ECT2019

17th European Conference on Thermoelectrics

23 - 25 September 2019

Limassol, Cyprus

Conference Abstracts

Monday, 23 Sep

Oral Presentations

Poster Presentations

Tuesday, 24 Sep

Oral Presentations

Poster Presentations

Wednesday, 25 Sep

Oral Presentations

Plenary & Invited I

9:00 - 10:45

Room: Panorama

Chair: Franck Gascoin

9:00 - 9:45

Understanding and Designing High Performance Thermoelectrics

M. Kanatzidis[1]

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The broad based push to develop highly efficient thermoelectric materials as a possible route to address the worldwide power generation from heat is ongoing. Today there is a variety of effective strategies to improve the properties of these narrow gap semiconductors such as achieving extremely low thermal conductivity and raising the power factors. The so-called nanostructuring and mesoscale approach has led to a new era of investigation for bulk thermoelectrics. Currently lead chalcogenides incorporating second phases hold the record in figure of merit ZT for power generation applications. Nanostructures enable effective phonon scattering of a significant portion of the phonon spectrum while mesostructures tend to scatter phonons with long mean free paths remain. By combining all relevant length-scales in a hierarchical fashion, from atomic-scale disorder and nanoscale endotaxial precipitates to mesoscale phonon scattering a large enhancement in the thermoelectric performance of bulk materials can be achieved. Progress on device and module assembly is excellent and modules with conversion efficiency of ?12% for a delta T of 590 K have been demonstrated using nanostructured PbTe-based materials. Interestingly, nanostructuring is not necessary to obtain record high thermoelectric performance. Several systems based on PbTe and PbSe will be described that lack nanostructuring but feature mesoscale structuring and point defects, which can also achieve very low thermal conductivity. Comparisons with nanostructured materials will be made. Finally, SnSe is a new striking example of a single-phase material which has disrupted our thinking of how high ZT performance can arise will be discussed.

9:45 - 10:15

Tailoring thermal and electronic properties of bulk $Cu_{26}T_2(Ge,Sn)_6S_{32}$ colusite through defects engineering and functionalization of the conductive network

E. Guilmeau[1], V. Pavan Kumar[1], P. Lemoine[2], B. Raveau[3], C. Bourgès[3], V. Nassif[4], R. Al Rahal Al Orabi[5], A.R. Supka[6], M. Fornari[6], K. Suekuni[7], O.I. Lebedev[1], Y. Bouyrie[8], M. Ohta[8]

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A complete study of the structure and thermoelectric properties of colusite Cu26T2(Ge,Sn)6S32 (T = V, Cr, Mo, W) is presented. A brief introduction will provide a state-of-the-art/survey in thermoelectric sulfides, with a special focus on the structural features and transport properties of Cu-based sulfides. In the first part of the presentation, the key role of the densification process on the formation of short-to-medium range structural defects in Cu26V2Sn6S32 will be discussed [1]. A simple and powerful way to adjust carrier concentration combined with enhanced phonon scattering through point defects and disordered regions is described. By combining experiments with band structure and phonons calculations, we elucidate, for the first time, the underlying mechanism at the origin of intrinsically low thermal conductivity in colusite samples as well as the effect of S vacancies and antisite defects on the carrier concentration. In the second part, the spectacular role of the substitution of V5+ by hexavalent T6+ cations (Cr, Mo and W) on the electronic properties, leading to outstanding power factors [2], will be presented. In particular, Cu26Cr2Ge6S32 sample shows a PF value of 1.53 mW m-1 K-2 at RT that reaches a maximum value of 1.94 mW m-1 K-2 at 700 K. The rationale is based on the concept of conductive “Cu-S” network, which in colusites corresponds to the more symmetric parent sphalerite structure. The interactions within the mixed octahedral-tetrahedral [TS4]Cu6 complexes are shown to be responsible for the outstanding electronic transport properties.

[1] C. Bourgès et al., J. Amer. Chem. Soc. 140 (2018) 2186

[2] V. Pavan Kumar et al., Adv. Energy Mater. 9 (2019) 1803249

10:15 - 10:45

Screening thermoelectric materials with ab initio atomistic modelling and machine learning techniques

O.M. Løvvik[1], K. Berland[2], F. Remonato[1], E. Sagvolden[1], E. Flage-Larsen[1]

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The thermoelectric properties of various known and hypothetical materials have been assessed by first-principles calculations based on density functional theory and the Boltzmann transport equations for electrons and phonons. Half-Heusler alloys and silicides were two important classes of materials in the study. Trends and patterns of the results will be presented. Some of the results were fed to machine learning algorithms, in order to assess thermoelectric performance of a larger number of compositions. Possibilities and limitations of the investigated machine learning methods will be presented. Comparisons with available experiments are favourable; previously well-known materials with high thermoelectric performance are reproduced by the computations. Some materials show higher potential in this theoretical study than what has been proven experimentally, and reasons for this will be discussed.

Applications I

11:15 - 12:45

Room: Panorama

Chair: Jean-Pierre Fleurial

11:15 - 11:30

Thermoelectric Harvesters and the Internet of Things: Technological and Economic Drivers

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In 2006, devices autonomously exchanging information were reported to have outnumbered humans connected to Internet worldwide. In most situations, the Internet of Things (IoT) is populated by remotely deployed devices, so that a need raises for sensing nodes not only exchanging data wirelessly but also operating maintenance-free over their whole predicted lifetime. This implies that either energy sources or renewable energy converters must be embedded in the sensor. Among renewable converters, thermoelectric generators may play a relevant role, whenever temperature differences are available at sensor deployment sites. Aim of this communication is to analyse contexts where TEGs may compete with batteries as power supplies in the IoT. The analysis compares batteries and TEGs (both conventional and integrated) by considering energy and power requirements of the sensing nodes; and in view of the economic competitiveness of both power sources, also accounting for the key issue of their maintenance. It is found that TEGs fully meet power requirements of low-power sensing nodes and that they outperform batteries as of the installation and ownership costs. Moreover, applications where battery replacement is unfeasible will further motivate TEG initial deployment, overcoming the present reluctance to modify sensor design to optimize heat intake and dissipation. Embedded sensors to monitor the stability of bridges and buildings are among the possible examples. Thus, the development of IoT over the next years might provide thermoelectric research and development with the long-awaited opportunity to emerge as a fully recognized tool not only to recover wasted heat but also to locally convert it into the critical, high-value low power needed to support specific applications in the IoT.

