximity with the 1111 Fe superconducting compounds.

In the present communication, we report inelastic neutron scattering experiments as well as Raman scattering and infrared absorption spectroscopies on polycrystalline sample of BiCuSeO as a function of the temperature. We find a large broadening of the phonon density of states (DOS) when the temperature increases, a fingerprint of the large anharmonicity of this system. We also observe a rather large thermal variation of a shoulder at 32cm^{-1} in the phonon DOS, corresponding to the flattening of the transverse acoustic modes at the Brillouin zone boundary We identify 6 out of 8 predicted Raman-active modes and all 6 predicted infrared-active modes. The 2 infrared-active E_u modes of lowest energy have large Grüneisen parameters and anharmonicity. Other manifestations of these anharmonic properties are the large thermal expansion and thermodynamic Grüneisen parameter. Our results will be discussed via an analysis of the DFT calculations of the anharmonic properties of the lattice dynamics and of the thermal conductivity of BiCuSeO.

ID: 05149
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Topic: Advanced characterization

Fe Segregation as a Tool to Enhance Electrical Conductivity of Grain Boundaries in Ti(Co,Fe)Sb Half Heusler Thermoelectrics

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Complex microstructures can be used to optimize transport properties in thermoelectric materials. Grain boundaries are known to scatter phonons, but they often also impede charge carrier transfer. Fe dopants in TiCoSb half Heusler materials segregate to the grain boundaries and simultaneously increase the electrical conductivity and reduce the thermal conductivity. To study these phenomena, samples with different grain sizes are synthesized and a model is developed that relates the electrical conductivity with the area fraction of grain boundaries and allows the calculation of electrical conductivity of grain interior and grain boundaries. In addition, the atomic structure of grain boundaries is studied in detail using high resolution scanning transmission electron microscopy (TEM) and atom probe tomography (APT) to understand the role of complexions in the creation of conductive grain boundaries. Segregation engineering is proposed in nanocrystalline thermoelectric materials as a new design tool to optimize transport properties and reduce thermal conductivity.

ID: 05203
Type: Poster
Topic: Advanced characterization

I want a simple tool to characterise my thermoelectric device and my generator. Use impedance spectroscopy

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The fabrication of thermoelectric devices is not a simple task, since it involves the optimisation of many parameters, such as the thermoelectric materials themselves, their connection with the metallic strips, the thermal influence of the electrically insulating layers, etc. Impedance spectroscopy offers many advantages to characterize thermoelectric devices, since from simple measurements that just require the connection of the device to the impedance equipment and vacuum, it is able to quantify many of the key properties of the device, such as the materials properties and the thermal contact resistances at the thermoelectric material/metallic strip junctions [1].

In addition, when integrating the devices into generators the efficiency of conversion of heat into electricity is not only influenced by the material properties, but it also depends on the temperature of operation, which is governed by the thermal resistances from the thermoelectric legs up to the heat source/sink. The thermal contact resistances between the outer ceramics of the thermoelectric devices and the heat exchangers is essential to achieve a good efficiency of the entire generator.

Impedance spectroscopy has also been proved to be a useful method for the characterization of thermoelectric systems. In fact, we recently proved that these thermal contacts can be determined by performing a measurement in suspended conditions and a measurement with the device assembled. In this work, we show the benefits of using impedance spectroscopy to characterise devices, and also for the very first time the characterization of an entire thermoelectric generator, showing the potential of the impedance to evaluate, monitor, and identify issues during the fabrication of devices and their assembly in thermoelectric generators.

References

[1] B. Beltrán-Pitarch, J. Maassen and J. García-Cañadas. Comprehensive impedance spectroscopy equivalent circuit of a thermoelectric device which includes the internal thermal contact resistances. **Applied Energy** 299, 117287 (2021)

ID: 05204
Type: Poster
Topic: Thermoelectric materials and materials processing

Phonon characterization by neutron inelastic scattering experiments

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The performance of thermoelectric materials is characterized by the figure of merit $Z = S^2?/(k_e+k_l)$ with the Seebeck coefficient S, electrical conductivity *?,* and the electronic k_e and lattice k_l thermal conductivities. Consequently, to optimize Z highest power factors $S^2?$ and lowest thermal conductivities k_e and k_l are required. Whereas S, *?* and k_e reflect the electronic properties, k_l represents the thermal transport by the materials' lattice and is thus dominated by its vibrational properties. To certain extent k_l can be modified independently from the electronic properties allowing a tailoring towards lower values and higher Z.

Concepts such as the notorious 'phonon glass and electron crystal' draw attention to peculiar vibrational properties of thermoelectric materials. They highlight that a wide distribution of 'soft' anharmonic vibrations with energies extending down to characteristic energies of mass transport as present in glasses and liquids, is favorable for the thermoelectric performance. A 'phonon glass' is realized in many ways, such as by the complexity of crystal structures, by an extended spread of element masses in multi-component compounds or by a hierarchic organization of chemical bonds.

Whatever the origin of the vibrational peculiarities is, a comprehensive experimental study of the inelastic response from the ground state properties to the thermal regime of thermoelectric applications is necessary to understand the functioning of phonons in k_l. Inelastic neutron scattering is a powerful experimental tool to tackle this task. Its strength is the covered momentum and energy space matching the regime of vibrations in thermoelectric compounds. The European Neutron Source, Institut Laue Langevin, introduced the new spectrometer PANTHER [1] adapted for such material studies. Its sample environment covers temperatures from 1.5 K to 1500 K and pressures up to 1 GPa. We will show examples of its application to different thermoelectric compounds (chalcogenides, silicides, tellurides).

[1] https://www.ill.eu/users/instruments/instruments-list/panther/description/instrument-layout

ID: 05221
Type: Poster
Topic: Advanced characterization

Atomic site distributions in medium / high temperature range application thermoelectrics: an HRTEM and electron channeling study

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Electron spectroscopy techniques in analytical transmission electron microscopy (TEM), such as energy dispersive X-ray spectroscopy (EDS) or electron energy loss spectroscopy (EELS) provide a powerful tool for structure refinement, by precise identification of atomic positions in crystal structures. In this aspect, the yield of element-characteristic X-ray emission is modified and manipulated under strong channeling conditions, dependent upon kind and position of atoms in the lattice. Such channeling effects are powerful in determining site locations in nanocrystals and techniques such as ALCHEMI (Atom Location by CHanneling Enhanced MIcroanalysis) have been developed and widely exploited.

Complementary high resolution TEM (HRTEM) and channeling studies have been recently focused in thermoelectric (TE) materials for medium and high temperature range applications, such as mixed silicides ($Mg_2Si_{1-x}Sn_x$) or MCoSb / MNiSn (M=Ti, Zr, Hf) half Heuslers (HH). Their advantages are low production costs, excellent mechanical and electrical properties, thermal stability, abundancy and atoxic nature of raw materials, as well as environmental-friendly approaches (e.g. Si recycling from photovoltaics). Synthesis of mixed silicides or HHs in nanocrystal morphologies are often coupled with incorporation of dopants (Bi, Sn, Sb) to significantly reduce thermal conductivity by enhanced phonon scattering, in addition to host atom alloying. As a result, the precise location and distribution of both host and dopant atoms remains controversial. Applications, therefore, of electron channeling are essential in order to accurately determine and refine structural characteristics in these TE compoundss. In this contribution, an overview and demonstrations of recent experimental outcomes of the channeling method will be exploited; in addition, complementary HRTEM imaging and post-experimental analysis results will be presented, in a comparable fashion.

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ID: 05251
Type: Poster
Topic: Advanced characterization

Study of the annealing effects on thin films prepared with phase vapour deposition of Bi2Te3 and Sb2Te3 compounds with full figure of merit characterization.

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Thermoelectric (TE) devices enable the direct conversion between heat and electricity and vice versa. The demand of micro TE harvesting or Peltier cooling devices for application in autonomous sensor systems required for the internet of things (IoT) will prospectively drastically increase in the coming years. Such microdevices are typically fabricated using electrodeposition or physical vapor deposition and photolithography. However, by using photolithography heat treatment during deposition is often not possible. Therefore, the use of post-deposition heat treatment for optimization of the thermoelectric figure of merit, zT, which is the key parameter of these devices, is of high interest. In this study, we developed a thickness depended post-deposition heat treatment process for both n-type Bi2Te3 and p-type Sb2Te3 films and observed a 400% increase of *zT*. Moreover, we support these investigations with EDX, XRD, SEM measurements. For the in-plane Seebeck coefficient, Hall coefficient, electrical, and thermal conductivity measurement a thin film analyzer (TFA) has been used. We will discuss the influence of temperature effects on the transport properties, including in-situ annealing experiments and the relation to the structure, grain size, and chemical composition. Furthermore, we support these findings with finite element method (FEM) simulations and discuss possible device designs and applications.

ECT'22

Theory & modelling

ID: 03467
Type: Poster
Topic: Theory and modelling

Advanced simulation tools for thermoelectric materials

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The new generation of thermoelectrics involves physics-based concepts and transport complexities. Hierarchical nanostructuring, energy filtering, modulation doping, band engineering, alloying, topological states, etc., are design ‘tools’ that can lead to unprecedented performance towards the realization of economically scalable materials. Theory and simulation can play an enormous part by providing the means to optimize material designs that utilize those ‘tools’. However, a higher degree of sophistication in simulation approaches is required. Large scale, computationally robust simulators that adequately capture all necessary physics and transport details at reasonable computational cost can provide both qualitative and quantitative insight and assist the design and identification of new, high performance materials.

This work, describes the development of advanced simulators related to the extraction of thermoelectric transport properties of: i) nanostructures and ii) complex bandstructure materials. The first group requires simulators that utilize ‘real-space’ treatment, and we elaborate on the development of a quantum transport simulator and a promising design concept for extremely large power factors. The second group, requires coupling of DFT with Boltzmann transport, and for this we present a simulator developed based on deformation potential theory, and a study for identification of high performance materials. In both cases, we provide deeper understanding in thermoelectric transport, that could not have been reached from simplified considerations, and introduce advance software that can be utilized by the community.

ID: 05026
Type: Poster
Topic: Theory and modelling

Screening quaternary Heusler by machine learning for application in thermoelectricity

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Heusler alloys, full and half-, thanks to their high versatility of compositions as well as their very interesting properties, are good candidates for thermoelectric applications. In the Heusler family, quaternary alloys also exist and allow to further increase the chemical diversity and so one to achieve more complex properties. However, due to the high number of combinations, traditional screening methods are not effective to target relevant compounds. To accelerate this research, it is advantageous to use machine learning methods.

In our project, we are looking for new promising quaternary Heusler compounds screened within a dataset of 24 selected elements. First, a database of calculated thermodynamic, electronic and magnetic properties, obtain from DFT calculations (Density Functional Theory) on binary and ternary compounds was constructed. Then, a supervised learning with the neural network model was built to predict the enthalpy of formation and the density of state at the Fermi level (metallic or semiconductor character) of quaternary Heusler compounds. Our model presents comparable or superior performance than the state of art and allow to identify promising compounds among the 24^4 possible configurations of our dataset.

