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ABSTRACT BOOK

ORAL PRESENTATIONS

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ECT'22 

Session VII - Auditorium

**MATERIALS &
PROCESSING IV**

ID: 05042

Type: Oral Presentation

Topic: Thermoelectric materials and materials processing

Organic-inorganic hybrids based on mesoporous silicon and functionalized molecules for thermoelectrics

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As part of the ongoing efforts to develop novel thermoelectric materials with superior performance as usually expressed by the figure of merit zT or the power factor PF, organic-inorganic hybrids aspire to overcome drawbacks of conventional materials such as low flexibility and limited performance at room temperature by synergetically combining complementary properties of their constituents.

Inorganic mesoporous silicon (pSi) is considered for thermoelectric applications due to its low thermal conductivity caused by increased phonon scattering at the pore boundaries. However, its electrical conductivity is impaired by charge carrier depletion, limiting the overall zT . One idea to overcome the low electrical conductivity of pSi is to incorporate functional molecules into the mesopores (2nm - 50nm wide). Among materials suitable to confine inside the pore space are conjugated polymers - emerging materials in electronics but also appealing thermoelectric candidates. The P3HT conjugated polymer is an outstanding candidate as it displays high charge carrier mobility and easy processability.

In this contribution, we present synthesis and thermoelectric characterization of pSi-P3HT hybrids. The synthesis consists of two steps. First, we produce 200 microns thick mesoporous silicon membranes by electrochemical anodization of bulk silicon in hydrofluoric acid-based electrolytes. In the second step the porous membranes with pores about 8nm - 10nm are infiltrated by polymer melt at 553K for 48h. Sorption isotherms, gravimetry and SEM imaging with energy dispersive x-ray spectroscopy mapping are performed to determine pore filling and morphology. Small angle and wide angle x-ray scattering techniques are employed to determine the polymer morphology in confinement to identify the interplay between chain ordering and high electrical conductive pathways. Resulting pSi-P3HT systems are characterized after the confined polymer is doped with $FeCl_3$. Hall effect, SBA and LFA measurements are essential for a comprehensive thermoelectric characterization and highlight an improved power factor PF compared to pristine porous silicon.

ID: 05066

Type: Oral Presentation

Topic: Thermoelectric materials and materials processing

Flexible thermoelectric thin films based on layered nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$

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Flexible thermoelectrics is an emerging area of research, in particular for wearable applications. One strategy used for the flexible thermoelectrics is to combine an inorganic and organic material as composite/hybrid material. In a bi-layer approach, $\text{Ca}_3\text{Co}_4\text{O}_9$ and PEDOT:PSS composite have shown their potential for application in thermoelectrics. The electronic, thermal, and mechanical properties of thin films can be altered by porosity but is controllable by engineering of the nanoporosity in layered crystalline inorganic materials such as $\text{Ca}_3\text{Co}_4\text{O}_9$ remains a challenge. In order to improve the flexibility and thermoelectric properties of the composite, thus the inorganic layer, the nanoporosity of the $\text{Ca}_3\text{Co}_4\text{O}_9$ layer was synthesized in a controlled fashion way. The porosity and average pore size of $\text{Ca}_3\text{Co}_4\text{O}_9$ films can be tuned by adjusting individual layer thickness in the multilayers ($\text{Ca}(\text{OH})_2/\text{Co}_3\text{O}_4$). With decreasing Co thickness, the morphology of pure $\text{Ca}_3\text{Co}_4\text{O}_9$ in the annealed films on mica change from a nanoporous continuous film morphology, via larger pores, to a discontinuous film of textured islands. The oriented nanopores formation in textured $\text{Ca}_3\text{Co}_4\text{O}_9$ is driven by local epitaxy and strain relaxation between $\text{Ca}(\text{OH})_2$ and Co_3O_4 during annealing. The nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ films not only exhibit a high electrical conductivity of $\sim 90 \text{ S cm}^{-1}$ and a high Seebeck coefficient of $\sim 135 \text{ } \mu\text{V K}^{-1}$, but also a thermal conductivity as low as $\sim 1 \text{ Wm}^{-1} \text{ K}^{-1}$. Moreover, the nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ films exhibit a greater mechanical compliance and resilience to bending than the bulk. The nanoporous $\text{Ca}_3\text{Co}_4\text{O}_9$ films incorporating organic PEDOT:PSS fillers can form hybrid films and show high mechanical flexibility maintaining the initial thermoelectric properties, with potential use in mechanically flexible energy-harvesting applications.

ID: 05084

Type: Oral Presentation

Topic: Thermoelectric materials and materials processing

Millimeter thick mesoporous PEDOT: PSS aerogels exhibiting high power output for promising integration in vertical TEGs

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Here, we propose to investigate the effect of porosity on the thermoelectric properties of conducting polymers. A novel architecture for organic thermoelectrics was designed using highly porous poly(3,4-ethylenedioxy thiophene):poly(styrene sulfonate) (PEDOT:PSS). Thanks to an innovative process of gelation and solvent removal with supercritical drying technique, we demonstrate the possibility to produce mechanically robust mesoporous materials (a few mm thick). The fibrillar native structure of the PEDOT:PSS gel is conserved after drying as demonstrated by Scanning and Transmission Electron microscopy (SEM and TEM) and by Wide and Small Angle X-Ray Scattering (WAXS and SAXS).

The interconnected fibrillar morphology of the aerogel maintains good electrical conductivity and mechanical properties despite the high porosity (93%). The Seebeck coefficient is not impacted by the porosity as compared to the dense film. Moreover, the mesoporosity of these aerogels allows obtaining a thermal conductivity about 5 times lower than that observed in thin films ($65 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). We demonstrate therefore the possibility to decrease the lattice part of the thermal conductivity of PEDOT:PSS. Finally, the output power of $2.6 \mu\text{W}/\text{cm}^2$, measured for a temperature gradient of 36.5 K on a single aerogel, highlights the possibility of integrating these PEDOT:PSS aerogels in vertical thermoelectric generators. ^[1]

References :

[1] Q. Weinbach, S. V. Thakkar, A. Carvalho, G. Chaplais, J. Combet, D. Constantin, N. Stein, D. Collin, L. Biniak (2022) *Front. Electron. Mater.* 2:875856. doi: 10.3389/femat.2022.875856.