11:30 - 11:45

Modeling and Design Optimization of a Thermoelectric Generator for Reducing Fuel Consumption in a Heavy-Duty Vehicle

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Heavy-duty vehicles are responsible for a large proportion of road traffic emissions in the European Union due to their high annual mileage and increasing freight traffic. For this reason, carbon dioxide limits will be introduced in this vehicle segment for the first time. Technological innovations are essential to meet these emission limits. Increasing the efficiency of modern heavy-duty vehicles is an important approach. Today, about 60% of the chemical energy of fuel is lost through waste heat. The use of a waste heat recovery system offers the potential to increase efficiency in order to reduce fuel consumption and thus emissions. The state of the art, however, was not convincing in terms of system efficiency and costs.

Thermoelectric generators provide an attractive solution for a waste heat recovery system with low system complexity. Based on the Seebeck effect, they convert the existing thermal energy of the exhaust gas directly into electrical current. Integrated into the exhaust system of the current vehicle architecture, thermoelectric generators can convert part of the previously unused energy for supplying the vehicle electrical system or charging the battery and relieve the generator. The system advantages are low costs, low system weight and low installation volume.

This paper presents a thermoelectric generator system for modern Euro VI heavy-duty vehicles. For this purpose, a novel approach is presented, which allows a holistic system modelling. Innovative segmented thermoelectric modules and heat exchanger structures will be used to demonstrate how efficiency can be increased. By optimizing the thermoelectric generator system, a significant fuel consumption of 1-2% under dynamic driving conditions is to be achieved. The challenge of optimizing a waste heat recovery system with regard to the total cost of ownership and amortization in 2 years of use is to be demonstrated.

11:45 - 12:00

Radioisotope Power for an Autonomous Ice-Penetrating Cryobot to Explore Icy Worlds

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Ice-penetrating probes for missions to Ocean Worlds have been considered for nearly 20 years. JPL recently funded the development of an end-to-end mission concept for an ice penetrator or cryobot to Ceres, Enceladus, and Europa. The conceptual mission was designed from pre-flight to arrival at an Ice-Ocean Interface (IOI). Since the cryobot would not be tethered to the surface, it would need independent, on-board power sources as it descended through the ice shell over the ocean. The cryobot carries a mix of four different radioisotope thermoelectric generators (RTGs).

The conceptual cryobot carries two Cryobot RTGs (CRTGs) each producing approximately 400 We from 4000Wth. These are the primary power and heat sources for the cryobot. The power would be used for the typical spacecraft functions such a guidance, navigation, and control, and also for powering a drill/cutter head at the nose of the vehicle, and supplying thermal control to various cryobot subsystems as well heating streams of water from melted ice to further enhance drilling/cutting. The cryobot would also deploy communications pucks in the ice. Each would be deployed 1-2 km from each other and enable telecommunications between the lander and the cryobot. The pucks would each be powered by milliwatt RTGs (mW-RTGs) that would store-and-forward commands, troubleshooting information, and positioning, velocity ,and health telemetry. The last of the RTGs would be the Lander Electronics RTG (LERTG), and this one would provide electrical power (~100We) from 1000Wth inventory to power the RF equipment for Direct-to-Earth (DTE) communications.

The mission concept will be summarized along with some of the challenges such as RTG integration, planetary protection, thermal control, communications, and a concept of operations through various mission phases. The information presented about the cryobot and the notional RTGs it would use is pre-decisional and is provided for planning and discussion purposes only.

12:00 - 12:15

Thermoelectric Generator Design and Experimentation for Wast-heat Recovery in a Manufacturing Plant

M. Araiz[1, 2], D. Astrain[1, 2], P. Aranguren[1, 2], Á. Martínez[1, 3], L. Catalan[1, 2], Á. Casi[1]

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There is a need to develop and invest on alternative energy sources in order to fight against the current unsustainable energy situation based on fossil fuels. Thermoelectric generation is one of the technologies that can help us on this matter, being able to produce electric power from waste-heat, a byproduct of several industrial and domestic processes. This would increase the efficiency of the whole process and would reduce the dependency on fossil fuels. One of the ways to improve the performance of the thermoelectric devices is to optimize the heat exchangers, increasing the temperature difference between the faces of the thermoelectric modules, which leads to an increase in the power generation.

This work presents a prototype of a thermoelectric generator developed and tested to recover waste-heat from a combustion process in a manufacturing plant located in Navarre (Spain) where the exhaust gases exit the combustion chamber at 350 °C. The work includes the design and optimization of the heat exchangers used in the hot side of the device in charge of absorbing the heat from the inside duct and drive it to the hot face of the thermoelectric modules. Four bismuth-telluride modules transform part of this heat into electricity and an optimized heat exchanger on the cold side helps to release the rest of the thermal power not converted to the ambient. This cold side dissipator is a heat-pipe that uses free convection to evacuate the heat. This configuration offers a passive with no moving parts device, increasing the lifetime of the thermoelectric generator and reducing any maintenance tasks involved.

12:15 - 12:30

Autonomous volcanic monitoring stations at Teide national park (Spain)

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Volcanic monitoring and vigilance becomes indispensable in any volcanic system in the world. Nevertheless, energy supply of the necessary equipment (seismographs, gas sensors…) constitutes a challenge due to the absence of power grid, the access difficulties, the climatology and the acidic environment associated with volcanoes. Nowadays, energy supply is fulfilled by means of photovoltaic panels and batteries. However, this solution does not guarantee a permanent energy supply: during long snow periods or in case of any failure, due to the access difficulties, data acquisition is lost. In order to face this situation, one of the objectives of ELECTROVOLCAN project (RTC-2017-6628-3) consists in the development of thermoelectric generators that make use of the temperature of the fumaroles available at Teide National Park (Spain) to directly supply electricity to the stations in a robust, compact and reliable way. A first prototype has already been installed at Teide volcano, where there exist 83.5°C fumaroles. The prototype is made of high efficiency heat exchangers based on phase change that try to maximize power generation with no moving parts. The obtained results show the viability of this patented solution, being able to generate 300 mW per thermoelectric module in a continuous, robust, reliable and compact way.