ID: 05029
Type: Poster
Topic: Theory and modelling

Optimal alloying site for reducing lattice thermal conductivity of Half-Heusler

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Iso-valent (sub-lattice) alloying is a standard strategy to improve thermoelectric material properties. It can be used to engineer band convergence which enhances the power factor. It also generally causes a significant reduction in the lattice thermal conductivity (LTC) by scattering high-frequency phonons. Despite these merits, alloying is seldom taken into account in computational material screening, and general guidelines for which site to alloy on are missing. Here, we will present the results of a recent computational screening study [Electron. Mater. 2022, 3, 1] based on the TDEP code systematically probing the effect of sub-lattice substitution on LTC for all sites of 122 half-Heusler compounds. We identify the site hosting the heaviest atom as the most effective substitution site. Moreover, we find that the reduction in LTC is particularly large for materials with large mass contrast between elements of the parent compound and provide examples. Finally, we discuss the consequences of our results of the hunt and the design of improved thermoelectric materials in general.

ID: 05032
Type: Poster
Topic: Theory and modelling

Efficient and reliable scattering rate extraction in complex band thermoelectric materials from first principles: The case of Mg3Sb2

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Thermoelectric materials are characterized by crystal complexity, electronic and phononic structure complexity, and electronic and phononic transport complexities. Theoretical methods to compute their electronic transport properties and thermoelectric power factor have been developed, and they consist of two parts: the computation of the scattering times, which are then used within the Boltzmann Transport equation (BTE). The computation of the scattering times is challenging. The most common direction uses rather strong approximations, such as the constant relaxation time (CRT) approximation. Full ab initio methods also exist, but they are computationally enormously expensive, requiring the computation of billions of electron-phonon matrix elements, and thus are rarely used.

In this work, we describe a novel method that we have recently developed in order to compute the electron-phonon scattering times of complex band structure materials from fully ab initio considerations, but with one tenth of their computational cost. Based on density functional theory (DFT) and density functional perturbation theory (DFPT), we have developed a first-principles framework to extract acoustic and optical deformation potentials [1], which can then be incorporation within the BTE. We test our method for common semiconductors such as Si, but also for high-potential materials such as Mg_3Sb_2, which otherwise present significant computational challenges. Using our own-developed BTE software ElecTra [2], we further compute the mobility and thermoelectric coefficients of this material, and explain complex phenomena that appear such as the intra- versus inter-band/valley scattering and its immunity to ionized impurity scattering.

Our method presents the middle ground between the simplistic CRT, and the immensely computationally expensive Wannier methods. However, it can still provide first principles accuracy at a portion of the cost, which can allow proper and robust assessment of the thermoelectric properties of materials.

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ID: 05038
Type: Poster
Topic: Theory and modelling

Impact of doping on the lattice thermal conductivity of PEDOT:PSS

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Organic materials for thermoelectric applications have attracted a fair amount of attention in recent years due to remarkable advances achieved in terms of their *ZT* (the thermoelectric figure of merit): a value of 0.42 has been reported by [1]Kim et al. for poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) films treated with dimethyl sulfoxide (DMSO), while 0.25 has been obtained for PEDOT:Tosylate by [2]Bubnova et al.
Despite these remarkable advances, we feel there is still much to do on the theoretical aspects of this material. For this reason, in this work we investigate the thermal properties of pristine PEDOT in its neutral and doped (bipolaronic) state and doped PEDOT:PSS, varying the distribution of oligomer lengths and the concentration of PSS. To this aim, we take advantage of the all-atom force field recently developed by [3]Micheals et al. We find that in neutral PEDOT lattice thermal conductivity ($?_{lat}$) scales with average oligomer length (l_{avg}), while in doped PEDOT there is a maximum $?_{lat}$ at intermediate l_{avg}. We also find that in doped PEDOT density (?) scales inversely with l_{avg}, which would explain the non-linear relation $?_{lat}(l_{avg})$. Additionally, we find that doped PEDOT has generally higher $?_{lat}$ and ? than neutral PEDOT. The introduction of small amounts of PSS polyanions is sufficient to disrupt the already low degree of order of these systems, bringing both $?_{lat}$ and ? to values lower than neutral PEDOT. Morphological properties are also studied by calculating radial distribution functions, XRD patterns and measures of local degree of crystallinity.

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ID: 05070
Type: Poster
Topic: Theory and modelling

Machine learning enabled thermoelectric generator modelling and optimisation

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Modelling and optimising thermoelectric generators is one of the essential tasks in developing thermoelectric generators (TEGs) with high performance. However, a compromise of either the computational accuracy or speed is always inevitable when using conventional modelling methods such as the finite element method (e.g. ANSYS simulation) and mathematical modelling. The artificial neural network (ANN), a type of deep learning technique, can serve as a suitable forward modeller for TEGs that balances accuracy and computational speed without prior knowledge of the thermoelectric device. This work demonstrates the application of the deep learning technique in forward modelling the power performance of different TEGs. The ANN-based modeller considers a range of design parameters (e.g., leg height, width, and filling factor) with varying operating conditions (i.e., heat flux and electrical contact resistivity). After training using datasets from 3-D COMSOL simulations, the ANNs showed extremely high prediction accuracy, over 98% and 95% on conventional symmetric and asymmetric thermoelectric generators, respectively. Such high accuracy is also accompanied by a significantly reduced prediction time – 1 ms, 60,000 times faster than the finite element method (FEM) approach. Furthermore, for the more complex segmented thermoelectric generators, we introduced an iterative training approach that significantly improved the accuracy of ANN in predicting high-performing TEG designs. The fast and accurate modelling of TEG enables short TEG design optimisation. Coupling with an optimisation algorithm (i.e. genetic algorithm), our trained ANN can perform geometrical and structural optimisation for TEG under different operating conditions. With almost identical optimised values obtained, our ANNs demonstrate superior optimisation efficiencies over 1000 times better than the COMSOL simulation coupled with genetic algorithm optimisation. The success of this work indeed points towards using ANN for modelling complex TEG designs and other renewable energy technologies.

ID: 05161
Type: Indiferrent
Topic: Theory and modelling

More than 500 new low bandgap materials identified in a hybrid functional screening study – some with very promising thermoelectric properties

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The underestimation of electronic bandgaps is a well-known problem in standard density functional theory (DFT). A non-zero bandgap is a standard filter in high-throughput (HT) screenings of thermoelectric (TE) materials as the electronic transport properties greatly depend on the existence of a bandgap. In our recent work, a group of 7500 materials in the Materials Project database were selected for a HT screening based on stability, unit cell size, and elements. All structures were re-relaxed with a functional that includes van der Waals interaction (vdW-DF-cx) for more accurate lattice constants, in particular for layered systems. For the 4869 materials with a reported bandgap of less than 0.3 eV, the electronic band structure was re-evaluated with the hybrid functional HSE06 for more accurate predictions of the bandgap. Among the 4159 materials previously reported to have no bandgap, we found more than 500 materials with a non-zero bandgap at an average of 0.52 eV. Further, we found that the choice of functional also changes the relative energy of band structure valleys resulting in different degrees of band alignment. Based on the hybrid-level band structures several materials were found to have promising TE properties. Among them, $MgSc_2Hg$ and Li_2CaSi were both predicted to have a high thermoelectric figure of merit, even at medium-range temperatures.

ID: 05168
Type: Indiferrent
Topic: Theory and modelling

Finding Low Lattice Thermal Conductivity Compounds in Materials Space: Machine Learning with Active Sampling

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Low lattice thermal conductivity (LTC) is essential for high thermoelectric performance. Assessing the LTC typically involves time consuming experiments or computations, making the discovery of low LTC compounds challenging. Machine learning (ML) methods can accelerate the identification of low LTC compounds at a lower computational cost. As there are few low LTC compounds, there are few in typical training sets, ML models can misclassify new low LTC compounds. In this work, we present an active sampling scheme that iteratively selects the compounds to include in the ML training set. The training set LTC is obtained from density functional theory and the temperature-dependent effective potential method. We also adopt ML descriptors that are less sensitive when transitioning to different compound classes. The ML model can accurately assess the LTC, and is used to identify over 50 cubic compounds with ultra low LTC (< 1 W/Km) from the MaterialsProject database.

ID: 05191
Type: Poster
Topic: Theory and modelling

Stability, Electronic Structure and Thermoelectric Properties of Functionalized 2D Molybdenum Nitrides – MXenes

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MXenes are relatively new family of low dimensional materials, which has been gaining more and more popularity in recent years. MXenes are mainly carbides and nitrides of early transition metals and they combine the properties of both components. Bare MXenes typically exhibit metallic behaviour and, therefore, are known to be good electric conductors. Interestingly, this property changes with functionalization of their surfaces. It occurs that functionalizing groups can change metallic MXenes into semiconducting ones, and not only open the band gap but also influence other properties, just opening the path towards many potential applications, e.g., in electronics, optoelectronics, and thermoelectricity.

In this communication, we present probably the first reported studies of geometry, stability, and electronic structure of bare and functionalized molybdenum nitrides Mo2N (MXenes). The studies are based on first-principles calculations in the framework of density functional theory (DFT) employing pseudo-potentials and plane-wave basis as implemented in the QUANTUM ESPRESSO package. Here, we discuss the results for the bare, and functionalized with oxygen and fluorine Mo2N layers. All three systems are predicted to be stable at room temperature. The bare Mo2N is metallic with good electric conductivity. Functionalization of Mo2N with F leads to opening of the band gap by 0.09 eV and emergence of n-type semiconductor, whereas the Mo2N functionalization with O creates p-type semiconductor with energy gap of 0.49 eV.

The thermal properties of these two-dimensional materials have been calculated. Further, we consider the influence of the functionalization of Mo2N with Cl and OH groups on the effectiveness of energy band gap tuning. We have started also the calculations of physical quantities that determine the thermoelectric properties of these materials.

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Topic: Theory and modelling

Dual-phase-lagging heat conduction for porous media thermoelectric materials

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Porous theromoelectric materials such as CNT do not follow Fourier heat conduction during transient conditions. This affects directly to the accuracy of current thermoelectric models that cannot predict the electrical and thermal behaviouir correctly. The obective of this work is to mathematically model the thermal and electrical behaviour of this type of materials mixing the thermal model with dual phase lagging (DPL) outlined by Tzou and our thermoelectric model for non-porous materials.

ID: 05226
Type: Indiferrent
Topic: Theory and modelling

Thermoelectric properties of Cobalt doped n-type Bi2Te3

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Bi_2Te_3 is a known thermoelectric material [1]. To emphasize the fundamental transport mechanism in the $Bi_{2-x}Co_xTe_3$ (x=0, 0.05, and 0.1) samples, the temperature dependences of resistivity (?), Hall concentration of charge carriers (n_H) and Seebeck coefficient (S) have been calculated in frame of Boltzmann equation approach for single isotropic electron band with parabolic dispersion. Two mechanism of electron scattering have been included in the model: 1) Acoustic phonon scattering in deformation potential approximation; 2) Ionized donor scattering. Thermal variation of resistivity (*?*), thermopower (*S*), Hall Effect (*nH*) measurements have been performed on cobalt (Co) doped *n*-type $Bi_{2-x}Co_xTe_3$ (x=0, 0.05, and 0.1) bulk samples. The thermoelectric performance, as estimated through power factor is found to increase with Co doping, with an enhancement of ~ 50% is observed for Bi1.9Co0.1Te3 sample.