ID: 05151

Type: Oral Presentation

Topic: Thermoelectric materials and materials processing

Sustainable thermoelectric materials based on lignocellulose biomass

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Lignocellulosic biomass from agriculture and forestry have shown enormous potential for high value products . Lignin along with cellulose is one of the most prevalent components of lignocellulosic biomass. Lignin is amorphous and the only aromatic biopolymer present in the cell of plants. The aromatic molecular structure of lignin generated by the condensation of the three different monolignols (coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol) allows great potential for carbon fibre production as well as the crosslinking with hydrophilic molecules to produce hydrogels. The aim of this work is to improve lignin processability for the production of materials that can produce and storage energy such as hybrid carbon fibre electrodes and hydrogels as platforms for ionic thermoelectric materials for energy harvesting. For the case of lignin hydrogels, different crosslinker ratios were used to determine their influence on the structural and chemical properties of the resulting hydrogels. It has been found that pore size was reduced by increasing crosslinker amount. The greater crosslinking density increased the swelling capacity of the hydrogels due to the presence of more hydrophilic groups in the hydrogel network. The results for ionic thermopower measured in lignin hydrogels systems were very promising achieving Seebeck coefficient values of 3-4mV/K, indicating an enormous potential to be use as platforms for ionic thermoelectric systems to harvest energy from low-grade heat.

ID: 05328

Type: Oral Presentation

Topic: Thermoelectric materials and materials processing

Does microstructure govern the thermal conductivity in semiconducting polymers?

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The thermal conductivity is the main parameter defining how heat propagates in a solid. It is of paramount importance for heat dissipation in electronics and transmission lines, but also in thermoelectrics. Despite its importance, little attention has been paid to its actual value, in part due to the general belief that the thermal conductivity in organic semiconductors “should be” small. Literature shows, however, values spanning more than two orders of magnitude.

In this invited talk, we will show a combined experimental/theoretical study, in which we have measured the thermal conductivity for a large polymer library and discovered the coexistence of two fundamentally distinct regimes. Semicrystalline conjugated polymers behave as conventional theory predicts, with increasing order leading to an increase in thermal conductivity, and this correlates also with an increase in charge carrier mobility. In other words, thermal and electrical transport go hand in hand. On the other hand, materials that do not show long range order in GIWAXS behave very differently, not following the same classic theory. As a consequence, for the latter, charge carrier mobility and thermal conductivity appear to be anticorrelated. We rationalize our results using Spearman statistics as well as theoretical calculations, which allow us to provide simple and exploitable design rules for materials that are able to decouple thermal and electronic transport, namely, texture/orientation and monomer/sidechain weight. Our results open a new avenue for highly efficient organic thermoelectrics.

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Session VIII - Parallel room

**TRANSPORT
PHENOMENA**

ID: 04957

Type: Oral Presentation

Topic: Transport phenomena

Considering the role of ion transport in diffuson-dominated thermal transport

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Superionic materials spark tremendous interest in the field of thermoelectrics due to their low lattice thermal conductivities. The material class of argyrodites shows thermal conductivities as low as ~ 0.2 W/mK, with that often falling underneath the predictions of the phonon-gas model. The role of ion transport in achieving those desired thermal transport properties often has been elusive, given the lack of reported ion conductivities.

Here, the thermal conductivities of the Ag-argyrodites Ag_8MSe_6 ($M = \text{Ge}_{1-x}\text{Si}_x, \text{Ge}_{1-x}\text{Sn}_x$) are experimentally assessed. Lattice dynamical calculations and 2-channel modelling are utilized to show that diffusive heat transport (by diffusons) is prevalent in Ag_8GeSe_6 above ~ 100 K. Temperature-dependent X-ray diffraction and sound velocity measurements are utilized to determine Einstein and Debye frequencies, that allow the generalization of this result to all here investigated argyrodites.

Furthermore, Impedance and NMR spectroscopy are used to measure the magnitude and temperature-dependence of ionic conduction. While the material foundation of ionic conductors, e.g. large anharmonicity, structural complexity and lattice softness, facilitate diffusons, the magnitude of ion transport does not influence thermal conduction. Here, the lattice thermal conductivities remain approximately constant over a large temperature and compositional range, while the ionic conduction changes multiple orders of magnitude.

Ongoing work shows that increasing the structural complexity in the argyrodites, i.e. as shown in the $\text{Ag}_{9-x}\text{Ga}_{1-x}\text{Ge}_x\text{Se}_6$ series, further suppresses the phonon-gas transport, leading to almost exclusive diffuson transport. Since diffuson signatures are found in solid electrolyte materials for battery applications, there is an outstanding question if thermal diffuson transport and fast ionic conduction are fundamentally coupled.

ID: 05171

Type: Oral Presentation

Topic: Transport phenomena

Anderson transition in stoichiometric Fe₂VAl: High thermoelectric power factor driven by antisite disorder

Fabian Garmroudi¹, Michael Parzer¹, Alexander Riss¹, Andrei V. Ruban², Sergii Khmelevskiy³, Michele Reticcioli⁴, Matthias Knopf¹, Herwig Michor¹, Andrej Pustogow¹, Takao Mori^{5,6}, Ernst Bauer¹

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In their seminal work, Mahan and Sofo mathematically derived the conditions for 'the best thermoelectric' ? a delta-distribution-shaped electronic transport function, where charge carriers contribute to transport only in an infinitely narrow energy interval. So far, however, only approximations to this concept were expected to exist in nature. Here, we propose the Anderson transition in a narrow impurity band as a physical realisation of this seemingly unrealisable scenario. An innovative approach of continuous disorder tuning allows us to drive the Anderson transition within a single sample: variable amounts of antisite defects are introduced in a controlled fashion by thermal quenching from high temperatures. Consequently, we obtained a significant enhancement and dramatic change of the thermoelectric properties from *p*-type to *n*-type in stoichiometric Fe₂VAl, which we assign to a narrow region of delocalised electrons in the energy spectrum near the Fermi energy. Our results demonstrate that high thermoelectric performance can be found at the metallic side of the Anderson insulator-metal transition. The obtained maximum power factor for the stoichiometric disorder-tuned Fe₂VAl reaches up to 7.6 mW m⁻¹ K⁻², one of the highest power factors among *n*-type thermoelectric materials. Simultaneously, the high lattice thermal conductivity is reduced by a factor 3?4, which makes disorder tuning via thermal quenching a promising novel enhancement strategy.

ID: 05252

Type: Oral Presentation

Topic: Transport phenomena

Transport and magnetothermoelectric properties of some Co-based sulfides

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Searching for ecofriendly and low cost thermoelectric (TE) materials has led us to investigate sulfides. The latter are of interest as sulfur is an abundant and cheap element, and some sulfides exhibit large TE power factor ($PF=S^2/\rho$; S = Seebeck coefficient and ρ = electrical resistivity).¹ Moreover, in 2018, we reported the first magnetothermopower (MTEP) effect in the $CuCrTiS_4$ thiospinel,² containing high spin $S=3/2$ Cr^{3+} cations, which motivated a more systematic study of magnetic sulfides.