12:30 - 12:45

Assessment of Thermoelectric Generator Concepts incorporating Thermal Control during Driving Cycles

F.P. Brito[1], R. Vieira[1], N. Pacheco[1], J. Martins[1], L. Goncalves[1]

[1]University of Minho, Portugal

The commercial use of thermoelectric generators (TEGs) to harvest the energy wasted through the exhaust of road vehicles has been a long but unfulfilled promise. Exhaust power is highly variable during realistic driving conditions, being a challenge to design a TEG that is able to operate efficiently under those conditions. Conventional systems can be optimized either for low thermal loads, by-passing high power events to avoid over-heating, or they will be designed to absorb high load events and then have a poor performance during low load operation due to thermal dilution. Actual prototypes generally aim towards a compromise between the two situations, leading to less than optimal performance under low loads and substantial heat rejection under high loads.

The lack of thermal performance might be one of the main reasons for the really low global conversion efficiency of most existing TEG prototypes under realistic driving conditions. This efficiency is substantially lower than the already modest nominal efficiency of currently available TEG modules. Bearing in mind the advantages of TEGs (modularity, low to no maintenance needs) and the recent advances in cheap, higher performance thermoelectric materials, TEGs might well become a viable solution for automotive energy recovery, if the aforementioned thermal performance issues of TEGs are addressed.

The present work assesses the performance of TEGs incorporating thermal control through the use of variable conductance thermosiphons/heat pipes. These are embedded in the system, located between the heat source and the TE modules and act as temperature-controlled thermal spreaders. The aim is to maximize the generator output under all driving conditions as the TEGs will be operating close to their optimal temperature without overheating risk. When compared to simple by-pass systems, the proposed concept was able to approximately double the average electric power produced during the driving cycle while still avoiding over-heating.

Chalcogenides I

11:15 - 12:45

Room: Megaron B

Chair: Antonio Goncalves

11:15 - 11:30

Copper iron sulfides as promising thermoelectric materials

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Several minerals containing the earth-abundant elements copper and sulfur, as exemplified by tetrahedrite, colusite and bornite, exhibit promising thermoelectric performances at moderate temperatures. The complex structures adopted by these p-type semiconducting minerals result in very low thermal conductivities and hence values of ZT near or above unity. However, fewer n-type thermoelectric copper sulfides are known (e.g. chalcopyrite, CuFeS2), and their performance is comparatively poor. In our search for cost-effective thermoelectric materials, we are exploring the potential of copper iron sulfides adopting stuffed superstructures of sphalerite as n-type thermoelectric materials. Here were present our recent work on the synthesis and properties the minerals talnakhite (Cu9Fe8S16) and mooihoekite (Cu9Fe9S16).

Samples with composition Cu9Fe8S16 and Cu9Fe9S16 were synthesised by high-temperature reactions as well as by ball milling. Samples with composition Cu9Fe8S16 adopt the chalcopyrite structure. Although initial analysis of X-ray diffraction data indicated that samples with stoichiometry Cu9Fe9S16 adopt the mooihoekite structure, powder neutron diffraction data are consistent with a mixture of mooihoekite (Cu9Fe9S16) and talnakhite (Cu9Fe8S16). Hot pressing Cu9Fe9S16 produces a material that consists primarily of a talnakhite phase. Electrical transport property measurements indicate that Cu9Fe9S16 is an n-type semiconductor. The thermal conductivity of Cu9Fe9S16 is ca. 1.4 W m-1 K-1 at room temperature, significantly lower than that of chalcopyrite (ca. 6 W m-1 K-1), due to structural disorder. This leads to a higher figure of merit than that of chalcopyrite.

11:30 - 11:45

Crystal structure reinvestigation of synthetic thermoelectric $Cu_{22}Fe_8Ge_4S_{32}$ germanite from multi-scale characterizations

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The design and optimization of thermoelectric (TE) materials rely on the intricate balance between thermopower, electrical resistivity and thermal conductivity. Perfecting such a balance is key to reach high values of the figure of merit ZT necessary to improve energy recovery systems. Among the most promising TE materials at medium temperature, complex copper-based sulfides are of double interests as they are usually made of eco-friendly and low cost elements and exhibit intrinsically low thermal conductivity. While those materials have a potential to be used in TE devices, the understanding of their (micro)structure-properties relationships is mandatory to optimize their efficiency through synthesis process and/or chemical substitutions. For instance, we have shown recently that introduction of hexavalent T6+ cations in the synthetic Cu26T2Ge6S32 colusites leads to outstanding electronic transport properties with the highest powder factors among iono-covalent sulfides.1 A detailed structural analysis shows that the electronic properties are governed by the conductive “Cu-S” network distortion through interactions between mixed octahedral-tetrahedral [TS4]Cu6 complexes.1 The TE properties of the synthetic Cu22Fe8Ge4S32 germanite, a derivative structure of colusite, were also reported.2 Despite their closely related crystal structures, the TE properties of germanite remain lower than those of colusites.1,3 Moreover, from thorough structural investigations, we have shown that the crystallographic structure of synthetic germanite is highly different to that reported for natural one. In order to understand the structure-properties relationships leading to different properties in germanite and colusite, a careful knowledge of their structures is necessary. In this presentation will be discussed the crystal structure reinvestigation of the title compound from multi-scale characterizations: Mössbauer spectroscopy, single-crystal XRD, neutron powder diffraction, and anomalous X-ray scattering.

[1] Pavan Kumar et al., Adv. Energy Mater. 2019, 9, 1803249

[2] Pavan Kumar et al., Inorg. Chem. 2017, 56, 13376-13381

[3] Bourgès et al., J. Am. Chem. Soc. 2018, 140, 2186-2195

11:45 - 12:00

Kesterite-Type Chalcogenides as Potential Thermoelectric Materials

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Quaternary chalcogenides of general formula A2BCQ4, where A, B and C are elements from groups 11, 12, and 14 respectively and Q = S, Se, have applications in thermoelectric and photovoltaic devices. The presence of cations with similar atomic numbers hampers X-ray investigations of the detailed structure that plays a key role in the functionality of these materials. Using a combination of neutron diffraction and density functional theory (DFT) we have established that the ground-state structure of a series of materials in which A = Cu, Ag; B = Zn and C = Ge, Sn is that of kesterite. Whilst silver-containing phases are fully ordered, those containing copper show Cu/Zn disorder. DFT reveals that this is associated with minimisation of the inter-planar Zn2+---Zn2+ repulsions.