It should be stressed here that in the frame of the rather simple model including acoustic phonon and ionized impurity scattering, it is possible to fit the experimental data of *?(T)*, $n_H(T)$ and *S(T)* not only qualitatively but also quantitatively. The model gives reasonable agreement with the experimental data for x= 0.05 and 0.1 Co content. Proposed model explains effect of Co doping by change of donor concentration and disorder. Donor concentration decreases with the increase of Co content. Tail parameter also decreases with increase of Co content and can be partially explained by decrease of disorder with the decrease of ionized donor concentration. Decrease in ionized donor concentration furthermore designates that scattering decreases in Bi2-xCoxTe3 system and mobility (m) accordingly increases with Co (x=0.05, 0.1) doping.

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ID: 05257
Type: Poster
Topic: Advanced characterization

Thermoelectric properties and electronic structure of high-strength martensitic AISI 4340 steel

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Hydrogen embrittlement and the interaction of hydrogen with steel have recently been of interest to many research group. To our best knowledge, thermoelectric properties of high-strength steel have not been unequivocally correlated with the hydrogen content. AISI 4340 martensitic steel is very susceptible to hydrogen absorption and trapping due to its crystal structure. It is well-known that the hydrogen adsorbed by steel may occupy octahedral or tetrahedral interstitial positions in bcc (or tbc) structures. In our study, after electrochemical hydrogenation of steel, the surface Seebeck coefficient was measured. The experimental results are interpreted on the basis of *ab initio* electronic structure calculations performed by the KKR-CPA method, which appears to be especially well-adapted to treat multi-atom chemical disorder, appearing on Fe site (Mn, Ni, Cr impurities) and interstitial sites (C and H). The KKR-CPA total energy computations allowed to determine variation of equilibrium lattice constant and bulk modulus with hydrogen content, assuming different H positions in the unit cell. Theoretical results were compared with the experimentally investigated mechanical properties of 4340 steel samples. Furthermore, bearing in mind that the investigated steel systems are magnetic, the spin-polarized KKR-CPA calculations were carried out in order to analyze evolution of total and site-decomposed density of states (DOS) as well as total and local magnetic moments on transition metal atoms in 4340 steel with different H content. Finally, based on the analysis of DOS changes in the vicinity of the Fermi energy, the linear part of the Seebeck coefficient for steel samples with different hydrogen content was estimated.

On the whole, it was found from our theoretical study that lattice constant markedly increases with H content in the steel materials, which is accompanied by strong decrease of magnetic moment due to disappearance of spin-polarization of d-DOS mostly on Fe atoms.

ID: 05268
Type: Poster
Topic: Theory and modelling

Anomalous Paramagnon Thermopower: The Role of Inter-Layer Spin-Spin Correlations

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The heat capacity can directly measure the entropy transport; hence it is a strong tool for studying the spin-driven thermopower in magnetic thermoelectric materials. The relation between the thermopower and heat capacity can be extended above the magnetic ordering temperature, where the enhancement in the thermoelectric figure of merit is expected to happen. However, since the heat capacity of paramagnons is rarely reported, its application to study paramagnon-driven thermopower has not been considered so far. To close this gap, we investigate the paramagnon heat capacity using different approaches, including mean-field approximation (MFA), spin-wave theory (SWT), and cluster mean-field theory (CMFT). We consider manganese telluride (MnTe), with hexagonal spin 5/2 model and large paramagnon thermopower, as a case study in this work. The heat capacity from MFA increases with temperature and drops suddenly above the magnetic transition temperature; therefore, it cannot explain the paramagnon heat capacity. SWT is also not applicable to high temperatures and is reliable only at temperatures significantly lower than the transition temperature. In contrast, the paramagnon heat capacity from the CMFT, which includes the spin quantum correlations, agrees with the experimental results below and above the transition temperature. Moreover, these results show that the large spin-spin correlations between the inter-layer nearest neighbor (NN) spins are responsible for the finite paramagnon heat capacity observed experimentally in the disordered phase. To validate this concept with larger clusters, we examine the S=1 system. We show that the correlations between further neighbors in the inter-layer NN direction are even more significant than correlations with direct spin-spin interactions. Therefore, we conclude that the NN spin-spin correlations have a fundamental role in the paramagnon specific heat hence the paramagnon drag thermopower. These results can guide the material selection for designing efficient spin-driven thermoelectric materials.

ID: 05273
Type: Indiferrent
Topic: Theory and modelling

When Power Factor Supersedes zT to Determine Power in a Thermocouple

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The primary material parameter determining power in a thermoelectric is the figure of merit zT. This figure of merit comes from the requirement for thermal impedance matching between the thermoelectric legs and heat exchangers in an optimally designed thermoelectric module. However, in a thermocouple temperature sensor, the geometry is constrained for temperature sensing. If the geometry is constrained so that the length of the thermoelectric elements is greater than a characteristic length, then the material thermal conductivity becomes less relevant. This makes the power factor the determining material metric for power output in such a device designed for temperature sensing.

ECT'22

Thermoelectric materials & materials processing

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Type: Poster
Topic: Thermoelectric materials and materials processing

BISMUTH DOPING IN Cu-Sb-S SYSTEM : SCALABLE MECHANOCHEMICAL SYNTHESIS AND THERMOELECTRIC PERFORMANCE

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In this study we demonstrate the use of Cu, Sb, Bi and S precursors with the aim to synthetize Bi-doped tetrahedrite $Cu_{12}Sb_{4-x}Bi_xS_{13}$ (x=0-0.2) in an industrial eccentric vibratory mill. High-energy milling was followed by spark plasma sintering. XPS, XRD and thermoelectric methods for product characterization were applied. In all milled samples bismuth in Bi^{3+} form was identified by XPS. However, if this trivalent form belongs to bismuth in Sb site of tetrahedrite or to bismuth in Bi_2S_3 which can be formed as an intermediate remains undisclosed. XRD analysis has shown presence of chalcostibnite $CuSbS_2$, skinnerite Cu_3SbS_3, famatinite Cu_3SbS_4 and tetrahedrite $Cu_{12}Sb_4S_{13}$.

The most prominent effect of doping was a decrease in total thermal conductivity with increasing Bi content. The lowest value (1.1 W/mK at 675 K) was achieved for sample doped with 0.2 Bi content. However, this sample also manifests the lowest elctrical conductivity. Summing up with values for Seebeck coefficient, the figure of merit values show degradable effect of Bi doping on the thermoelectric properties [1]. This result is in accord with paper [2] where in contrast to our study the high temperature synthesis and higher Bi-content (x=0.2-0.8) was applied.

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ID: 04860
Type: Poster
Topic: Thermoelectric materials and materials processing

Post-treatment effects on the performance of p-type Te/PEDOT:PSS and n-type Ag2Te/PEDOT:PSS hybrid materials for thin film thermoelectrics

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Since 2010, the interest in hybrid organic/inorganic materials has seen a profound increase due to their enhanced thermoelectric (TE) performance. By combining the low thermal conductivity of organic materials with the high Seebeck coefficient and high electrical conductivity of inorganic materials, it is possible to design hybrid materials that outperform their constituents. Furthermore, it is well established that the TE performance of organic materials can be enhanced through post-treatment methods by modulating their morphological conformation and degree of oxidation. These post-treatment methods have been applied to hybrid TE materials, but surprisingly, there is a lack of systematic analysis of their impact on TE performance.

In this work, we investigate the effects of sulfuric acid, ethylene glycol, and tetrakis(dimethylamino)ethylene post-treatments on the performance of p-type Te/PEDOT:PSS and n-type Ag_2Te/PEDOT:PSS thin film hybrid TE materials. By analyzing the materials with X-ray diffraction, Raman spectroscopy, hard X-ray photoelectron spectroscopy, and Hall measurements, we are able to determine the impact that the post-treatments have on the morphological and chemical structure of the PEDOT:PSS constituent, as well as details and changes to the composition of the inorganic component. This study provides an improved understanding of the effects that post-treatments have on hybrid TE materials, which will enable further enhancement of their performance.

ID: 04999
Type: Poster
Topic: Thermoelectric materials and materials processing

Thermoelectric performance of natural and mechanochemically synthesized copper (I) selenide

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This work studied the electrical and thermoelectrical properties of copper (I) selenide Cu_2Se synthesized by laboratory high-energy milling in a planetary ball mill. Chemical and phase composition studies were carried out by X-ray diffraction analysis and scanning electron microscopy. For densification of Cu_2Se, the method of Spark Plasma Sintering was applied to prepare suitable samples for thermoelectric characterization above and below room temperature. High-temperature thermoelectric properties of synthetic Cu_2Se were interestingly compared to its natural analogue-mineral berzelianite in terms of its potential application. The measurements of low and high thermoelectric transport properties, i.e., electrical conductivity, the Seebeck coefficient, and thermal conductivity in the temperature range from 0 to 750 K were carried out. Based on these results, the temperature dependence of the thermoelectric figure of merit ZT was determined. A relatively high ZT parameter (ZT~1.32, T=740 K) for undoped Cu_2Se was obtained.

ID: 05000
Type: Poster
Topic: Thermoelectric materials and materials processing

High thermoelectric efficiency in electrodeposited silver selenide films: from Pourbaix diagram to a flexible thermoelectric module

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In the last few years, the exploration of new thermoelectric materials with low-toxicity, earth-abundance, and high-efficiency has become essential. Following this trend, sustainable, easily scalable, and cost-effective fabrication methods, such as electrochemical deposition, are also desirable. In this work, the Pourbaix diagram of silver–selenium–water was developed to find an adequate pH and reduction potential for the electrodeposition of stable silver selenide. Based on this diagram, a solution without the incorporation of additives was developed. Silver selenide films were electrodeposited at different reduction potentials, and after the deposition, the compositional, morphological, and structural characterizations of the silver selenide thin films were analysed. The thermoelectric properties of the electrodeposited silver selenide films were measured at room temperature. The maximum power factor was found for the films grown at 0.071 V with a value of 3421 ± 705 mW/·m^{-1}·K^{-2} and a thermal conductivity of 0.56 ± 0.06 W/m^{-1}·K^{-1}. Even better, when it can be done by employing a technique that

is easily scalable to an industrial level and allows large areas to be obtained, such as electrodeposition. Finally, films with similar properties were deposited on a flexible Kapton substrate. A unileg thermoelectric power generator was produced with maximum output powers of 14.7, 29.4, and 37 mW under temperature differences of 10, 15, and 19 K, respectively; and maximum power densities of 55.1, 110.1, and 138.6 mW·m^{-2} under temperature differences of 10, 15, and 19 K, respectively.

ID: 05025
Type: Poster
Topic: Thermoelectric materials and materials processing

Electrophoretic deposition of Bi2Te3 nanoparticles through electrolyte optimization and substrate design

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Assembly of thermoelectric (TE) nanostructures with pre-defined morphology and surface chemistry on solid substrates has been one of the challenges for in-plane TE devices. Electrophoretic deposition (EPD) has the potential to be used for this purpose, as it utilizes pre-made nanoparticles stabilized in a solution migrated under an electric field. For electronically active materials, a non-conductive substrate is required to benefit from the potential of the deposited films. EPD deposition has been scarcely used in the field of TEs, mostly using commercial particles in the order of 10-20 ?m.