Searching for simple structures, the Co-S binary was chosen considering the PF of CoS_2 , large and constant over a broad T range ($PF \sim 1mW.m^{-1}.K^{-2}$ from $T_C= 122K$ to $650K$).^{3,4} Interestingly, S has been found to be driven by the magnons below T_C and by the asymmetry between the spin up and spin down density of states in the spin polarized state below T_C .⁵ Co_9S_8 is another interesting member of this binary,⁶ especially for its different crystal structure with both tetrahedral and octahedral cages, contrasting with that of CoS_2 , where Co^{2+} cations form a 3D network of CoS_6 octahedras.

We will present a comparison between Co_9S_8 and CoS_2 ceramics to reveal how spin polarized transport is responsible for a strong S increase in CoS_2 . Moreover, the too high thermal conductivity, e.g. close to $10 W.m^{-1}.K^{-1}$ in Co_9S_8 at $300K$, motivated the study of the magnetic and thermoelectric properties, including MTEP, for the more complex Cu_2CoSnS_4 stannite.

[1] A. V. Powell, *J. Appl. Phys.* 2019, **126**, 100901.

[2] D. Berthebaud et al, *J. Appl. Phys.* 2018, **124**, 063905.

[3] H. S. Jarrett et al, *Phys. Rev. Lett.* 1968, **21**, 617.

[4] S. Hébert et al, *J. of Appl. Phys.* 2013, **114**, 103703.

[5] U. Acevedo Salas et al, *Phil. Trans. R. Soc.* 2019, **A 377**, 20180337.

[6] S. Hébert et al, *The Journal of Physical Chemistry C* 2021, **125 (9)**, 5386-5391.

ID: 05280

Type: Oral Presentation

Topic: Transport phenomena

Charge and heat transport in calcium-manganate oxides for thermoelectric energy harvesting

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Coupling between thermal and charge transport in crystalline materials has always been one of the greatest challenges in understanding the underlying physics of thermoelectric materials, which are useful for generating electric power from waste heat. In this sense, $\text{CaO}(\text{CaMnO})_m$ Ruddlesden-Popper layered perovskites, comprising m -perovskite sub-cells separated by CaO-planes, exhibit intriguing thermal and electronic transport properties that can be tuned by altering their crystal periodicities. Applying the well-established phonon glass electron crystal (PGEC) concept enables us to increase the transparency of these CaO-planes to electron transport at the same time with preserving their opacity to phonon transport. First-principles calculations indicate that the total local potential at the CaO planes, where Y substitutes for Ca, is lower by ca. 50 % compared to La-substitution. Measurements of the electrical conductivity and Seebeck coefficients for $\text{Ca}_{2-x}\text{R}_x\text{MnO}$ ($\text{R} = \text{La}$ or Y , and $x = 0.01, 0.05, 0.1, \text{ and } 0.15$) bulk materials in the range of 300-1000 K confirm that compounds doped with Y exhibit higher electrical conductivity values than their La-doped counterparts. We attribute this to lower polaron hopping energy values (up to 23 %) evaluated using the small polaron hopping model. This study introduces an original way to employ the PGEC approach for thermoelectric oxides.

ID: 05283

Type: Oral Presentation

Topic: Transport phenomena

From phonons to the thermal properties of complex crystals

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Crystals with a high structural complexity and chemical bonding inhomogeneity, such as tetrahedrites or type-I clathrates, often have a very low and almost temperature independent lattice thermal conductivity. On the other hand, phonons measurements have revealed the existence of long-living acoustic phonons in the clathrates questioning the origin of their low lattice thermal conductivity [1]. Another interesting case is that of High Entropy Alloys which exhibits a strong chemical disorder at the level of their unit cell leading also to a poor lattice thermal conduction. In this talk, I will first review spectroscopic measurements by means of neutrons and/or X-rays of the phonon spectrum and transport properties and the comparison with perturbative *ab initio* DFT calculation [2]. We will see how the complexity acts on propagative phonons and is responsible for the anomalous behaviors in temperature of the lattice thermal conductivity without requiring the presence of strong anharmonicity or defects in clathrates. From this knowledge of the phonon, I will propose a simplified description of it and describe meaningful model which, I believe, is enough to capture the dominant features for analyzing their thermal properties and extract microscopic properties from macroscopic measurements. In a second part, I will introduce our recent measurements of phonons in High Entropy Alloys and show that these systems present a unique phonon dynamics at the frontier between fully disordered and ordered materials, characterized by long-propagating acoustic phonons in the whole Brillouin zone. We will see that the whole attenuation behavior can be understood in terms of scattering from force-constant fluctuations [1].

[1] P.F. Lory, S. Pailhès et al., Nat. Comm. 8 (2017) 491.; 747-754.; SR Turner, S. Pailhès et al., Physical Review Research 3 (1), 013021 (2021); SR Turner, S. Pailhès et al, submitted

[2] T. Tadano and S. Tsuneyuki, Phys. Rev. Lett 120, (2018) 105901

ID: 05329

Type: Oral Presentation

Topic: Advanced characterization

Engineering thermal transport in nanowire: material design and innovative experimental techniques

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The recently growing research field called “Nanophononics” deals with the investigation and control of vibrations in solids at the nanoscale. Phonon engineering leads to a controlled modification of phonon dispersion, phonon interactions, and transport [1,2]. However, engineering and probing phonons and phonon transport at the nanoscale is a non-trivial problem.

In this talk, we discuss how phononic properties and thermal transport can be engineered and measured in nanowires [3,4] and the challenges and progresses in the measurement of the thermal conductivity of nanostructures and low dimensional systems [5].

The concept of phonon engineering in NWs is exploited in superlattice (SL) NWs.

References

[1] M. Maldovan, *Nature* **503**, 209 (2013).

[2] S. Voltz et al., *Eur. Phys. J. B* **89**, 15 (2016)

[3] M. De Luca et al. *Nano Lett.* **19**, 4702 (2019)

[4] D. de Matteis et al. *ACS Nano* **14**, 6845-6856 (2020)

[5] D. Vakulov et al. *Nano Lett.* **20**, 2703-2709 (2020)

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Session IX - Auditorium

**MATERIALS &
PROCESSING V**

ID: 05024

Type: Oral Presentation

Topic: Thermoelectric materials and materials processing

Thermoelectric Inks and Power Factor Tunability in Hybrid Films through All Solution Process

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Thermoelectric (TE) materials can have a strong benefit to harvest thermal energy if they can be applied to large areas without losing their performance over time. One way of achieving large-area films is through hybrid materials, where a blend of TE materials with polymers can be applied as coating. Here we present the development of all solution-processed TE ink and hybrid films with varying content of TE Sb_2Te_3 and Bi_2Te_3 nanomaterials, along with their characterization. Using (1-methoxy-2-propyl) acetate as the solvent, and poly(methyl-methacrylate) as the durable polymer, large-area hybrid TE films have been fabricated.^[1] Sb_2Te_3 and Bi_2Te_3 are synthesized through microwave-assisted thermolysis route. The conductivity and TE power-factor improve with nanoparticle volume fraction, peaking around 60-70% fill factor. For larger fill factors the conductivity drops, possibly because of an increase in the interface resistance through interface defects and reduced connectivity between the platelets in the medium. The use of dodecanethiol as an additive in the ink formulation, enabled an improvement in the electrical conductivity through modification of interfaces and the compactness of the resultant films, leading to a 4-5 times increase in the power factor for both p- and n-type hybrid TE films, respectively. The observed trends were captured by combining percolation theory with analytical resistive theory, with the above assumption of increasing interface resistance and connectivity with polymer volume reduction. The results obtained on these hybrid films open a new low-cost route to produce and implement TE coatings on a large scale, which can be ideal for driving flexible, large-area energy scavenging technologies such as personal medical devices and the IoT.