The electrical transport properties of these materials make stoichiometric kesterite-type phases poor thermoelectrics. However, Cu2GeZnSe4 is unusual in showing an apparent semiconductor to metal transition on heating above 500 K. Structural investigations indicate that this is associated with the delocalisation of copper cations, suggesting this phase may exhibit characteristics of the class of thermoelectric termed phonon-liquid-electron-crystals. We have used chemical substitution to improve the electrical transport properties of Cu2GeZnSe4. Here, two complementary approaches to introduce holes into the conduction band of kesterites will be described. The substitution of the group 14 cation with copper produces a marked reduction in both resistivity and Seebeck coefficient, whilst also suppressing the electronic phase transition. The power factor is more than doubled from that of the stoichiometric phase and figure-of-merit of ZT = 0.2 is achieved at 573 K. The introduction of copper vacancies also leads to partial oxidation of copper, impacting on both the electrical transport properties and the thermal conductivity.

12:00 - 12:15

Effect of order-disorder transition and crystal symmetry on the thermoelectric properties of nanostructured kesterite $Cu_2Zn_nS_nS_4$

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Bulk samples of kesterite (Cu2ZnSnS4, CZTS) were produced by cold-pressing and sintering of CZTS powders obtained via reactive ball-milling [1,2]. Based on the sintering temperature, different polymorphs are observed from the XRD: the starting powder, up to 300°C, forms a cubic F-43m phase with high stoichiometric disorder [3], while for a higher sintering temperature the stable tetragonal I-4 crystal structure is obtained. Thermoelectric measurements point out two main facts: a reversible second-order transition from ordered I-4 to disordered I-42m kesterite structure is observed at 260°C, as the Seebeck coefficient presents a sharp increase [2] (see Figure), and thermal analyses confirm the transition character; at low temperatures, below the phase transition, the cubic kesterite has a greater Seebeck coefficient and a much lower thermal diffusivity than the tetragonal polymorph. This suggests that the increased crystal symmetry and cation-disorder, progressively obtained with disordered I-42m and cubic F-43m structures, may lead to thermopower enhancement due to increased band degeneracy, and suppression of lattice thermal conductivity, possibily due to enhanced phonon scattering [3].

1. Isotta, E.; Pugno, N.M.; Scardi, P. Nanostructured kesterite (Cu2ZnSnS4) for applications in thermoelectric devices. Powder Diffr. 2019, 1–6.

2. Isotta; Fanciulli; Pugno; Scardi Effect of the Order-Disorder Transition on the Seebeck Coefficient of Nanostructured Thermoelectric Cu2ZnSnS4. Nanomaterials 2019, 9, 762.

3. Thermoelectric properties of cubic kesterite produced by high-energy mechanical alloying. (in preparation)

12:15 - 12:30

Process-controlled transport properties of scaled-up synthetic mineral colusite

G. Guélou[1], C. Couder[1], C. Manière[1], G. Marnier[1], P. Martin[1], E. Hug[1], P. Lemoine[2], C. Coureau[3], E. Guilmeau[1]

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Recently, the mineral colusite Cu26T2M6S32, where T is a group 5 or 6 transition metal and M is Sn or Ge, has been the subject of an increased level of attention due to its peculiar transport properties and excellent thermoelectric performance. Despite being identified only 5 years ago as a potential candidate for thermoelectric application,[1] and despite relatively few studies, colusite-based materials stand out by their high figure of merit, around unity at medium-range temperature, and the deep level of understanding of the structure-property relationship that was achieved in a relatively short time.[2,3]

In an effort to drive colusite towards industrial scale and another step closer to reaching global application, we have undertaken multiple studies regarding large scale synthesis, impact of processing conditions, stability and mechanical properties of environmentally-friendly Cu26V2Sn6S32. Our latest fundamental research, carried out using a wide range of tools including experimental and theoretical contributions, will also be discussed.

[1] K. Suekuni, F. S. Kim, T. Takabatake, J. Appl. Phys. 2014, 116, 2.

[2] C. Bourgès, Y. Bouyrie, A. R. Supka, R. Al Rahal Al Orabi, P. Lemoine, O. I. Lebedev, M. Ohta, K. Suekuni, V. Nassif, V. Hardy, R. Daou, Y. Miyazaki, M. Fornari, E. Guilmeau, J. Am. Chem. Soc. 2018, 140, 2186.

[3] V. Pavan Kumar, A. R. Supka, P. Lemoine, O. I. Lebedev, B. Raveau, K. Suekuni, V. Nassif, R. Al Rahal Al Orabi, M. Fornari, E. Guilmeau, Adv. Energy Mater. 2018, 9, 1803249.

12:30 - 12:45

Nanograined low doped chalcopyrite – route to the optimization of thermoelectric properties

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The thermoelectric potential of chalcopyrite CuFeS2 is underlined by its chemical benignity and economic affordability. The thermoelectric efficiency, however, is at moderate temperatures essentially limited by the high lattice thermal conductivity. Most concretely at optimized doping the thermal conductivity of dense ceramics amounts to □~7 Wm-1K-1 with promising and robust, temperature independent, power factor of ~10-3 Wm-1K-2 as demonstrated recently for e.g. Cu1-xZnxFeS2 and Cu1-xPdxFeS2 ceramics [1,2]. We have probed various substitutions, which should theoretically induce both the n-and p-type doping. Our experimental data unambiguously confirm the highest thermoelectric potential of n-type chalcopyrite. Moreover, we demonstrate, that high-energy milling can be used for (i) rapid mechanochemical synthesis of chalcopyrite phase from elemental copper, iron and sulfur, for (ii) mechanical activation of natural mineral and for (iii) one-pot synthesis of doped chalcopyrite. Most importantly mechanochemical synthesis leads to the nanograined ceramics with highly depressed thermal conductivity comparing to micrograin ceramics [3]. As chalcopyrite CuFeS2 is one of the strongest known antiferromagnets with Neel temperature exceeding 800 K and due to the close interconnection between the thermal, electric transport and magnetic interactions we study besides the impact of grain size/nanostructuration the thermoelectric characteristics in connection to the magnetism. Among all the thermal conductivity and magnetoresistance are discussed both with respect to the grain size, doping, and magnetic response. The observed results on nanostructured chalcopyrite confirm the promising technological potential of high-energy milling with respect to thermoelectric properties of CuFeS2.