In this work we have synthesized Bi_2Te_3 nanoparticles using microwave-assisted hydrothermal route [1], which were subsequently used for the EPD of TE films on various substrates. Glass-based substrates with special pattern design were prepared via maskless photolithography, to evaluate the electronic transport properties of the TE films without the interference of the substrate.

Synthesized Bi_2Te_3 nanoparticles possess hexagonal platelet morphology, which were used to fabricate EPD films with deposition rate reaching 10 ?m/min in an optimized media mixture. The initial EPD films are highly resistive, due to the surface oxidation and surface capping ligands. The resistance is significantly reduced by using a dithiol molecular linker which is capable of interconnecting the Bi_2Te_3 particles through ligand exchange. Seebeck coefficient in the order of 160 ?V/K, and a power factor of 422 nW/K^2m was measured on the EPD films, revealing the potential for the application of this technology to large area TE films. The progress on this activity will be presented, as a part of the on-going EU project - UncorrelaTEd [2].

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ID: 05030
Type: Poster
Topic: Thermoelectric materials and materials processing

Nano Structured PbTe and PbSe Thermoelectric Films with Reduced Thermal Conductivity and Increased Seebeck Coefficient

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Promising advances have been achieved with patterned phononic crystal nanostructures in thermoelectric materials, because the thermal conductivity is lower compared to non-patterned thermoelectric samples due to phonon-boundary scattering. In this study we report on the successful synthesis of PbTe and PbSe thermoelectric layers on patterned porous silicon templates by a thermal ALD system. PbTe/PbSe nanolaminates grown on porous silicon membranes exhibit higher Seebeck coefficients compared to non-patterned ones grown on regular planar silicon wafers. The higher Seebeck values result from the lower thermal conductivity *k* in porous structures, which in turn lead to a higher power factor and figure of merit ZT. We demonstrate the feasibility to enhance the figure of merit ZT further by modulating the size and periodicity of the pattern and the thickness of the thermoelectric film in relation to the mean free path of the phonons of the thermoelectric material. In our study PbTe and PbSe thin films and nanolaminates were synthesized by Atomic Layer Deposition (ALD) technology on regular planar silicon wafers and on macro-porous silicon templates. ALD is a surface saturating, self-limiting, conformal thin film synthesis technique reacting two pulsed precursors that enable film growth of one atomic layer per growth cycle. Lead bis(2,2,6,6-tetramethyl-3,5-heptanedionato) [$Pb(C_{11}H_{19}O_2)_2$], plus (trimethylsilyl) telluride ($(Me_3Si)_2Te$) and (trimethylsilyl) selenide ($(Me_3Si)_2Se$) were employed as the chemical ALD precursors for lead, tellurium, and selenium, respectively. The surface morphology observations indicate Volmer–Weber growth mechanism of PbTe/PbSe nanolaminates during the thermal ALD deposition process rather than classic layer-by-layer growth. The ALD PbTe/PbSe nanolaminates exhibited complete surface coverage on planar silicon substrates and inside the pores of microporous silicon membranes. For the case of porous Si templates, the Seebeck measurements in both the horizontal and vertical directions revealed significant enhancements in Seebeck coefficients for PbTe/PbSe thermoelectric nanolaminates synthesized inside nanostructured lithographically defined porous silicon templates.

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Type: Poster
Topic: Thermoelectric materials and materials processing

Low pressure chemical vapour deposition (LPCVD) of thermoelectric GeTe thin films and generators via a novel single source precurso

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With escalating energy costs and global warming, the need for efficient and sustainable energy conversion processes has never been more prevalent. With predictions claiming 72% of primary energy is lost as heat, thermoelectric generators offer a solution to reclaim a portion of this wasted energy. A potential nontoxic replacement of PbTe based thermoelectrics is germanium telluride (GeTe), owed to its highly competitive thermoelectric performance at comparatively lower operational temperatures. High quality, stoichiometric chalcogenide based thin films are often challenging to achieve *via* conventional methods such as sputtering. Previously, our group has demonstrated the development of single sources precursors (SSPs) that facilitate the LPCVD of a range of thermoelectric thin films including Bi_2Te_3, Sb_2Te_3, SnTe, etc. Apart from achieving high quality thermoelectric films, these precursors also displayed selective deposition characteristics which could lead to streamlining mass production methods.

In this work, we will present a low-cost LPCVD method for growth of GeTe films *via* a novel SSP – $Ge_nBu_3(Te_nBu)$. Stoichiometric and high quality GeTe films deposited on silica substrates will be demonstrated and characterised with a range of techniques, including SEM, EDX, XRD and Raman spectroscopy. The temperature-dependent thermoelectric measurements (i.e. Seebeck, electrical conductivity) will also be presented, demonstrating the highly-competitive performance of our GeTe films. Additionally, our CVD approach also demonstrates the capability of tuning thermoelectric performance *via* deposition conditions. By controlling the deposition temperature, the as-deposited GeTe films display significantly improved thermoelectric properties with maximum power factor of 40 ?W/K^{2}cm achieved at 629 K. Moreover, a GeTe-based lateral thermoelectric generator designed for integration into hot pipe systems tested experimentally, achieving a linear power density of 170 nW/m per device. This is also supported by FEM simulations to reveal potential linear power densities of up to 8 W/m for water-cooled hot pipes at a temperature difference of 100^{o}C.

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Topic: Thermoelectric materials and materials processing

Screen-printing of thermoelectric thin films from PbSe colloidal nanocrystals

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Thin-film thermoelectrics (TEs) with a small thickness of below 10 ?m present an increasing opportunity to power wearable electronics and the internet of things. Besides improved thermoelectric efficiency, more inexpensive materials and low-energy demand fabrication routes are needed to satisfy the current need for thin-film TEs. Here, we propose screen-printing as an easy to scale-up and industry-relevant technology to fabricate TE thin films from colloidal nanocrystal (NC) building blocks.

Monodisperse colloidal PbSe NCs with spherical morphology and size of 14 nm were synthesized by heating-up method. Next, PbSe ink was formulated, and then used for the fabrication of the TE thin films by means of screen-printing. The small size of the NCs as well as their phase composition was maintained after subsequent heat treatment at 600 ºC. The treatment is essential to remove organic matter from the screen-printed TE thin films, since carbon residues, which remain in the thin film, can reduce electron mobility within the film. Electrical properties measured at room temperature by Hall effect revealed that PbSe thin films have a bulk carrier concentration of 3.8×10^{18} cm^{-3}, electron mobility of 7.9×10^{-1} $cm^2 V^{-1} s^{-1}$ and electrical conductivity of 50 S m^{-1}. A maximum Seebeck coefficient of 561 ?V K^{-1} was obtained at 143 ºC and the highest electrical conductivity of 123 S m^{-1} was reached at 197 °C. Positive Seebeck coefficient indicates that as-fabricated PbSe thin films behave like a *p*-type material. Power factor calculations resulted in maximum of 2.47×10^{-5} W $m^{-1}K^{-2}$ at 143 °C. Since TE characterization of thin films with thickness of few microns is yet a very challenging task, different methods for measuring electrical conductivity and Seebeck coefficient were assessed and will be discussed.

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Topic: Thermoelectric materials and materials processing

Effect of powder's particle size on the thermoelectric performance of BixSb2-xTe3 alloys fabricated via melting and mechanical alloying

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The best commercial thermoelectric materials for near room-temperature applications are still bismuth telluride-based alloys. Even though $Bi_xSb_{2-x}Te_3$ is by far the most studied thermoelectric material, its ZT had remained around 1 for more than 50 years. During the past decade high ZTs have been recorded in nano-composite materials prepared using different tecniques. According to recent reported results it is worthwhile to "revisit" this material system. To this end, the aim of this work was the improvement of the thermoelectric efficiency of bismuth telluride-based materials by tuning both the microstructure and the carrier concentration.

P-type hot-pressed $Bi_xSb_{2-x}Te_3$ materials were prepared using different methods: melting and mechanical alloying. The experimental results indicate that the presence of high-density grain boundaries and interfaces in materials prepared using nano-powders and powders consisting of sub-micron and micron-sized particles (?45?m) significantly reduced the lattice thermal conductivity while the formation of antisite defects, caused by hand-grinding and ball milling, resulted in lower carrier concentrations and, therefore, in higher Seebeck coefficient values. As a consequence, a high ZT(350K) ~ 1.13 was obtained for $Bi_{0.3}Sb_{1.7}Te_3$ composition. In a second step, nano-composite $Bi_{0.3}Sb_{1.7}Te_3$ materials were prepared via mixing nano-powders and micron-sized powders in an attempt to further reduce the lattice thermal conductivity. However, the unexpected increasing trend of $?_{lattice}$ indicated the presence of significant grain boundary electrical resistance which leads to an overestimation of $?_{lattice}$ by using the conventional Wiedemann-Franz law.

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Topic: Thermoelectric materials and materials processing

Additive manufacturing of thermoelectric modules based on Fe_2 VAl Heusler compound,a feasibility study

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The digitalization of our society relies on an increased availability of electrical energy sources to power interconnected sensors, transmitters, actuators, ... Surrounding thermal energy could offer the opportunity of autonomous devices owing to thermoelectric (TE) generators. However, widespread use of such thermoelectric generators requires both the availability of materials and the efficiency of assembled modules . This study focuses on the fabrication of TE modules based on the Heusler compound owing to Laser Powder Bed Fusion (L-PBF) manufacturing. This process allows obtaining complex and topologically optimized parts while limiting the assembly steps, bringing a significant advantage.

In order to optimize the process parameters window, a "bottom-up" strategy was developed consisting in building successively 1D (single tracks), 2D and finally 3D objects. The relationship between defects (density, cracks, …), manufacturing parameters and resulting thermoelectric properties was scrutinized. Properties of best samples densified by L-PBF have then been compared to samples processed by conventional methods.

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Topic: Thermoelectric materials and materials processing

Flexible n-type abundant chalcopyrite/ PEDOT:PSS /graphene hybrid film for thermoelectric device utilizing low grade heat

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Thermoelectric (TE) materials that can stably and directly convert ubiquitous heat or industrial waste heat into electric energy have become a hot topic in recent decades, especially now for their applicable potential in flexible TE (FTE) devices that can present conformal interactions with heat sources to maximize heat harvesting. Combining inorganic TE materials with conductive polymers (CPs) is one promising strategy to develop FTE films and devices. So far, PEDOT:PSS has been widely studied as the polymer matrix in FTE composites due to its promising characteristics. However, most inorganic materials used in the composites have main constituents of the scarce Te or toxic Se element, and/or expensive Ag element. Moreover, the most reported CP-related composites are mainly *p*-type while their *n*-type counterpart is still lacking. For the completion of a flexible TE module, *n*-type flexible composites are particularly desired. One compelling TE inorganic material, Zn-doped $CuFeS_2$ which is composed of very cheap and abundant elements in the earth crust, and is a stable material, has been widely studied as a potential *n*-type TE material. Accordingly, instead of aiming for just high performance but for *n*-type FTE films, the fundamental study was developed that combining the Zn-doped $CuFeS_2$ with a flexible electrical network constituted by PEDOT:PSS and graphene on a flexible substrate. The flexibility of $Cu_{0.98}Zn_{0.02}FeS_2$/PEDOT:PSS/graphene films and a five-leg TE module made of optimum flexible films will be presented. The thermoelectric inorganic materials with high performance were also hybrized and will be presented.