Reference

[1] Serrano-Claumarchiran J. F., Hamawandi B., Ergül A. B., et al. Thermoelectric Inks and Power Factor Tunability in Hybrid Films through All Solution Process. in press in *ACS Applied Materials and Interfaces* 2022 *ACS Appl. Mater. Interfaces* 2022, <https://doi.org/10.1021/acsami.1c24392>

ID: 05045

Type: Oral Presentation

Topic: Thermoelectric materials and materials processing

High Thermoelectric Performance in Lithium Germanium Bismuth Tellurides by Optimizing Microstructure and Transport Properties

Matthias Jakob¹, Christopher Benndorf¹, Robert Michael¹, Timm Reimann¹, Aryan Sankhla², Johannes de Boor², Oliver Oeckler¹

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Alloying GeTe with Sb_2Te_3 or Bi_2Te_3 leads to GeTe-like rhombohedral compounds with high concentrations of planar vacancy layers.^[1,2] However, these nanostructures do not cause pronounced phonon scattering that would decrease thermal conductivity significantly. In contrast, decreasing charge carrier mobility leads to low ZT values especially at temperatures where the rhombohedral structure is present ($\sim < 250$ °C). Decreasing the vacancy concentration on the cationic site of $\text{Ge}_{17}\text{Bi}_2\text{Te}_{20}$ by substituting Ge by twice the amount of Li leads to compounds like $(\text{GeTe})_{17-x}(\text{Li}_2\text{Te})_{2x}\text{Bi}_2\text{Te}_3$ ($x = 0 - 1$) with variable Li content while the average crystal structures are similar. Atom emission spectroscopy confirms the integration of Li in the structure. SEM-EDX and powder diffraction confirm phase purity. TEM shows that compounds with no cation vacancies like $\text{Li}_2\text{Ge}_{16}\text{Bi}_2\text{Te}_{20}$ do not exhibit pronounced planar defects in contrast to $\text{Ge}_{17}\text{Bi}_2\text{Te}_{20}$. Addition of Li increases carrier mobility from ~ 8.0 to 21.2 cm^2/Vs at RT which – in combination with an increase of carrier concentration – leads to a fourfold increase of electrical conductivity. Since phononic thermal conductivity is nearly the same in this compounds, the total κ is only increased by about 50%. This leads to higher ZT values over the whole temperature range up to 450 °C but the increase is most significant in the temperature regime up to 225 °C. The highest reached ZT value was ~ 1.7 at 400 °C for $\text{Li}_2\text{Ge}_{16}\text{Bi}_2\text{Te}_{20}$. The average ZT of $\text{Li}_2\text{Ge}_{16}\text{Bi}_2\text{Te}_{20}$ from RT up to 450 °C is nearly doubled from 0.61 to 1.17 in comparison to $\text{Ge}_{17}\text{Bi}_2\text{Te}_{20}$. Applying an SPB model underlines that decreasing the vacancy concentration leads to higher possible ZT values of up to 1.4 at 225 °C which is more than a fourfold increase compared to the Li free compound. This underlines the necessity of discussing the influence of nanostructures on electron transport.

[1] T. Rosenthal, M. N. Schneider, C. Stiewe, M. Döblinger, O. Oeckler, Chem.Mater. 2011, 21, 4349.

[2]. N. Madar, T. Givon, D. Mogilyansky, Y. Gelbstein, J. Appl. Phys. 2011, 120, 035102.

ID: 05174

Type: Oral Presentation

Topic: Thermoelectric materials and materials processing

As-grown nanostructured thermoelectric thin films

Pablo Cerviño-Solana¹, Álvaro Rodríguez-Martín¹, Marisol Martín-González¹, Olga Caballero-Calero¹

1) CSIC

Nanostructured bismuth telluride thin films fabricated by electrochemical deposition in the presence of specific additives into the solution have been prepared. For this purpose, a nitric acid bath with sodium lignosulfonate has been used [M. S. Martín-González, A. L. Prieto, R. Gronsky, T. Sands, A. M. Stacy, J. Electrochem. Soc. (2002) C546-C554] as electrochemical bath, along with a three-electrode cell with reference electrode Ag/AgCl, Pt counter electrode and a Si covered with 150 nm of gold for working electrode. This technique has been previously studied aiming to improve the thermoelectric properties and morphology of bismuth telluride thin films [Olga Caballero-Calero, Pablo Díaz-Chao, B Abad, Cristina V Manzano, MD Ynsa, JJ Romero, M Munoz Rojo, MS Martín-González, Electrochimica Acta, 123 (2014) 117].

The deposition conditions have been modified in order to optimize the final result. We have observed that, with the proper parameters, it is possible to grow the bismuth telluride with a nanostructured morphology of highly oriented nanoplatelets without the need of a template. The thickness of this nanoplatelets is close to 10 nm, while their lengths stretches up to 2 or 3 microns.

The objective of this work is to optimize the thermoelectric properties of the films, controlling the growth parameters to modify their stoichiometry, morphology and crystallographic. The measurement of the transport properties is not straightforward in these films, given that the conductive substrate has to be removed while maintaining the integrity of the nanostructure. Different detaching approaches have been studied to obtain measurable samples. The first thermoelectric measurements done in these films are quite promising.

ID: 05211

Type: Oral Presentation

Topic: Thermoelectric materials and materials processing

Surface functionalization of surfactant-free particles to tailor nanocomposite's properties and enhance thermoelectric performance

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The broad implementation of thermoelectricity requires finding high-performance materials and reducing their production costs. Inorganic nanocomposites are among the most suitable materials for achieving high performance. There are plenty of methods to produce inorganic nanocomposites, the most common in thermoelectric materials being spinodal decomposition in high-temperature reactions. However, it requires large amounts of energy, long reaction times, and ultra-high purity reagents, therefore, yielding materials that are too expensive for large-scale implementation. One possibility for reducing costs is employing solution synthesis to produce semiconducting powders and consolidate them into dense materials. Among the most economical solution synthetic strategies are the so-called surfactant-free as they usually require low-cost reagents and mild reaction conditions yet deliver high yields.