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References

1. H. Y. Xie et al., Adv. Energy Mater. 7, 1601299 (2017)

2. J. Navratil et al., J. Electron. Mater. 48, 1795 (2019).

3. E. Dutková et al., Advanced Powder Technology 29 (2018) 1820–1826

Theory and Modeling I

11:15 - 12:45

Room: Megaron C

Chair: Neophytos Neophytou

11:15 - 11:30

Estimations of thermal conductivity and thermoelectric performance through phase transitions

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The accurate characterization of thermal conductivity κ, particularly at high temperature, is of paramount importance to many materials, thermoelectrics in particular. The ease and access of thermal diffusivity D measurements allows for the calculation of κ when the volumetric heat capacity, ρc, of the material is known. However, in the relation κ=ρcD, there is some confusion as to what value of heat capacity should be used in materials undergoing phase transformations. Herein, it is demonstrated that the Dulong-Petit estimate of heat capacity at high temperature is not appropriate for materials having phase transformations with kinetic timescales relevant to thermal transport. In these materials, there is an additional capacity to store heat in the material through the enthalpy of transformation ΔH. Namely,

$$\rho c = C + \Delta H \, d\phi/dT$$

is the total heat capacity for a material that has an order parameter ϕ that can respond “instantly” to temperature changes. Here, C is the intrinsic heat capacity (e.g. the Dulong-Petit heat capacity). It is shown in a model Zn4Sb3 system that the decrease in D through the phase transition at 250 K is fully accounted for by the increase in total heat capacity. Importantly, κ changes smoothly through the phase transition. Consequently, reports of κ diverging through phase transitions have likely overlooked the effects of excess heat capacity on thermal properties measurements and overestimated the thermoelectric efficiency, zT.

11:30 - 11:45

The annealed-nanograin phase for simultaneous increase of the conductivity and the Seebeck coefficient and large thermoelectric power factor enhancement

X. Zianni[1]

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We propose the annealed-nanograin (a-NG) phase as a new route for high thermoelectric performance. Thermal annealing of originally defective nanograins decreases ionized defects in the core of the grains and can simultaneously stimulate higher concentration of ionized defects at grain boundaries to fulfill overall charge neutrality. Then, a transition takes place from dominant ionized impurity scattering to dominant phonon scattering. Charged grain boundaries form energy barriers that filter carriers. Synergy between defects, charge neutrality and energy filtering activated by thermal annealing leads to high mobility, simultaneous increase of the conductivity and the Seebeck coefficient and large enhancement of the thermoelectric power factor. We will present the theoretical model and experimental validation [1]. We will compare the transport properties of the a-NG phase and of the two-phase grain emphasizing the transition from two-phase transport to single-phase transport that leads to enhancement of the thermoelectric efficiency.

[1] X.Zianni and D.Narducci, Nanoscale 11, 7667 (2019)

11:45 - 12:00

Looking for new thermoelectric materials among ternary intermetallics using high-throughput calculations

C. Barreteau[1], J. Crivello[1], J. Joubert[1], E. Alleno[1]

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Novel high-performance materials are needed for developing thermoelectric devices. One way to answer this need is to screen a large number of compounds by first-principles calculations and to synthesize the most promising compounds.

We focus our investigation on the ternary intermetallic compounds T-M-X, with T a transition metal, a rare earth or an alkaline earth metal, M an element from the first line of the transition metal and X, a metalloid. For each prototype, all the possible T-M-X combinations are investigated by DFT calculations. Among all these candidates, those which are predicted as thermodynamically unstable and metallic are dismissed. For the most promising compounds, predicted as stable and semiconductor, complementary calculations as the phonon band structure and additional BoltzTrap electronic transport calculations are carried out to better assess their thermoelectric properties. After those theoretical steps, experimental investigations are performed to confirm calculations.

The study of the equimolar TMX in four different prototypes lead to the investigation of 2280 possible configurations. Then our screening process allowed us to highlight more than 45 possible new semiconductors. Among these, new compositions such as HfCoP, SrCuSb or TaFeSb were predicted to be stable and non-metallic. Complementary calculations allowed to estimate their lattice thermal conductivity and Seebeck coefficient.

[1] Barreteau C. et al., Looking for new thermoelectric materials among TMX intermetallics using high-throughput calculations, Comput. Mater. Sci., 156 (2019) 96-103

12:00 - 12:15

A theoretical model for the Seebeck coefficient in superlattices and nanocomposite materials with partial energy relaxation

V. Vargiamidis[1], M. Thesberg[2], N. Neophytou[1]

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[2]Technical University of Vienna, Austria

Nanostructured materials have shown great potential to achieve improved thermoelectric performance, not only due to lower thermal conductivities, but also due to higher power factors. The power factor improvements come primarily from energy filtering, which results in a higher Seebeck coefficient S. In nanocomposites with feature sizes similar to the electronic mean-free-paths, however, S is not only determined by the bulk Seebeck values of the individual materials but, in addition, by the energy relaxation process of electrons as they propagate over the potential barriers and lose energy to relax into the wells. The intermixture of the properties of the two regions requires involved computational modelling to accurately determine the composite S, usually through ‘real-space’ Monte Carlo or the quantum mechanical non-equilibrium Green’s function (NEGF) method. However, these methods are either complex or time-consuming, or both.