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Type: Poster
Topic: Thermoelectric materials and materials processing

Flexible Bi2Te3 Films on Polymer Sheets Prepared by the Powder Aerosol Deposition Method at Room Temperature

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The development of flexible thermoelectric generators (TEG), especially for near-body applications, has become increasingly important. However, it is challenging to produce them because flexible substrates such as polymers are temperature-sensitive and efficient thermoelectric materials such as Bi_2Te_3 usually require high temperature manufacturing steps.

With the powder aerosol deposition (PAD), we present a spray-coating process that allows the fabrication of dense metallic or ceramic films at room temperature. The films are produced directly from the starting powder without a thermal treatment. The PAD can be used to coat ceramic, glass, metallic, as well as temperature-sensitive polymer substrates.

In our contribution, we report on the fabrication of flexible Bi_2Te_3 films on polymer substrates using the PAD. The films were prepared using commercially available 99.9% Bi_2Te_3 and subsequently thermoelectrically characterized. In order to evaluate the flexibility of the films (width 10 mm, length 25 mm, thickness 10 ± 5 µm), the thermoelectric characterization is carried out both in the non-bent and in the bent state, the latter down to a radius of 10 mm. The Seebeck coefficient remains unaffected by both the number of bends and the bending radius in all measurements. In contrary, the electrical conductivity slightly decreases with decreasing radius. However, the conductivity partially recovers after measuring in the non-bent state again. A possible explanation therefore could be the nanocrystalline morphology, a typical PAD feature, which may lead to small microcracks during bending, which subsequently recover after bending in the planar state.

Overall, it can be summarized that the PAD offers enormous potential for the further development of rigid or flexible TEGs.

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Type: Poster
Topic: Thermoelectric materials and materials processing

Thermoelectric enhancement in composite half Heusler (hH): TiNbFeCoSb2

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Inspired by the recent advancement in the high entropy / composite half Heusler (hH), we have tried to design a new hH composite by mixing two 18 Valance electron Count (VEC) hHs, NbFeSb and TiCoSb. The intrinsic properties of NbFeSb and TiCoSb are known to be p-type and n-type respectively. This gives an advantage of having tunable p-type or n-type properties. Our first-principle electronic structure calculation shows the bandgap of the composite lies in between that of NbFeSb and TiCoSb. We have used the Simple Quasi-random Structure (SQS) method to generate the structure. Transport properties calculation indicates many folds enhancement in the power factor (PF) at a certain doping percentage of electrons and holes. With computed results at hand, we synthesized $Ti_{1+y}Nb_{1-y}Fe_{1+x}Co_{1-x}Sb_2$ with x and y having values between ± 0.2. All the synthesized compositions were found to be stable at room temperature and above. Samples with excess Co/Nb (x,y < 0) showed n-type properties having maximum Seebeck of -244 ?VK^{-1} and PF of 22 ?$Wcm^{-1}K^{-2}$ at 1073 K for $Ti_{0.9}Nb_{1.1}Fe_{0.85}Co_{1.15}Sb_2$, whereas maximum Seebeck of 170 ?VK^{-1} is recorded for p-type sample. The thermal conductivity is significantly suppressed compared to the individual hHs. HRTEM imaging shows the presence of dislocation and lattice distortion, which contributes to the low thermal conductivity. A very limited number of high entropy/composites have been reported so far in hH. Having low thermal conductivity along with carrier tunability and thermal stability up to very high temperatures makes these classes of materials interesting as potential thermoelectrics for mid-to-high temperature range applications.

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Type: Indiferrent
Topic: Thermoelectric materials and materials processing

Impact of side-chain length on the thermoelectric and mechanical properties of oligoether-substituted polythiophenes

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Organic materials are appealing for the design of flexible, easily processable and inexpensive thermoelectric generators (TEGs) that can convert waste heat into electricity. Polythiophenes with oligoethylene glycol side chains are promising candidates for the design of TEGs due to their improved processability, good compatibility with common p-type molecular dopants and low elastic modulus. In this work, the impact of the side-chain length on the thermoelectric properties is explored. Structure-property relationships are elucidated and the ionization efficiency and mechanical properties of undoped and doped polymers are discussed. The role of the polymer nanostructure and anisotropy in tuning thermoelectrical performance, i.e. decoupling of the electrical conductivity and Seebeck coefficient, is studied by orienting the polymers through different processing techniques.

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Type: Poster
Topic: Thermoelectric materials and materials processing

Implementing porosity in n-type polymer hybrid aerogels for promising thermoelectric efficiency

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Current research trends in organic thermoelectricity mainly focuses on polymer materials that are developed as thin films. However, maintaining a stable temperature gradient is rather difficult in such thin films due to lack of control over thermal conductivity. Here, we present an alternative architecture to develop these materials as aerogels that present superior control over thermal conductivity (?) by phonon engineering via modulating the lattice component of thermal conductivity ($?_L$) [1].

Recent research progress has drawn the attention to TE property of metal coordination polymer Poly(M-ett) (M = metal, ett = ethylenetetrathiolate), which provides the best performance of n-type organic thermoelectric materials. These materials display good electronic features and exhibit excellent stability in air as their backbone structure is composed of air-stable ligands [2]. However, their only limitation stands in its low solubility restraining their processability either in the form of pristine pellets or hybrid films blended with other polymers [3].

Herein, we demonstrate a well-defined methodology to design and fabricate novel n-type polymer hybrid aerogels of scalable mm thickness. These ultra-light weight hybrid materials were characterized by a multiscale-correlative approach using electron microscopy and spectroscopy techniques to elucidate the microstructure and dispersibility of poly(M-ett) fillers in a porous matrix. The thermal transport property of the hybrid aerogel was investigated using the Transient Plane Source method, and these aerogels exhibit ? below 0.05 W/m K. An aerogel that exhibit superior thermoelectric features as compared to hybrid films but also pure poly(M-ett) pellet was developed.

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Topic: Thermoelectric materials and materials processing

Aikinite systems: ultra-low thermal conductivity for thermoelectric applications

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For the widespread implementation of thermoelectric (TE) energy recovery, it is important to identify tellurium-free materials with good TE performance. In this context, sulfide minerals such as tetrahedrites and colusites are attracting much interest. Here, we present work on the mineral aikinite, $CuPbBiS_3$, which adopts a structure closely related to that of Bi_2S_3, which itself exhibits promising TE properties. While Bi_2S_3 contains Bi_4S_6 ribbons in a herringbone pattern, in aikinite, half of the Bi^{3+} cations are replaced with Pb^{2+} and the Cu^{+} cations fill the tetrahedral holes between the $Bi_2Pb_2S_6$ ribbons.

Aikinite samples were prepared by mechanical alloying followed by heat treatment. Rietveld refinement of powder neutron diffraction data, collected on POWGEN (SNS, ORNL), indicate that the isoelectronic Pb^{2+} and Bi^{3+} cations are fully ordered. Moreover, Cu^{+} and Pb^{2+} have larger atomic displacement parameters than Bi^{3+}. The thermal conductivity, measured on hot-pressed pellets, exhibits a remarkably low value of ca. 0.54 W $m^{-1}K^{-1}$ at room temperature. The calculated vibrational density of states exhibits Einstein-like phonon modes at 100 cm^{-1}, attributed to Cu^{+} vibrations, and low-frequency optical phonon modes below 50 cm^{-1} (at ~ 4.5 meV), arising from Pb^{2+} vibrations. The experimentally-determined vibrational phonon density of states is in very good agreement with calculations. Inelastic neutron scattering data, collected on LET (ISIS), confirms the presence of low-energy vibrational modes (~ 4 meV), which are likely to be responsible for the ultralow thermal conductivity. The temperature dependence of the low-energy Pb^{2+} vibrational mode is consistent with anharmonic behaviour, while the Cu^{+} Einstein-like mode softens markedly with increasing temperature. Preliminary doping studies of p-type akinite demonstrate that the Cl-doping results in n-type behaviour, and that halide doping increases the electrical conductivity while further reducing the total thermal conductivity.

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Topic: Thermoelectric materials and materials processing

Understanding Oxidation Kinetics of RE3-xTe4 for Improved Corrosion Resistance

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$La_{3-x}Te_4$ is state-of-the-art n-type, high temperature thermoelectric (TE) material with ZT of 1.1 at 1275K and is currently being developed at JPL for potential use in radioisotope thermoelectric generators. Despite its high TE performance, it is sensitive to oxidation, which can deteriorate the TE properties over time. In order to better understand oxidation mechanisms in this $La_{3-x}Te_4$, we investigated the relationship between rare-earth (RE) doping on the La site and oxidation sensitivity. We prepared dense, fully occupied RE_3Te_4 and vacancy-rich $RE_{3-x}Te_4$ analogs of which RE= La, Pr, Nd. Isothermal thermogravimetric measurements were conducted under controlled oxidative environments to compare the oxidation kinetics of the materials at high temperature. Grazing incident X-ray diffraction (GIXRD) and X-ray Photoemission Spectroscopy (XPS) were utilized to characterize oxidation products and depth of the oxidation scale. Preliminary results on the oxidation resistance and kinetics of oxidation of the analog materials and as well as the development of potential protective coatings will be presented and discussed.

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Topic: Thermoelectric materials and materials processing

Investigation of anharmonicity of lattice vibration using Grüneisen parameter in BiCh2-based compounds

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The Grüneisen parameter ($?_G$) [1] is a parameter related to lattice anharmonicity. In this study, we investigated anharmonicity in a layered $BiCh_2$ (Ch: chalcogen) thermoelectric system $LaOBiS_{2-x}Se_x$. In previous work on inelastic neutron scattering [2], the enhancement of anharmonicity (lowering of phonon energy of Bi-rattling mode) by Se substitution was revealed. The Se concentration depended on $?_G$ for the system exhibited a trend similar to that of the Bi-rattling phonon energy. Therefore, we propose that the estimation of $?_G$ is useful for discussing lattice anharmonicity in $BiCh_2$-based layered thermoelectric materials. In the presentation, we will also show the results of the relationship between thermoelectric properties, physical properties, and anharmonicity in various $BiCh_2$-based compounds including high-entropy-alloy-type systems [4].

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Topic: Thermoelectric materials and materials processing

Synthesis and transport properties of the chalcogenide semiconductor Bi2Te2Se

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The state-of-the-art thermoelectric compound Bi_2Te_3 has been widely studied over the last few decades and recently revisited for its non-trivial topological character [1,2]. Attempts to enhance its thermoelectric properties through the introduction of a resonant level showed that Sn distorts the valence bands of Bi_2Te_3, leading to increased thermopower values [3]. The ternary derivative Bi_2Te_2Se has raised interest for its topologically-protected surface states and bulk insulating properties [4,5]. Thanks to the introduction of carefully chosen dopants, density functional theory calculations highlighted the opportunity to create such a resonant level in this compound, thereby inducing optimized transport properties near room temperature [6]. However, no detailed study of its thermoelectric properties and on the influence of various dopants has been undertaken so far.