Herein we employ such a synthetic method and propose the strategy of functionalizing the surface of the resulting "naked" particles by using inorganic molecules. We use the surface molecules' decomposition products to control the final material's structural and compositional properties to yield high thermoelectric performance. This strategy has barely been explored despite the vast number of possibilities to produce unique nanocomposites non-achievable by other means.

ID: 05230

Type: Oral Presentation

Topic: Thermoelectric materials and materials processing

Flexible Thermoelectric Paper and its thermoelectric generator from Bacterial Cellulose/Ag₂Se Nanocomposites

Dulyawich Palaporn¹, Wiyada Mongkoltharuk¹, Kajornsak Faungnawakij², Ken Kurosaki³, Supree Pinitsoontorn¹

1) Khon Kaen University 2) National Nanotechnology Center 3) Kyoto University

In this research, a flexible thermoelectric paper was fabricated from bacterial cellulose/silver selenide (BC/Ag₂Se) nanocomposites. Ag₂Se particles were *in situ* synthesized in the network of BC nanofibers. Several synthesis parameters that crucially affect the formation of Ag₂Se particles in the BC structure were investigated to understand the phase formation mechanism. Under the optimized conditions, the BC/Ag₂Se paper with a large proportion of Ag₂Se up to 75 wt.% was successfully obtained. The *in situ* synthesis limits the Ag₂Se formation within the nanopores of the BC structure. As a result, the sub-micro size Ag₂Se particles with narrow size distribution were homogeneously dispersed in the BC nanofiber network. The microstructure was further improved by hot-pressing, which increase the density of the BC/Ag₂Se paper and make the BC layered structure more compacted. These contributed to a significant enhancement of the thermoelectric properties, with the electrical conductivity of 23000 S/m and the Seebeck coefficient of -167 $\mu\text{V}/\text{K}$ at 400 K. The power factor was 642 $\mu\text{W}/\text{mK}^2$ at 400 K, a very high value compared to other flexible thermoelectric research. The measurement of thermal conductivity yielded the κ value of 0.36 W/mK at 400 K, which led to the maximum ZT of 0.70 at 400 K. To demonstrate the thermoelectric conversion, five BC/Ag₂Se paper pieces were connected in series to construct a thermoelectric module. The module is very flexible and can be curved to attach to any arbitrary shape of the hot/cold surfaces. In addition, the process for fabricating the BC/Ag₂Se paper is scalable without any use of advanced or expensive instruments. This makes it a very attractive choice as a flexible TEG.

ID: 05256

Type: Oral Presentation

Topic: Thermoelectric materials and materials processing

Grain growth engineering in solution processed silver selenide

Tobias Kleinhanns¹, Mariano Calcabrini¹, Cheng Chang¹, Christine Fiedler¹, Maria Ibáñez¹

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Silver selenide (Ag_2Se) is a promising thermoelectric material for high performance around room temperature, owing to its high charge carrier mobility and low thermal conductivity in this temperature range. Among the routes to produce silver selenide, solution processing stands out with low cost, high yield and the possibility to fine-tune structural parameters from the bottom-up. Here, we report a facile strategy to crystallize silver selenide from molecular solutes at room temperature, and consolidate the obtained powder into pellets using the spark-plasma sintering (SPS) technique at relatively low temperatures (below 200 °C).

Strikingly, different sintering conditions have tremendous effects on the microstructure: With increasing the sintering temperature, the average grain size can be changed by two orders of magnitude. Thus, dense samples with either small grain sizes or big grain sizes can be systematically synthesized. However, this trend is missed out in current literature. Therefore, we use processing conditions, annealing and SPS as our experimental knobs for controlling the grain growth and obtain a series of samples with different grain sizes. We then correlate the microstructure with the thermoelectric transport properties, to understand this material better and achieve the next generation of high performing silver selenide.

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Session X - Parallel room

**THEORY &
MODELLING I**

ID: 04992

Type: Oral Presentation

Topic: Theory and modelling

Dynamical tuning of the thermal conductivity via magnetophononic effects

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Strategies for tuning the thermal conductivity of crystals by means of external fields are rare. Here, we predict the existence of large magnetophononic effects in materials that undergo antiferromagnetic (AFM)-ferromagnetic (FM) phase transitions, which allow for the modulation of the lattice heat conductivity via the application of magnetic fields. Specifically, by using first-principles methods we predict a large and anomalous increase of the thermal conductivity of approximately 40% for the metamagnetic phase transition occurring in bulk FeRh near room temperature. The disclosed magnetophononic effects are caused by large anharmonic spin-phonon couplings, namely, significant differences in the phase space of allowed phonon-phonon collision processes taking place in the respective AFM and FM phases.

We expect that similar magnetophononic effects will exist also in other families of materials in which akin phase transitions are known to occur. The present study, therefore, opens up new avenues for the dynamical control of heat transport in functional materials, thus besides of its fundamental interest it may also provide useful guides for the design of emerging phonon devices and tunable thermoelectrics.

ID: 05041

Type: Oral Presentation

Topic: Theory and modelling

Efficient *ab initio*-based thermoelectric transport simulations beyond the constant relaxation time approximation using the ElecTra code

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In this work we describe a newly developed method to compute the electronic and thermoelectric transport properties of complex electronic structure materials and their alloys. Using density functional theory (DFT) and density functional perturbation theory (DFPT), we have developed a first-principles framework to extract deformation potentials and form all relevant electron-phonon scattering rates [1]. We then compute the material's transport properties using a new own-developed Boltzmann transport simulator, *ElecTra* [2], which takes into account the full energy/momentum/band dependence of the scattering processes, as well as all relevant scattering mechanisms such as acoustic, optical and polar phonons, ionized impurity scattering and alloy scattering. The code allows treatment beyond the commonly employed constant relaxation time approximation, but also *ab initio* accuracy at a fraction of the computation cost of state-of-the-art fully *ab initio* methods. Here we present details related to the methods and software, as well as indicating computational studies related to the properties of some promising materials [3], the development of relevant descriptors that can be used in machine learning studies [4], as well as some peculiar material features that can lead to ultra-high power factors [5, 6].

References

[1] Z. Li, P. Graziosi, and N. Neophytou, *Phys. Rev. B*, 104, 195201, 2021

[2] ElecTra - DOI: 10.5281/zenodo.5074943.

[3] P. Graziosi, C. Kumarasinghe, and N. Neophytou, *J. Appl. Phys.*, 126, 155701, 2019.