Here we present a simple analytical model for the Seebeck coefficient of a channel with embedded superlattice (SL) barriers for energy filtering, which explicitly takes into account the details of energy relaxation due to electron-optical phonon scattering. The model mimics either a SL or a nanocomposite, or any material in which carrier transport alternates between potential barriers and wells. Importantly, the model requires only four relatively easily determined parameters: the bulk Seebeck coefficients of the two materials that form the superlattice, the energy relaxation length of carriers in the wells, and the length of the wells. We validate the model against advanced NEGF simulations, and we find very good agreement for a range of structural and material physical properties (see attached Figure). The model would prove useful in the identification of material combinations and the estimation of ideal sizes of nano-engineered materials with enhanced power factors. As we show, only when energy relaxation is taken into account, significant power factor improvements can be achieved.

12:15 - 12:30

Accessing lattice thermal conductivity of complex crystal structures via machine learning interatomic potentials

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The properties of heat transfer via crystalline lattice are of prime importance for thermoelectric conversion, microelectronics, thermal insulation, etc. New materials with potentially attractable thermal properties could be developed, and many of them have complex crystal structures. To accelerate the discovery of such materials computational methods with predictable power are needed.

Unfortunately, the determination of lattice thermal conductivity of complex structures remains an issue even for modern computational techniques. The problem is two-fold. First, large (usually several tens) number of atoms in the unit cell make methods in reciprocal space, like Boltzmann transport equation (BTE) approach, unfeasible. Second, for large-scale molecular-dynamics (MD) simulations of heat transfer or heat dissipation accurate and reliable interatomic potentials are required.

In present work we merge the quantum-mechanical accuracy of lattice dynamics description with the speed of classical force-fields via machine-learning (ML) techniques. The ML interatomic potentials in MTP form [1] were obtained by active learning on the density functional theory (DFT) based calculations. As an example, we considered CoSb3 skutterudites. With only several hundreds of DFT calculations, accurate and reliable potentials were constructed. We use them to calculate thermal conductivity (TC) either via BTE for phonons, and via Green-Kubo method. The results are very close either to the result of ab-initio molecular dynamics, and to the experiments. We believe that such a technique will allow simple yet accurate prediction of TC of complex compounds.

12:30 - 12:45

Phonon Lifetimes in $S_rT_iO_3$ Investigated with High-Energy Resolution Neutron Spectroscopy

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[2]Max Planck Institute for Solid State Research Stuttgart, Germany
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Computational materials design based on first-principle calculations holds a huge potential in identifying novel compounds with superior functional properties. For single crystals, the progress made with ab initio methods allows to calculate wavevector-dependent relaxation rates for every phonon mode in the Brillouin zone. Essentially, it is thus possible to determine the macroscopic thermal conductivity from the lifetime-limiting phonon-phonon and phonon-electron interaction on the microscopic level. Since low intrinsic thermal conductivity is an asset for enhanced thermoelectric performance, numerical modelling of phonon lifetimes is an important ingredient to predict novel high-performance thermoelectric materials. However, it is mandatory to validate the underlying theoretical models which are based on approximations. Thus experimental data on phonon lifetimes is required which allows to test the predictive power of numerical calculations.

We have used inelastic neutron scattering techniques to measure phonon lifetimes in the perovskite SrTiO3 which is known to offer good thermoelectric properties. Both, triple-axis spectroscopy (TAS) which probes the scattering function S(Q,w) in the energy domain and neutron resonance spin-echo (NRSE) spectroscopy which probes the intermediate scattering function I(Q,t) have been employed. We discuss recent results obtained by neutron triple-axis spectroscopy and neutron resonance spin-echo spectroscopy pin-pointing phonon lifetimes on an absolute energy scale. We further discuss Larmor diffraction measurements which deliver important information about phonon scattering at the domain walls. These experiments provide a thorough basis to resolve discrepancies between the calculated and measured lifetimes and to further develop theoretical models for lattice-mediated heat propagation.

Nanomaterials I

14:15 - 15:30

Room: Panorama

Chair: Daryoosh Vashaee

14:15 - 14:30

Boosting the efficiency of thermoelectric materials using porous alumina: recent examples

M. Martin Gonzalez[1]

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Nowadays, it seems to be clear for a great majority of people that energy needs to be generated, conserved, and recycled in better ways. We need to prevent as much as possible to waste it, since every joule saved means less fossil fuel burnt. Because of that harvesting waste energy are becoming a popular among the scientific community. And, one of the most promising approaches is nano-engineering thermoelectric materials to produce devices.1,2 Thermoelectrics are a class of materials able to convert wasted heat energy into electricity. By controlling nano-structuration properly, their efficiency increase. And, since the devices have no moving parts, they are extremely reliable.

In this talk, different approaches to nanostructure different materials will be shown and how those approaches help to increase the final efficiency of the material and the final device. I will show recent examples: large area antidote SiGe nanomeshes,3 and a three-dimensional interconnected Bi2Te3 nanowires array.4,5

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2. JA Perez-Taborda, L Vera, O Caballero-Calero, EO Lopez, JJ Romero, F Briones, M. Martin-Gonzalez “Pulsed Hybrid Reactive Magnetron Sputtering for High zT Cu2Se Thermoelectric Films” Advanced Materials Technologies 2018, 2 (7), 1700012.

3. JA Perez-Taborda, MM Rojo, J Maiz, N Neophytou, M Martin-Gonzalez “Ultra-low thermal conductivities in large-area Si-Ge nanomeshes for thermoelectric applications” 2016, Scientific Reports 6, 32778.

4. A Ruiz-Clavijo, Y Tsurimaki, O Caballero-Calero, G Ni, G Chen, S.V. Boriskina, M. Martín-González, “Engineering a full gamut of structural colors in all-dielectric mesoporous network metamaterials” ACS Photonics, 2018, 5 (6), pp 2120–2128

5. A Ruiz-Clavijo, O Caballero-Calero, M Martín-González “Three-Dimensional Bi2Te3 Networks of Interconnected Nanowires: Synthesis and Optimization” Nanomaterials, 2018, 8 (5), 345

14:30 - 14:45

Hybrid thermoelectrics based on mesoporous silicon filled with functionalized molecules

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Mesoporous silicon (pSi) structured on nanometer-sized length scales is a promising yet challenging candidate material [1] for thermoelectric applications. Its exceptionally low thermal conductivity, originating in porosity and increased phonon boundary scattering, provides a promising route to overcome the poor thermoelectric performance of bulk-Si. However, electron boundary scattering and charge carrier depletion at interfaces need to be minimized because of their detrimental impact on the thermoelectric conversion efficiency. Low power-factors are severe obstacles for the implementation of pSi-based thermoelectrics.