In this communication, we will present the synthesis of polycrystalline samples of Bi_2Te_2Se doped with acceptor-like impurities. The samples were synthetized by using a conventional powder metallurgy route in sealed silica tubes followed by spark plasma sintering. Structural and chemical analyses were performed to assess the phase purity and chemical homogeneity. The transport properties were measured over a wide range of temperatures (2 - 700 K), both parallel and perpendicular to the pressing direction, in order to assess the influence of the selected impurities. High *ZT* values of up to 0.7 K near room temperature were achieved.

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Topic: Thermoelectric materials and materials processing

Achieving both p-type and n-type of thermoelectric performance in Zr2FeNiSb2 double half-heusler compounds

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The half-Heusler (hH) compounds are promising thermoelectric (TE) materials owing to their high power factor (PF) and good mechanical-thermal stability in mid-to-high temperature applications. However, an inherently large lattice thermal conductivity is observed in these simple crystal structures of ternary half-Heusler alloys, thus limiting their usage. Therefore, the concept of double half-Heusler (DhH) was introduced. The complex site occupancy in the DhH structure helps decrease the thermal conductivity and reduces the electronic transport properties. Thus, a need arises to optimize to achieve both high PF and high figure of merit (zT) in these DhH compounds. Doping or minor alloying is an effective way to simultaneously improve electronic and transport properties by introducing point defects in these compounds.

$Zr_2FeNiSb_2$ is the quaternary DhH compound with a valency electron count (VEC) of 18, comprising two aliovalent ternary hH compounds ZrFeSb (VEC: 17) and ZrNiSb (VEC: 19). The Seebeck coefficient (S) of this material exhibits bipolar behavior. Initially, the system exhibits p-type behavior and reverses the sign of S at ~ 888K.

The minor alloying of respective aliovalent elements at Zr and Sb sites suppresses the bipolar conduction in the $Zr_2FeNiSb_2$ compound. The Nb addition at the Zr site and Sn addition at the Sb site helps achieve a high Seebeck coefficient; n-type (~ -105 µV/K at T_{max} = 673 K) and p-type (~ 187 µV/K at T_{max} = 673 K), respectively. Hence, $Zr_2FeNiSb_2$ can be attractive for fabricating p-type and n-type legs of a thermoelectric device for power generation applications. The structure-property correlation for these systems is further studied in detail.

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Topic: Thermoelectric materials and materials processing

Thermoelectric Performance of n-Type Magnetic Element Doped Bi2S3

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Thermoelectric technology offers exciting potential for converting waste heat into electrical energy and is an emission-free technique for solid-state

cooling. Several methods have been used to increase the efficiency of thermoelectric materials including nanoprecipitation, modulation doping, nanostructured grain boundaries, and ionized impurities. In recent years, however, the emergence of research on spintronics and

magnetic effects on semiconductors has shown a new path to achieve higher efficiency materials by demonstrating that the presence of magnetic interactions on the material effectively drags the carriers and increase their effective mass. Here, we show the effects of a

magnetic element co-doping in Bi_2S_3. Achieving high efficiency in Bi_2S_3 is challenging due to its high electrical resistivity that reduces its power factor. Decreasing the electrical resistivity while maintaining a high Seebeck coefficient is key for improving its performance. In this work,

Bi_2S_3 was co-doped with Cr and Cl. An enhanced conductivity was achieved due to an increase in the carrier concentration by the substitution of S^{2-} with Cl^-. High values of the Seebeck coefficients were obtained despite high carrier concentrations; this is attributed to

an increase in the effective mass, resulting from the magnetic drag introduced by the magnetic covalent Cr dopant. A peak power factor of 566 ?W m?1 K?2 was obtained for $Bi_{2-x/3}Cr_{x/3}S_{3-x}Cl_x$ with x = 0.01 at 320 K. These effects resulted in a maximum zT of ~0.3 at 480

K, which is comparable to the highest values reported in literature at the same temperature. These results support the success of co-doping thermoelectric materials with magnetic and carrier concentration tuning elements to enhance the thermoelectric properties.

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Topic: Thermoelectric materials and materials processing

A novel method of obtaining bulk PbTe-CdTe nanocomposite

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Semiconductor composites are the practical implementation of the idea of nanostructuring, which is one of the promising strategies to increase the thermoelectric efficiency of known materials. In this work we describe the preparation method of bulk PbTe-CdTe semiconductor nanocomposite intended for thermoelectric generators working at mid temperature conditions. The method utilizes the extremely low mutual solubility of both semiconductors and is based on novel combination of the modified Bridgman growth method with proper preparation of constituent substances. While the method of obtaining an ordered low-dimensional PbTe-CdTe layered nanocomposite using the molecular beam epitaxy technique has already been successfully researched in the context of thermoelectric applications [1], there is little study on this type of composite in the form of bulk samples with high figure of merit parameter ZT [2]. In these studies, the formation of the composite is the result of the unintentional formation of CdTe precipitates in PbTe as a result of attempts to prepare Pb1-xCdxTe solid solution with a high Cd content. In our proposal, we deliberately use the tendency to segregate CdTe into PbTe. Of particular importance to presented novel method is the ability to introducing CdTe into the PbTe matrix in the form of uniformly distributed CdTe crystallites and the control of the amount of Cd into the PbTe crystal lattice. Moreover, the discussed growth procedure can be easily implemented in the industry as it is based on the basic material properties and requires non-advanced equipment.

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Type: Poster
Topic: Thermoelectric materials and materials processing

Textile thermoelectric generators based on carbon nanototubes and PEDOT bilayers

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Textile is indispensable for human life. Keeping apart its primary role to cover and protect the human body, it can contribute to produce energy as wearable thermoelectric (TE) for body heat conversion. In comparison to conventional rigid inorganic thermoelectrics conjugated/organic thermoelectric materials display many advantages for usage in thermoelectric generators. Organic textile thermoelectric materials/generators (T-TEG) can be prepared by in-situ polymerization of the conjugated polymers utilising textile substrates. Electrochemical polymerization has result to be a very promising method for coating fabrics with conducting polymers. However, a conductive fabric is needed as working electrode.

In this work, acrylic fabrics have been coating with carbon nanotubes (CNT) by layer-by-layer (LBL) method. Different bilayers made with positive and negatively charged surfactant modified CNTs have been used to turn conductive the fabrics. Afterwards, electrochemical deposition of PEDOT in presence of different counter ions has coated the CNT modified fabric with the conductive polymer. There is a good scope of improving thermoelectric efficiency of textiles like controlling morphology, improving crystallinity and molecular orientation of the polymer, doping and dedoping, suitable post-treatment, using a heat spreader, etc. The surface of the textile substrates has been optimally coated given place to a hybrid TE material with optimal electrical conductivity and Seebeck coefficient and low thermal conductivity. A thermoelectric device has been constructed with a maximum output power of 6 mW.

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Topic: Thermoelectric materials and materials processing

3D flexible nanostructured thermoelectric devices grown by scalable techniques

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In order to reduce the complexity of developing nanostructured thermoelectric materials, and thus, obtain enhanced properties for applications, we report the template-assisted electrochemical deposition of bismuth telluride inside commercial membranes. The objective is to develop efficient, cost-effective, flexible and wearable thermoelectric generators (TEGs) by the use of low cost and scalable fabrication techniques along with a reduction in the amount of material used when compared to thin films.

The use of different nanoporous membranes gives rise to different nanostructured morphologies, given that the electrochemical process produces a replica of the initial porous structure. Here we will fabricate thermoelectric 3D nanostructures inside flexible templates (made of polyester and cellulose) by electrochemical deposition as it has been previously done inside alumina templates [A. Ruiz-Clavijo., O. Caballero-Calero, M. Martín-González, Nanomaterials, 8 (2018) 345]. The morphology has been studied with SEM and Tomography, the crystalline orientation with XRD, the composition with EDX, and also Raman spectroscopy has been used to characterize the structures. Then, different transport measurements have been carried on. In fact, a certain increase is expected, as it was proved in [A. Ruiz-Clavijo., O. Caballero-Calero, C. V. Manzano, X. Maeder, A. Beardo, X. Cartoixa?, X. Álvarez, M. Martín-González, ACS Applied Energy Materials, 4 (2021). 13556-13566] for 3D interconnected nanowire networks of bismuth telluride inside alumina. In that paper we showed the importance of increasing surface to volume ratio, as well as the relevance of nano-features in the structure, in order to improve the efficiency. In this case, the nanostructure is not as ordered as 3D nanowire network, but similar features are present, and they should have an impact in the final efficiency. Finally, further metallic contacts made of electrodeposited gold and/or nickel will be also fabricated in order to improve their electrical contacts and test such nanostructures as thermoelectric generators.

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Topic: Thermoelectric materials and materials processing

A Tunable Structural Family with Ultralow Thermal Conductivity: Copper-Deficient Cu1–x?xPb1–xBi1+xS3

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Understanding the mechanism that connects heat transport with crystal structures and order/disorder phenomena is crucial to develop materials with ultralow thermal conductivity (?), for thermoelectric and thermal barrier applications, and requires the study of highly pure materials. We synthesized the n-type sulfide $CuPbBi_5S_9$ with an ultralow ? value of 0.6–0.4 W m^{-1} K^{-1} in the temperature range 300–700 K.[1] In contrast to prior studies, we show that this synthetic sulfide does not exhibit the ordered gladite mineral structure but instead forms a copper-deficient disordered aikinite structure with partial Pb replacement by Bi, according to the chemical formula $Cu_{1/3}â–¡_{2/3}Pb_{1/3}Bi_{5/3}S_3$.[1] By combining experiments and lattice dynamics calculations, we elucidated that the ultralow ? value of this compound is due to very low energy optical modes associated with Pb and Bi ions and, to a smaller extent, Cu. This vibrational complexity at low energy hints at substantial anharmonic effects that contribute to enhance phonon scattering. Importantly, we show that this aikinite-type sulfide, despite being a poor semiconductor, is a potential matrix for designing novel, efficient n-type thermoelectric compounds with ultralow ? values.[1] A drastic improvement in the carrier concentration and thermoelectric figure of merit have been obtained upon Cl for S and Bi for Pb substitution. The $Cu_{1–x}□_xPb_{1–x}Bi_{1+x}S_3$ series provides a new, interesting structural prototype for engineering n-type thermoelectric sulfides by controlling disorder and optimizing doping.

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Topic: Thermoelectric materials and materials processing

Thermopower enhancement driven by resonant states in semiconducting Fe2VAlx

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Exploring the Al-rich part of the Fe_2VAl_x full-Heusler phase, we find full solubility of Al up to Fe_2VAl_2. The enhanced thermoelectric properties of the Al-overdoped compounds are linked to the rise of resonant states and additionally a band-gap opening by the following experimental and theoretical results: Transport properties, measured in a wide temperature range from 4-800 K, indicate significant modifications of the electronic structure for the Al-rich full-Heusler compounds as the thermopower steadily increases up to $Fe_2VAl_{1.5}$. For undoped $Fe_2VAl_{1.5}$, we find an increase of the thermopower by nearly 50 % compared to all *p*-type Fe_2VAl-based compounds measured so far, leading to PF~2 mW/mK^2. Furthermore, the introduction of Fe/Al and V/Al antisites into the crystal lattice leads to a significant reduction of the thermal conductivity. We analyze the transport properties by modelling their temperature dependence using appropriate models and state-of-the-art density functional theory (DFT) calculations. Using the coherent-potential approximation, DFT calculations reveal resonant states arising close to the Fermi level due to Al antisites as a possible explanation for the high thermopower. This is also consistent with disordered supercell calculations performed using the *Vienna ab initio Simulation package*. Moreover, effective band structure calculations show a significant band-gap opening for the disordered compounds consistent with the results from our transport modelling. These findings therefore drastically extend the phase space of Fe-V-Al-based semiconducting Heusler compounds and pose a powerful starting point for future thermoelectric enhancement in this material class.