[4] P. Graziosi, C. Kumarasinghe, and N. Neophytou, *ACS Appl. Energy Mater.*, 3, 6, 5913–5926. 2020.

[5] P. Graziosi and N. Neophytou, *J. Phys. Chem. C*, 124, 34, 18462–18473, 2020.

[6] P. Graziosi, Z. Li, and N. Neophytou, *Appl. Phys. Lett.*, 120, 072102, 2022.

ID: 05086

Type: Oral Presentation

Topic: Theory and modelling

Finding Relationship Between the Local Structure and Electronic Orbital Occupation Using Machine Learning

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It is well understood how unique transport properties arise from the characteristics of compounds' electronic structure. However, it is less straightforward to find relationships between compounds' crystal structure and its electronic structure, which can speed up the discovery of high-performance thermoelectric materials, for example. One of the earliest such attempts, by Hoffmann to study electronic structures from local interactions, provides an intuitive and instructive understanding of this structure-electronic property relationship [1]. It is valid in 3*d* transition metal (TM) compounds where 3*d* orbitals are in general localized, and when TM ions do not form direct bonding. This provides a starting point where we can develop methods to determine electronic properties following the simple but well-understood bonding theory in solids.

In this study, we take advantage of the recently developed structure fingerprints that faithfully encode spatial atomic positions [2] to study how well, from a local structure, the machine learning (ML) model can determine the TM 3*d* orbital occupation (up and down). Importantly, we discuss different strategies to choose the scope (how many atoms) of the input local structure. We show that overfitting is very likely to occur when the scope is large and, in the end, nearest neighbor atoms are enough to achieve good prediction accuracy for the orbital occupation on TM atoms. We decompose the errors for different types of compounds. Finally, we compare the predicted spin-only magnetic moment with available experimental data. Our study would shed light on improving the ML methods in learning the structure-electronic property relationship as well as fast screening of electronic properties for thermoelectric material development in the future.

References:

[1] R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* 26, 846–878 (1987).

[2] M. Uhrin, *Phys. Rev. B* 104, 144110 (2021).

ID: 05154

Type: Oral Presentation

Topic: Theory and modelling

Thermoelectric properties of multiple component (high entropy) silicides

Ole Martin Løvvik^{1,2}, Jørn-Marcus Høylo-Rosenberg², Patricia Almeida Carvalho¹

1) SINTEF 2) University of Oslo

Multiple component or high entropy compounds (HECs) can be constructed by substituting one site of a master compound (e.g. FeSi_2) with five or more equimolar (or near equimolar) components (e.g. $\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Si}_2$). Similar to high entropy alloys, HECs can exhibit properties that differ significantly from their constituting compounds. Thermoelectric properties can thus be influenced by the compositional complexity of HECs in various ways: The enhanced alloy scattering of phonons can strongly reduce the lattice thermal conductivity; the complex band structure can exhibit multiple valleys, optimizing the electronic thermoelectric properties; the large compositional flexibility can be used to fine-tune the bandgap and electronic bandstructure; the variation in local environments can lead to a rich source of intrinsic defects and a correspondingly high intrinsic doping and charge carrier concentration.

The large array of possibilities does not come without a penalty. The entropy stabilization of multiple components may be competing with the enthalpy of formation, which can lead to phase separation into simpler compounds (e.g. CoSi_2 , FeSi_2 , etc. in the example above). Also, synthesis and processing can be challenging if the melting and boiling points of the elements differ significantly. Furthermore, atomistic modelling is challenging due to the solid solution of elements, explicitly breaking the periodicity requirement of band structure codes.

The present work is a joint experimental and modelling effort on new HECs based on the master silicides FeSi_2 , FeSi , and Fe_2Si . The experimental efforts have focused on providing single-phase materials with multiple components. This proved to be difficult for some compositions, but a number of new stable HECs could be identified. Transport properties were measured for selected compositions. The modelling work was a semi-high throughput search for HECs with a bandgap. A series of new compositions with small bandgaps were discovered. Their electronic and phonon properties were investigated to estimate thermoelectric transport properties.

ID: 05162

Type: Oral Presentation

Topic: Theory and modelling

Inherent anharmonicity of harmonic solids

Matthias Agne¹, Jeffrey Snyder²

1) WWU Muenster 2) Northwestern University

Nonlinear “anharmonic” forces between atoms are responsible for many behaviors of thermoelectric and other energy materials. Yet, the ubiquity of anharmonicity does not mean that it is well understood. Without a detailed study of the vibrational properties of a material (i.e., phonons), it is nearly impossible to make any prediction about the magnitude of thermal expansion, thermal conductivity, or other so-called anharmonic properties of solids. Here, we demonstrate a fundamental relation between harmonicity (e.g., elasticity), which is well characterized in every kind of solid, and anharmonicity, which is not well characterized and is a highly active field of research. We show that the kinetic energy of atoms in a solid produces a pressure much like the kinetic energy of atoms in a gas does. This vibrational or *phonon pressure* naturally increases with temperature, as it does in a gas and therefore results in a thermal expansion. Because thermal expansion thermodynamically defines a Grüneisen parameter, which is a typical metric of anharmonicity, we show that even a harmonic solid will necessarily have some anharmonicity. A consequence of this phonon pressure model is a harmonic estimation of the Grüneisen parameter from a ratio of bulk and shear elastic moduli. This work provides a new framework by which anharmonicity may be characterized from harmonic properties of solids, subsequently leading to metrics of anharmonicity useful for material screening and design.

ID: 05197

Type: Oral Presentation

Topic: Theory and modelling

Thermoelectricity by spontaneous particle-hole symmetry breaking.

Alessandro Braggio¹

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Thermoelectrical effects in systems with good particle-hole symmetry are usually weak. Here we will report some relevant exceptions. Even superconductors can be strongly thermoactive materials due to the gap opening at the Fermi surface. Anyway, some tricks are required to clearly unveil their thermoelectrical potential.

Firstly we will show in topological Josephson junctions that nonlocal thermoelectrical effects can be very strong of the order of tens of $\mu\text{V}/\text{K}$ at sub-Kelvin temperatures and can be manipulated by magnetic flux[1] and phase biases[2]. This effect can be used to clearly identify the helical nature of the topologically protected edge states with only a three-terminal geometry.

Further, we will discuss that strong bipolar thermoelectricity can be generated by spontaneous breaking of the particle-hole symmetry in an asymmetric SIS' junction where the Josephson coupling is sufficiently suppressed[3]. Intriguingly the thermoelectricity is very strong and can be of the order of $300 \mu\text{V}/\text{K}$ for Aluminium based tunnel junctions at sub-Kelvin temperatures. This means a thermoelectric effect 10^5 bigger than a normal metal at the same temperature. We will discuss the generality of the effect for different materials reporting possible experimental evidence[4] and applications[5]. These results open a new intriguing route toward strong thermoelectricity also for particle-hole symmetric materials.