Thermoelectric polymers are of interest for lightweight and flexible applications and come along with low costs and easy synthesis routes [2]. Recent years have witnessed the emergence of highly performing, thermoelectric polymers that achieve power-factors up to hundreds of μWm-1K-1 and high figure of merits [2]. Their applications are however limited by a lack of thermal and longtime stability.

This contribution presents the synthesis and thermoelectric characterization of hybrid materials that combine pSi and conductive polymers. The main objective is to benefit from the complementary properties of organic and inorganic hybrid constituents and potentially to trigger synergy effects. We discuss the synthesis of pSi by electrochemical etching. P3HT, polypyrrole and other functionalized molecules are reviewed as candidates for fillers. Synthesis of hybrids by melt infiltration is one presented approach to incorporate the polymer into the pSi matrix. Nitrogen sorption isotherms and scanning electron microscopy reveal the morphology of pSi and synthesized hybrids. Hall effect, SBA and LFA measurements complete the thermoelectric characterization of our samples. An outlook on the application of scattering techniques like GISAXS/GIWAXS to elucidate the polymer morphology in the pores closes the presentation.

[1] J. de Boor et al., Appl Phys A (2012) 107:789–794

[2] Yao et al., Macromol. Rapid Commun. 2018, 39, 1700727

14:45 - 15:00

Thermoelectric properties of thin film of Graphene-Mesoporous semiconductor nanocomposites

S. Sauze[1, 2], A. Stolz[3], P. Brault[3], N. Semmar[3], M.R. Aziziyan[1, 2], R. Arès[1, 2], A. Boucherif[1, 2]

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Nanoporous semiconductors such as silicon (Si) and germanium (Ge) have been predicted, theoretically, to be one of the most appealing candidates for advanced thermoelectric applications. [1] In this respect, nanocomposites based on mesoporous semiconductors and 3D graphene-like coating allowed to obtain hybrid physical properties that results with an expected enhanced figure of merit. Therefore, they have attracted interest of many researchers for their performance in the thermoelectric devices and batteries. [2-4] In this work, we have evaluated the potential of nanocomposite materials, based on Si and Ge, for thermoelectric applications. The nanocomposites were synthesized in two steps; first, porous layer formation by means of electrochemical etching process; second, carbon coating with Chemical Vapor Infiltration (CVI) technique. Then, various material properties were studied using different characterization methods; namely, Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscopy (TEM). Moreover, Seebeck coefficient measurements were performed through the material (in depth) in addition to the in-plane characterizations. For this purpose, a new measurement bench was developed and tested. The bench is composed of two Peltier modules for the monitoring of the heating and the cooling stages. Furthermore, four electrical probes on each side of the samples are used to collect the voltage data. In this setup, the low voltage level (expecting few μV) can be measured accurately thanks to the Faraday cage tied to the common ground. Consequently, study of Seebeck effect through the samples have become possible and it has enabled us to distinguish thermoelectric properties of thin films from that of the employed substrates. In this report, we will discuss synthesis of graphene-like coated Si and Ge nanocomposites as well as their electrical and thermal behavior under investigated conditions.

15:00 - 15:15

Organic-inorganic hybrid thermoelectrics based on mesoporous silicon and poly(3,4-ethylene-dioxythiophene) (PEDOT) polymer blends

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This contribution presents synthesis and thermoelectric characterization of mesoporous silicon (pSi) and related organic-inorganic hybrid systems. We discuss the synthesis of freestanding pSi membranes by electrochemical etching. Infiltration of thiophene based conductive polymer blends, PEDOT:PSS, PEDOT:Tos and PEDOT:Anisole into pSi by top-down and bottom-up synthesis routes provides an attractive way to form novel organic-inorganic thermoelectric hybrids. Specifically, hybrid synthesis via drop casting, vapor phase polymerization and electro-polymerization are compared. Important morphological parameters of pSi membranes such as pore size distribution, specific surfaces and porosities are characterized by quantitative analysis of SEM micrographs and quantitative analysis of Nitrogen sorption isotherms. Nitrogen sorption isotherms, as a volume sensitive probe, particularly show overall changes in pore size distributions, specific surfaces and porosities of pSi membranes upon changing etching parameters. Our characterization demonstrates successful incorporation of polymers into the pSi pore space. Macroscopic transport measurements that probe electrical and thermal conductivity, Hall mobility, charge carrier concentration and Seebeck coefficient reveal the effect of the morphology on thermoelectric properties of the pSi membranes. A comparative analysis of thermoelectric properties of pSi membranes and pSi/PEDOT hybrids concludes our presentation.

15:15 - 15:30

Ionic liquid ferrofluids for thermoelectrics applications

A. Talone[1, 2], A.M. Testa[1], S. Jovanovic[3, 4], S. Laureti[1], A. Capobianchi[1], E. Agostinelli[1], G. Varvaro[1], P. Imperatori[1], M. Salvador[1, 5], D. Peddis[1, 6]

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[2]Dipartimento di Scienze, Università degli Studi di Roma Tre, Italy
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[5]Department of Physics, University of Oviedo, Spain
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Spinel magnetic nanoparticles (MNPs) with different stoichiometry (Fe3O4, CoFe2O4 and Co0,5Zn0,5Fe2O4), has been prepared by the polyol method, in which metal (II) and iron (III) nitrates are dissolved in polyol and refluxed. X-Ray Diffraction (XRD) shows the presence only of cubic spinel phase (Pdf-3-864) with crystallites size around 4,5 nm (determined by Scherrer's equation). No other phases have been detected. Transmission Electron Microscopy (TEM) confirms the presence of almost spherical particles, with mean particles equal, within the experimental error, to values extracted from XRD. This indicate the high crystalline degree of the materials. By an exchange ligand process, MNPs has been coated by hydrocaffeic acid (HCA) and then dispersed in water. Thermogravimetric analysis (TGA) and Fourier Transform Infrared spectroscopy (FT-IR) have been used in order to investigate molecular coating of the particles and relative percentage of organic and inorganic (i.e. magnetic) part. In order to disperse in ionic liquid, water is added to create an aqueous dispersion, to which the 1-ethyl-3-methylimidazolium acetate (EMIMAC) will subsequently be added. This mixture thus formed is placed under vacuum. In addition, direct dispersion in EMIMAC was performed. Field and temperature dependence of magnetization of the powder and the dispersions in water and ionic liquid has been investigated. All the samples show superparamagnetic behaviour (i.e. Hc = 0, Mr = 0) at room temperature with value of saturation magnetization in line with expected for nanoparticles (Ms=70 Am^2/Kg). Measures at 5K, in the case of cobalt ferrite, the powder has values of Hc of 0,93 T and Ms of 90 Am^2/Kg. The direct dispersion presents Hc of 0,90 T and Ms 81 Am^2/Kg, higher values respect to indirect method (0,86 T and 76,5 Am^2/Kg). Interparticle interactions has been investigate by remanent magnetic measurement (i.e. DCD, IRM): dipolar interactions decrease in ILs dispersion respect to powder.