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Topic: Thermoelectric materials and materials processing

Solvothermal synthesis of Cu-rich tetrahedrite - phase analysis and thermoelectric properties

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Tetrahedrites are promising thermoelectric materials because of their considerable Seebeck coefficient, low thermal conductivity and earth-abundant nature of components. Obtained DFT calculations results show that the additional copper atoms in Cu-rich $Cu_{14}Sb_4S_{13}$ tetrahedrite effectively engineer the chemical potential towards high thermoelectric performance. In this paper the Cu-rich tetrahedrite phase was prepared using a novel approach. A solvothermal method with piperazine serving both as solvent and reagent was used. The presented method allows us to avoid the typically observed inorganic salts contaminations in products, as only pure elements were used for the synthesis. Prepared in such a way $Cu_{14}Sb_4S_{13}$ tetrahedrite materials possess a very high Seebeck coefficient (above 400 ?VK^{-1}) and low thermal conductivity (below 0.3 $Wm^{-1}K^{-1}$) yielding to an excellent dimensionless thermoelectric figure of merit *ZT* ? 0.65 at 723 K. The further enhancement of the thermoelectric performance is expected after attuning the carrier concentration to the optimal value for achieving the highest possible power factor in this system.

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Topic: Thermoelectric materials and materials processing

Synthesis and characterization of n-type TaCoSn half-Heusler compound

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In this work, an experimental and computational combined study of the TaCoSn Half Heusler compound was performed.

Elemental powders of Ta, Co and Sn were mechanically alloyed. As milling proceeded, crystallographic reflections disappeared leaving place to a broad halo, indicating the progressive amorphization of the powders. The DSC trace of the as milled powders showed an exothermic peak around 540 °C related to the crystallization of the amorphous phase into a crystalline phase with Half Heusler structure. After crystallization, an endothermic peak around 860 °C revealed the decomposition of the half Heusler phase into CoTa and Sn (liquid) through a peritectic reaction.

Bulk samples for thermoelectric characterization were obtained by consolidation of amorphous powders using Open Die Pressing (ODP) and Spark Plasma Sintering (SPS). When consolidation was performed below the peritectic temperature, both ODP and SPS samples showed a single phase and relative density around 75%. When SPS consolidation was performed above the peritectic temperature (e.g. 875 °C), a larger relative density (~ 85%) was achieved thanks to the reaction involving liquid Sn. In this case, the as sintered sample contained a relevant amount of secondary phases due to the incomplete peritectic reaction upon cooling. Thus, annealing below the peritectic temperature (e.g. 850 °C) was needed to return the sample into the equilibrium single phase region.

The experimental thermoelectric properties, showing a semiconducting behaviour of the electrical conductivity and n-type behaviour of the Seebeck coefficient, were discussed on the basis of the structural and microstructural features of the sintered samples. The measured transport properties were compared with the computed ones and the role of point defect was discussed.

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Topic: Thermoelectric materials and materials processing

Ultralow lattice thermal conductivity in filled ?-manganese-type phases: role of lone-pair-like interaction and bonding inhomogeneity

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Finding the way to interlink heat transport with crystal structure and order/disorder phenomena is crucial for designing materials with ultralow lattice thermal conductivity. Here, we revisited the crystal structure and explored the thermoelectric properties of several compounds from the family of the filled ?-Mn-type phases $M_{2/n^{n+}}Ga_6Te_{10}$ (*M* = Pb, Sn, Ca, Na, Na+Ag). The strongly disturbed thermal transport observed in the investigated materials originates from a three-dimensional Te-Ga network with lone-pair-like interactions, which results in the large variations of the Ga-Te and *M*-Te interatomic distances and substantial anharmonic effects. In the particular case of $NaAgGa_6Te_{10}$, additional presence of different cations, leads to bonding inhomogeneity and strong structural disorder resulting in the dramatically low lattice thermal conductivity (~0.25 $Wm^{-1}K^{-1}$ at 298 K), being the lowest among reported ?-Mn-type phases. This study offers a way to develop materials with ultralow lattice thermal conductivity by considering bonding inhomogeneity and lone-pair-like interactions.

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Topic: Thermoelectric materials and materials processing

Direct current stability of composites with copper chalcogenides under application conditions

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Copper chalcogenides, particularly $Cu_{1.97}S$ and Cu_2Se, are of great interest as thermoelectric materials due to the abundance of elements they contain and, in the case of the sulfide, their low toxicity compared to more established materials like PbTe.[1] Copper chalcogenides are high zT thermoelectric materials, but they have a major drawback: electrolysis occurs under direct current at a critical voltage specific to each material.[2] Since this decomposition is irreversible, the maximum power is limited for both power generation and Peltier cooling . To increase the critical voltage, one concept is to distribute the applied voltage over multiple segments by separating them with carbon.[3]

This concept can be applied to structured composites composed of copper chalcogenide microparticles coated with a secondary phase. In order to evaluate this hypothesis, two model systems were studied: one in which microparticles of Cu_2Se were mixed with graphite flakes, and one consisting of microparticles that reacted with iodine to form CuI on their surface. These composites have been characterized in terms of their performance and critical voltage. The graphite containing composites show similar thermoelectric performance and critical voltages as pristine materials, probably due to conduction paths. The composites containing copper iodine show inferior thermoelectric performance and decreased critical voltage with increased proportion of CuI in the composites.

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Type: Indiferrent
Topic: Thermoelectric materials and materials processing

Effect of Annealing on Structural and Thermoelectric Properties of Electrodeposited Ternary CuSbTe Thin Films

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Green and sustainable energy harvesting has become a vital technological drive over the past few decades. Thermoelectric energy harvesting provides a promising roadmap in finding the new energy solutions to overwhelming future energy demand and related environmental issues. Antimony Telluride (SbTe) is a well-known room temperature thermoelectric material. Particularly, doped SbTe alloy shows interesting thermoelectric transport properties, especially after thermal treatment at elevated temperatures. In this work, the effect of annealing (100 – 300 °C) on the ternary CuSbTe thin films in terms of their thermal and electric transport properties has been investigated. These electrodeposited films have different Cu concentrations in the range of 3 to 16 at.% (0.2 – 1 mM). The phase formation and valence state of Cu in the alloy has been investigated by X-ray diffraction and photoemission spectroscopy techniques. With increasing Cu concentration, the films become smooth and dense as compared to pure SbTe. The as-deposited CuSbTe films exhibit n-type behaviour at room temperature. After annealing at 150 °C and beyond, the charge carrier switching occurs and all the ternary alloy films become p-type. The CuSbTe shows an enhanced electrical conductivity for all the Cu concentrations when compared to SbTe. It appears that, before annealing Cu act as an electron donor and becomes an acceptor after thermal treatment. A maximum Seebeck coefficient of 42.5 μV/K and a power factor of 80 μW/mK^2 is observed for 9.84 at.% Cu doped SbTe film. This study concludes that annealing directly influences the crystalline structure of ternary CuSbTe alloy and can be a potential p-type material for thermoelectric energy generators at room temperature.

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Topic: Thermoelectric materials and materials processing

Conductive polymer with inorganic particles as elastic thermoelectric composite materials

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In recent years, development of portable and wearable electronic devices has increased. Compared to traditional batteries, thermoelectric generators which can convert body heat to useful electricity have drawn wide attention as energy-harvesting technology for wearable electronics. Polymer-based thermoelectric materials are particularly interesting to wearable devices due to their good flexibility, low density, easy processability and low toxicity. Furthermore, the transport properties of the thermoelectric polymers can be effectively modified by mixing the polymer matrix with the inorganic additives. Such composites usually demonstrate even better thermoelectric performance compared to the initial components. The improvement is mainly coming from the enhanced electric charge transport between the polymer and inorganic phase domains induced by inorganic particles.

The work aims to investigate the structural and thermoelectric properties of the conductive polymers (e.g. PEDOT:PSS) composites with the addition of inorganic particles (e.g. $Cu_{14}Sb_4S_{13,}$ Bi_2Te_3, PbTe, $SnGa_6Te$). Inorganic additives used for composites were characterized in terms of particle size distribution. All samples were prepared a with different inorganic particles volume content (25%, 50% and 75%) as films on glass and silicon substrates. The obtained samples were examined in terms of the highest ZT parameter by measured Seebeck coefficient, electrical and thermal conductivity. SEM was used to investigate the microstructure and to estimate the thickness of the films. It was found, that the tested properties changed with the weight fraction of inorganic particles and depended on the added inorganic phase. The performed tests confirmed that the examined composites are promising components to be used as elastic thermoelectric materials for wearable devices.

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Topic: Thermoelectric materials and materials processing

Enhancedthermoelectric performance of chalcogenide by band structure modification using Halide dping

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Over the past few decades, semiconducting chalcogenides compounds (A_2B_3 with A = Sb, Bi, As and B = S, Se, Te) received lot of attentions for thermoelectric applications. Among these chalcogenides sulphides-based (Bi_2S_3, $Cu_{2-x}S$, CdS, TiS_2, Ag_2S etc.) compounds have the advantage of having low cost, low toxic, more abundant elements. However their ZT values need to be improved. Various strategies such as doping have been used for improving its TE performance. Here we report the synthesis and thermoelectric properties of SPSed Bi_2S_3 and enhanced its performance by using x-mole% of $CuCl_2$ and x-mole% $CaCl_2$ as dopant. Powder in stoichiometric compositions were mixed and synthesised by melt and grow process inside a quartz evacuated tube. The as synthesised ingot were grounded and sintered by SPS. XRD of all samples shows single phase formation. All the compositions show a negative Seebeck coefficient suggesting n-type behaviour. The increasing dopant concentration leads to the improvement in its electrical property and after an optimised value it decreases. As a result a higher power factor ~2000 ?W/m-K^2 for $CuCl_2$ as dopant and ~1600 ?W/m-K^2 for $CaCl_2$ is obtained. ZT values greater than 1 was achieved in these halide doped chalcogenides. Further electron transport and heat transport mechanisms have been evaluated in co-relation with FESEM, XPS and TEM.