[1] G. Blasi et al. "Nonlocal Thermoelectricity in a S-TI-S Junction in Contact with a N-Metal Probe: Evidence for Helical Edge States" Phys. Rev. Lett. 124, 227701 (2020)

[2] G. Blasi et al. "Nonlocal thermoelectricity in a topological Andreev interferometer" Phys. Rev. B 102, 241302(R) (2020);

[3] G. Marchegiani et al. "Nonlinear thermoelectricity with with Electron-Hole Symmetric Systems" Phys. Rev. Lett. 124, 106801 (2020)

[4] G. Germanese et al. "Bipolar Thermoelectric Josephson Engine" arXiv:2202.02121

[5] F. Giazotto et al. Superconducting bipolar thermoelectric memory and method for writing a superconducting bipolar thermoelectric memory. Patent (Filling number: 102021000032042 (21/12/2021)).

ECT'22 

Session XI - Auditorium

**MATERIALS &
PROCESSING VI**

ID: 04915

Type: Oral Presentation

Topic: Thermoelectric materials and materials processing

LOW DIMENSIONAL METAL HALIDE PEROVSKITES FOR THERMOELECTRIC APPLICATIONS

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In recent years, metal halide perovskites have been considered as thermoelectric materials due to their efficient electronic transport properties combined with exceptionally low thermal conductivity. However, the studies for overcoming their low electrical conductivity and stability problems are still in its infancy. Our group focuses on development of thermoelectric materials and doping strategies through introducing intrinsic and extrinsic defects in the lattice. In this presentation, we will review our recent results on substitutional doping of MAPbBr₃ single crystals and self-doping of CsSnI₃ thin films. Furthermore, low dimensional semiconductors can exhibit quantum confinement effects that give the possibility of enhanced Seebeck coefficients and further reduced thermal conductivity. There is a vast family of 2D, 1D and 0D derivatives of halide perovskites whose thermoelectric performance (ZT) remains relatively unexplored. We will present our initial work on low dimensional derivatives of halide perovskites, focussing on barium doped Cs₃Cu₂I₅ pellets which exhibit high Seebeck coefficients and ultralow thermal conductivities.

In recent years, metal halide perovskites have been considered as thermoelectric materials due to their efficient electronic transport properties combined with exceptionally low thermal conductivity.[1] However, the studies for overcoming their low electrical conductivity and stability problems are still in its infancy. Our group focuses on development of thermoelectric materials and doping strategies through introducing intrinsic and extrinsic defects in the lattice. In this presentation, we will review our recent results on substitutional doping of MAPbBr₃ single crystals[2] and self-doping of CsSnI₃ thin films[3, 4]. Furthermore, low dimensional semiconductors can exhibit quantum confinement effects that give the possibility of enhanced Seebeck coefficients and further reduced thermal conductivity. There is a vast family of 2D, 1D and 0D derivatives of halide perovskites whose thermoelectric performance (ZT) remains relatively unexplored. We will present our initial work on low dimensional derivatives of halide perovskites, focussing on barium doped Cs₃Cu₂I₅ pellets which exhibit high Seebeck coefficients and ultralow thermal conductivities.

ID: 05012

Type: Oral Presentation

Topic: Thermoelectric materials and materials processing

Magnetism and defect enhanced thermoelectric materials and devices

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Development of thermoelectric materials is important as power generation for waste-heat energy-saving and IoT sensors [1]. I will present some especial routes where we have enhanced thermoelectric properties, also high device performance cases.

First, magnetism utilized to enhance power factor [2]: Strong coupling leading to effective magnon-drag, e.g. like for CuFeS_2 chalcopyrite and recently indicated origin of the huge power factor in metastable Fe_2VAl -based thin films, and also paramagnon-drag and spin-fluctuation.

Second, defect engineering [3]: Doping in GeTe serendipitously lowered the formation energy of Ge defects leading to Ge precipitations and vacancies to obtain $ZT \sim 2$. A high-entropy approach led to first stable n-type conduction in GeTe, while vacancy-crystal structure relation utilized to lead to high power factor.

Third, for selective low thermal conductivity [4]: Doping in SnTe led to lattice softening, with significantly stronger effect than phonon scattering. A new descriptor of partial occupancy, to construct a material catalogue with low thermal conductivity.

Most recently an interesting dual effect of minute Cu doping in Mg_3Sb_2 was revealed. Interstitial Cu doping indicated to lower phonon group velocity, while Cu doping into grain boundaries led to very high mobilities comparable to single-crystals, despite low thermal conductivity. An initial 8-pair module composed of original Mg-Sb based materials, exhibited efficiency of 7.3% @ 320°C, rivalling the Bi_2Te_3 -type best module for the first time [5].

Acknowledgments: Thanks to members of JST Mirai Large-Scale Program.

1) MRS Bull. 43, 176 (2018), Sci. Tech. Adv. Mater. 19, 836 (2018).

2) Small 13, 1702013 (2017), Phys. Rev. B, 104, 214421 (2021), Mater. Today Phys. 9, 100090 (2019), Sci. Adv., 5, eaat5935 (2019).

3) Small, 16, 1906921 (2020), NPG Asia Materials, 12:66 (2020), Adv. Energy Mater., 10, 2002588 (2020).

4) Adv. Energy Mater. 11, 2101122 (2021), Energy Environ. Sci. 14, 3579-3587 (2021).

5) Joule, 5, 1196-1208 (2021), Nature Commun., 13, 1120 (2022).

ID: 05037

Type: Oral Presentation

Topic: Emerging topics

Exploration of the thermoelectric properties of Cu and Ag ternary metal phosphides

Robert Quinn¹, Callum Stevens², Hector Leong², Andrew Huxley², Jan-Willem Bos¹

1) Heriot-Watt University 2) University of Edinburgh

Many leading thermoelectric materials contain heavy main group elements, with high mass correlating with low lattice thermal conductivity (κ_L) and low electronegativity differences yielding low band gaps (E_g). While phosphide materials might therefore be assumed to suffer from large κ_L or E_g , there are in fact many reports of phosphide materials displaying low κ_L (CaZn_2P_2 ,¹ $\text{Ag}_6\text{Ge}_{10}\text{P}_{12}$,² ZnCu_2P_8 ,³ Cd_3P_2 ,⁴), with Cd_3P_2 recently being reported to have a maximum figure of merit (zT) of 0.9 at 673 K.⁴

In this presentation, we will discuss the thermoelectric properties of three unexplored Cu and Ag based ternary phosphide materials. These are $\text{CaAg}_{0.9}\text{P}$,⁵ MgCuP , and CaCuP , which all have $zT \sim 0.5$ at 790 K. Each material has a different structure, but all are degenerately p-type doped due to Cu/Ag vacancies and have $\kappa_L < 5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ above 300 K. All compositions are stable under ambient conditions and are mechanically unchanged after thermal cycling under Helium atmosphere, demonstrating their potential for further investigation. Synchrotron X-ray powder diffraction and Hall measurements have been used to gain insight into the defect chemistry and underlying bandstructures of these materials. Initial work on the next steps to improve performance, reduction of κ_L by isoelectronic alloying and control of carrier doping will also be presented.