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Topic: Thermoelectric materials and materials processing

Synthesis and characterization of flexibe thermoelectric Bi2Se3/CNT hybrid structures

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Flexible thermoelectric materials are one of the most promising materials for powering future wearable electronics, offering a great thermal contact with curved surfaces as well as a much higher variety in the possible geometric configurations of the thermoelectric elements. Nevertheless, the low chemical stability of n-type conductive polymers is a major disadvantage for the further development of polymer-based flexible thermoelectrics. [1]

In this work we developed an original technique for preparing flexible n-type thermoelectric nanocomposites by encapsulating networks Bi_2Se_3-CNT hybrid structures. [2] Hybrid networks of Bi_2Se_3 and carbon nanotubes (CNTs) were used as a thermoelectrically active material. The properties of such thermoelectric hybrid networks have recently attracted the attention of many researchers worldwide. [3]

Bi_2Se_3 nanostructures were synthesized on CNT networks via a catalyst-free vapour-solid deposition technique. [4] The obtained networks Bi_2Se_3/CNT hybrid structures were encapsulated in non-conductive polyvinyl alcohol (PVOH) polymer matrices. The morphology and chemical composition of the obtained hybdrid structures and nanocomposites were analysed by using scanning electron microscopy and energy dispersive X-ray analysis. Thermoelectric and electric properties, as well as the mechanical stability of the flexible nanocomposites, were characterized by using a laboratory-made experiment setup and a physical property measurement system. Possible applications in flexible thermoelectric generators are discussed

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Type: Poster
Topic: Thermoelectric materials and materials processing

Enhanced thermoelectric performance of Bi0.3Sb1.7Te3.0+x milled with yttria-stabilized zirconia balls and vessels

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Many researchers have focused on improving the thermoelectric properties of bismuth antimony telluride BiSbTe materials. We focused on the effects of the milling media materials on the thermoelectric properties of undoped $Bi_{0.3}Sb_{1.7}Te_{3.0}$. We found that yttria-stabilized zirconia ceramic (YSZ) milling was superior to metal milling [M. Bumrungpon et al. *Ceram. Int.* 46 (2020) 13869?13876]. In present study, $Bi_{0.3}Sb_{1.7}Te_{3.0+x}$ (x = 0?0.05) was fabricated by mechanical alloying using YSZ balls and vessels, followed by hot pressing. The effects of the added tellurium on the thermoelectric properties of $Bi_{0.3}Sb_{1.7}Te_{3.0}$ fabricated with YSZ milling media were investigated. All sintered samples were dense and showed *p*-type conduction, with a grain size of approximately 1 ?m. X-ray diffraction (XRD) indicated a single-phase Bi_2Te_3-Sb_2Te_3 solid-solution that was isotropic. On the other hand, differential thermal analysis (DTA) of the x = 0.05 sample showed tellurium precipitation and formation of a Bi_2Te_3-Te solid-solution. The tellurium solid-solubility limit for $Bi_{0.3}Sb_{1.7}Te_{3.0}$ was determined to be x = 0.01. The solid-solubility limit of the sample fabricated using YSZ was narrower than that of the congener prepared with Si_3N_4 balls and stainless-steel vessels. Among the evaluated compositions, the $Bi_{0.3}Sb_{1.7}Te_{3.01}$ sintered disk had the highest dimensionless figure of merit, ZT = 1.30 ($?$ = 227 ?V $K^{?1}$, $?$ = 9.81 × 10^4 S $m^{?1}$, $?$ = 1.17 W $m^{?1}$ $K^{?1}$), at room temperature. This value was superior to that of $Bi_{0.3}Sb_{1.7}Te_{3.0+x}$ fabricated using Si_3N_4 balls and stainless-steel vessels. Thus, selection of the milling media affected the optimum doping amount and maximum ZT.

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The importance of the different synthetic steps in the production of thermoelectric materials from solution-processed particles: the case of SnSe

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The production of thermoelectric materials from solution-processed particles involves the following performance-determining steps: synthesis, purification, pre-consolidation thermal treatments and consolidation. Despite the importance of detailing how each of these steps have been done, we found that strictly following many publish works often results in blanks in the procedure where we have to decide our own methodology. Surprisingly, those missing details in the synthetic methods can be key to controlling material performance.

Herein, We evaluate the effect of the most relevant parameters within the entire process on the material properties and explain the reasons behind those significant differences in the thermal and electronic transport. Our case study is SnSe produced by an aqueous synthetic method. We selected this material as it is one of the most studied and relevant materials in thermoelectrics. The synthetic strategy was chosen due to its low cost and extended use in producing particles.

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Surface ions' role in the properties of polycrystalline SnSe produced in water

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Single crystal SnSe shows an intrinsic ultralow lattice thermal conductivity and the highest performance reported to date (average zT of 1.7 between 300K to 800K)[1]. However, the high production cost and the mechanical instability of the single crystal have limited its applications. Alternatively, polycrystalline SnSe has been investigated. Among the different ways to produce solution methods are of interest as they can further reduce material and production costs.

However, these solution syntheses generally involve the presence of additional molecules or ions belonging to the precursors or added to enable solubility and/or regulate nucleation and growth. These molecules or ions can end up in the particles as surface adsorbates and interfere with material properties. In previous works, we have proven that Na^+ ions are electrostatically adsorbed in SnSe particles and play a crucial role not only in defining the material nano/microstructure but also in determining the transport properties of the consolidated material[2]. Those results highlighted the importance of considering all the possible unintentional impurities to establish proper structure-property relationships and control material properties in solution-processed thermoelectric materials.

Herein, we use different alkaline-based precursors besides the typical sodium salts. We study the effects of the corresponding electrostatically adsorbed ions on the structure and transport properties of the final material.

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Application of DT-FGTM approach for the development of thermoelectric modules

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Typical commercial modules are constructed using uniform semiconductors with carrier concentration optimized for the assumed temperatures of heat sink T_c and heat source T_h. To enhance the efficiency in of thermoelectric conversion, the concepts of segmented (i.e. composed of different materials) or functionally graded thermoelectric materials (FGTM), with carrier concentration adjusted to the temperature gradient, are used. In our work, we propose a new extended concept of Double Tuned Functionally Graded Thermoelectric Material (DT-FGTM). Our approach assumes the simultaneous tuning of two electronic parameters i.e. the bandgap E_g and the Fermi level E_F to gain a high averaged figure of merit ZT_{ave} over the operational temperature range. Additionally, we propose to utilize the resonance effect in PbTe and adjust E_F with selected donor and acceptor impurities. We have shown that within the developed DT-FGTM approach, a high efficiency in energy conversion of at least 15 % can be achieved.

We have found that co-doping PbTe with resonance elements (In and Tl) significantly improves the homogeneity of the Seebeck coefficient distribution along the thermoelectric leg due to the stabilization of E_F position. Moreover, we have shown that in the specific case of In the negative process of In diffusion into the PbTe matrix could be reduced, which can extensively prolong the service time of the TE generator.

Prototypical DT-FGTM modules have been fabricated using Pulsed Electric Current Sintering (PECS) technique. The operational parameters of the module have been measured and compared with the results of numerical calculations.

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Morphologically Tuned, Thermoelectric Bi2Te3 Nanoparticles- Effect of polar solvents

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Nanostructuring and morphological tuning draws great attention for the fabrication of efficient thermoelectric material for power generation. Morphologically tuned Bi_2Te_3 nanostructures were synthesized to enhance the value of ZT through rise in the density of sates near the Fermi level and spatial confinement of acoustic phonons leading to reduction in thermal conductivity. The purity, size, morphology and thermoelectric properties of Bi_2Te_3 nanostructures were found to be greatly influenced by using different polar solvents in solvothermal synthesis. The physical and chemical properties of the solvent play the key role in tuning the final morphology of nanostructures. The carrier concentration values and thermoelectric properties were highly affected by morphology of the nanostructures. Besides the quantum confinement and phonon scattering the increased interfaces also improves the thermoelectric performance in nanostructured samples.

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Solution synthesis, processing, and characterisation of nanostructured n- and p-type thermoelectric materials

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The development of scalable synthetic techniques to produce large-scale and reproducible quality thermoelectric (TE) materials is critical for the advancement of the TE technology. To achieve this, here we coupled fast, facile, and environment-friendly microwave (MW)-assisted heating with the solution-based chemical route of thermolysis, complying with green chemistry perspectives. The focus is to fabricate bismuth telluride (Bi_2Te_3) and antimony telluride (Sb_2Te_3) alloys that are the best-known n- and p-type TE materials for temperatures below 200 $^{\circ}$C. This novel technique provides a sustainable synthesis strategy for large-scale manufacture of high-performance nanostructured TE materials as strategic energy materials, with reduced time and carbon footprint. Bi_2Te_3 and Sb_2Te_3 were synthesized from a homogeneous solution of oleic acid, chloride salts of Bi and Sb, Te-tri-butylphosphine complex, and thioglycolic acid as a shape directing agent. Due to the choice of the solvent along with MW-assisted heating, pure phase materials with a high yield of 95% were achieved efficiently in terms of energy and time. As-synthesized TE nanomaterials were processed in two ways as (i) consolidated via Spark Plasma Sintering, and (ii) mixed with poly (methyl methacrylate) to make solid-state and hybrid TEs, respectively. Scanning electron microscopy micrographs of the synthesized powders showed hexagonal platelet morphology, with a lateral size of 50-500 nm and a thickness of 50 nm, while X-ray powder diffraction revealed the rhombohedral layered crystal structure with a high phase purity. Making a hybrid TE was an attempt to create a paint, containing TE nanoparticles in order to recover waste heat in a more convenient and scalable manner through conformal coatings. Different nanoparticle contents in the paint were prepared to improve the power factor of the dried paint on a glass substrate. The addition of hexanedithiol as a linker to the paint improved the electronic performance by means of enhancing charge carrier transportation.

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Metallic Bismuth Seed Transformation to Synthesize Multinary Pnictogen based Chalcogenide Nanocrystals with Low Thermal Conductivity

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The discovery of metal chalcogenide nanocrystals with intrinsically low thermal conductivity is imperative to improving thermoelectric efficiency.1 Most multinary metal chalcogenide nanocrystals involving pnictogens (Sb, Bi) possess ultralow thermal conductivity.[2,3] However, solution growth of these nanocrystals is challenging due to the affinity of binary metal chalcogenide formation. The metallic Bi seeds are used to synthesize binary and multinary chalcogenides, although the seed is solely a catalyst for nanocrystal nucleation, and the metal from the seed has never been exploited as active alloying nuclei. Here we form colloidal Cu–Bi–Zn–S nanorods (NRs) from Bi-seeded $Cu_{2-x}S$ heterostructures. The evolution of these homogeneously alloyed NRs is driven by the dissolution of the Bi-rich seed and recrystallization of the Cu-rich stem into a transitional segment, followed by the incorporation of Zn^{2+} to form the quaternary Cu–Bi–Zn–S composition. The present study also reveals that the variation of Zn concentration in the NRs modulates the aspect ratio and affects the nature of the majority charge carriers. The NRs exhibit promising thermoelectric properties with very low thermal conductivity values of 0.45 and 0.65 W/mK at 775 and 605 K, respectively, for Zn-poor and Zn-rich NRs. We have further utilized the transformation of insitu formed Bi metal seeds to synthesize colloidal alkali metal (Na, K)-pnictogen based chalcogenides, another promising class of intrinsically low thermally conductive materials. This study highlights the potential of Bi metal seed transformation as a direct solution route to achieving homogeneously alloyed nanocrystal compositions possessing significantly low thermal conductivity that are not possible by conventional direct methods or by post synthetic transformations.

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