References:

1. V. Ponnambalam et al. J. Phys. D: Appl. Phys. 2011, 44, 155406.
2. A. Suwardi et al. ACS Appl. Mater. Interfaces. 2020, 12, 9150.
3. J. Mark and T. Mori, ACS Appl. Ener. Mater. 2021, 4, 4861.
4. L. Fan et al. Chem. Mater. 2022, 34, 1620.
5. R. J. Quinn and J.-W. G. Bos, Applied Physics Letters, 2022, 120, 073903 (Editors' Pick).

ECT'22 

Session XII - Parallel room

**THEORY &
MODELLING II**

ID: 05071

Type: Oral Presentation

Topic: Theory and modelling

A new method for detecting resonant levels in thermoelectric semiconductors

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Resonant levels (RL) may be formed by impurity atoms in semiconductors and by forming narrow peaks in the density of states they strongly modify the host materials' electronic structure, violating the rigid band model. By giving rise to a local distortion of the electronic density of states, RL offer an elegant way to enhance the thermoelectric properties of semiconductors. However, the experimental detection of RL is not straightforward. A widely-used method to demonstrate experimentally the resonant nature of a given dopant relies on the observation of enhancement of the thermopower of the doped system above the thermopower vs carrier concentration $S(n)$ relation characteristic for a host material (so-called Ioffe–Pisarenko curve). However, deviations from this material-specific $S(n)$ dependence can also be induced by other non-rigid-band doping effects such as band convergence or a change in the band curvature, making this method inconclusive in many cases. Our recent theoretical and experimental studies have resulted in a novel methodology [1], based on the analysis of the residual electrical resistivity and charge carrier mobility. It enables to distinguish the RL from other mechanisms which enhance thermopower, and is applied for two canonical RL systems: In-doped SnTe and Tl-doped PbTe. Although best suited for the study of single-crystalline specimens, we show that this novel method can be equally applied to polycrystalline specimens. We demonstrate that the resonant scattering induced by the RL affects in a more pronounced manner the two above-mentioned physical quantities at low temperatures compared to rigid-band-like and other non-rigid-band-like dopants. Moreover, understanding of resonant scattering is critical to explain the enhanced performance of the resonantly doped thermoelectric materials at high temperature and helps to design further optimization the thermoelectric efficiency.

References:

[1] B. Wiendlocha et al, Materials Horizons 8, 1735 (2021).

ID: 05110
Type: Oral Presentation
Topic: Emerging topics

FROM LOW-DIMENSIONAL NANOSTRUCTURES TO THERMOELECTRIC METAMATERIALS

XANTHIPPI ZIANNI¹

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Low-dimensional nanostructures offer the ability to engineer electron and phonon states as well as scattering and achieve high thermoelectric efficiencies. For this reason, they have been intensively studied in the last 30 years. Geometry-modulated nanostructures is a class of metamaterials also promising for thermoelectric efficiency enhancement and heat management through engineering of carrier states and scattering at the nanoscale, that has been proposed more recently, nearly ten years ago [1,2]. Now, in the era of metamaterials, they are gaining increasing research interest. In the quantum confinement regime, coupling between propagating waves and discrete states (resonances) of the modulation units modifies the electron and phonon transmission coefficients and results in enhanced thermoelectric power factor and decreased thermal conduction. This effect is generic and can take place in many shapes of geometrical modulation in 1d, 2d and 3d, irrespectively of the material choice. Geometry-modulated metamaterial operating in this regime have attracted much research interest, mainly theoretical [3]. Above the quantum confinement regime, scattering can be controlled by designing the shape of the geometry-modulation. Ballistic or diffusive transport effects may dominate depending on characteristic dimensions of the geometry modulation [4]. The predicted significant and geometrically controlled decrease of the thermal conductivity has been confirmed experimentally. We will discuss physics aspects of electron and phonon transport in geometry-modulated nanostructures based on our work and the evolution of the research on this class of metamaterials that is promising for efficient thermoelectric energy conversion.

[1] X.Zianni, Applied Physics Letters **97**, 233106 (2010)

[2] X.Zianni, Journal of Solid State Chemistry **193** 53 (2012)

[3] X.Zianni, Adv. Electron. Mater. **2021**, 2100176 (2021)

[4] X.Zianni, [MRS Advances](#) **6** 707 (2021)

ID: 05237

Type: Oral Presentation

Topic: Theory and modelling

Thermopower and Short-range Order Parameter in Self-consistent Spin-Wave Theory: A Path for Designing Spin-driven Thermoelectric Materials

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1) North Carolina State University 2) Institute for Advanced Studies in Basic Sciences

The experimental data indicate that magnon-electron drag can dominate the thermopower of some antiferromagnetic materials near the Néel temperature (T_N). A prime example is manganese telluride (MnTe), with several folds excess thermopower than the electronic contribution due to magnon-electron drag near T_N . Interestingly, this excess drag thermopower continues above T_N and sustains its high magnitude where the disappearance of magnons is expected. To understand the underlying reason for the presence of the drag mechanism above T_N , we investigate the short-range magnetic order (SRO) and correlations versus temperature near and above T_N . The standard spin-wave theory (SWT) works well in magnetic materials at low temperatures. However, the theory fails to describe the SRO at high temperatures where corrections owing to spin-wave interactions become significant. Several approaches have been applied to two-dimensional (2D), quasi 2D, and three-dimensional (3D) systems, such as variational mean-field theory, the boson mean-field theory based on Schwinger bosons representation of spin operators, and modified SWT based on Dayson-Maleev representation. However, these formalisms fail to quantify the value of ordering temperature and the correct behavior of the magnetic order near and above the T_N correctly. To address these shortcomings, we consider the Heisenberg model and use the Baryakhtar-Krivoruchko-Jablonsky representation via Bose ideal magnon operators and auxiliary pseudofermion operators in self-consistent SWT. Using a mean-field approximation for decoupling the quartic terms in transformed Hamiltonian, we show that this representation proves the existence of a strong SRO above T_N for the MnTe case study, and adding fluctuation corrections to SSWT improves the ordering temperature. The theoretical results are presented and benchmarked against the experimental data from Inelastic Neutron Scattering, and an acceptable agreement is obtained.