Modules I

14:15 - 15:30

Room: Megaron B

Chair: Krzysztof Wojciechowski

14:15 - 14:30

Scalable and efficient ceramic interconnect technologies for the integration of Half-Heusler thermoelectric alloys in modules

J. Schilm[1], D. Zuckermann[2], A. Rost[1], J. Marien[2], M. Trache[1], V. Macin[2]

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The challenge in expanding the range for thermoelectric power generation to temperatures above 300 °C is not only an issue of thermoelectric materials but also for interconnect technology on the hot side of modules. Replacing bismuth telluride by much more environmentally friendlier Half-Heusler alloys results in a remarkable increase of exploitable temperatures of up to 800°C. In order to make optimum use of the properties of these materials, low-resistance and temperature-stable current collectors as well as dielectric substrates are required as separators. A commonly applied solution involves direct copper bonded alumina substrates (DCB) consisting of a copper sheet bonded on a ceramic substrate made of aluminium oxide. Beside the advantage of high temperature stability, notably of the ceramic component, this solution lacks on thermal cyclisability, critical thermomechanical stresses and cost targets to be met for commercially marketable modules.

Within the scope of this work new concepts for hot side interconnects are presented. When ceramic supported metallisations are applied it is necessary to achieve a maximum exploitation of the expensive ceramic material. This can be realized by module concepts with segmented hot side designs, which also minimizes thermomechanical stresses. Efficient metallisation (thick film and active metal brazing) and dicing technologies allow a localized usage of the ceramic material by covering the active material only. The use of metal supported hot side interconnects is possible by using inexpensive steel substrates. Customized glass-ceramic materials have been developed, which can be applied to steel substrates by screen printing as layers with thicknesses below 50µm. After firing the layers have a thermal stability up to 600°C. Commercial metallisation pastes based on copper and silver are used for producing metallisation layers on top of the glass ceramics. These concepts have been transferred to an automated production process for a new generation of cost efficient thermoelectric modules.

14:30 - 14:45

Reliability assessment of thermoelectric device for power generation

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Thermoelectric device has be paid attention by rising attention for renewable and sustainable energy. Especially thermoelectric devices for power generation (TEG) have been widely investigated for direct energy conversion and electricity generation from waste heat sources in automobiles, incinerators, etc. A large temperature gradient across the TEG is required for significant power generation, and this temperature gradient leads to significant thermal stress. The performance of TED degrades with thermal cycling as the constituent materials and interfaces are exposed to large temperature gradients [1].

In this study, reliability assessment system was developed to evaluate fatigue life of TEG under thermal cyclic loading. It consists of loading part, load cell, power supplier, cooling system, and data acquisition system. Thermal cyclic loading was applied to the TEG by applying current to TEG to increase the upper substrate temperature of TEG, and by changing the current direction to decrease the upper substrate temperature when the target temperature was reached. At the same time the lower substrate temperature of TEG was controlled by 30 ℃ using cooling system. By experiments, relationship between temperature difference and life (ΔT-N curve) was obtained. ΔT-N curve was changed stress – life (σ-N) curve through thermoelectric analysis and thermal stress analysis. If we use stress - life curve of TEG, we can expect the lifetime of the TEG for thermal cyclic loading. We also measured the changes of the electrical resistance, ZT (figure of merit) and power generation performance of TEG by thermal cyclic loading.

Keywords: Thermoelectric device, power generation, thermal cyclic loading, lifetime, power generation performance, figure of merit

References

[1] W. Park, M. T. Barako, A. M. Marconnet, M. Asheghi, and K. E. Goodson, “Effect of Thermal Cycling on Commercial Thermoelectric Modules”, 2012 13th IEEE Intersociety Conference on Thermal and Thermomechanical Phenomena in Electronic Systems (ITherm).

14:45 - 15:00

Development of thermoelectric segmented (FGM) n-leg with contacts over a wide temperature range (50 - 600 °C)

Z. Dashevsky[1], T. Parashchuk[1], K. Wojciechowski[1, 2]

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[2]AGH University of Science and Technology, Poland

The absence of mechanical parts makes thermoelectric (TE) devices very reliable for different applications. Today, they are used in situations, where reliability is the most important factor, e.g., for electricity generation in remote regions for extended periods up to 20 years and in the wide operating temperature range (50 °C- 600 °C). The work is proposed to develop high efficient thermoelectric n-leg with commutative contacts by one pulse electric current (PECS) process.

The segment of TE material, based on n-type Bi2Te3-xSex, is proposed for use from 50 °C up to 300 oC temperature range. PbTe semiconductor, doped by In and I, is a material which excellently fit the higher temperature range from 300 °C up to 600 °C. Such a combination of dopants gives the possibility for both attuning Fermi level at an optimal position and keeping the required concentration of carriers at high temperatures. The indium level is located close to the bottom of conduction band EC, which is required for the maximum value of power factor S2σ (S is the Seebeck coefficient, σ is the electrical conductivity). High electron concentration caused by indium and iodine dopants at high temperature minimizes the influence of minority carriers at n-PbTe, which drastically decreases their thermoelectric efficiency.

For the fabrication of the metallic (commutative) contacts, we propose to use chromium for the cold side and iron for the hot side (Th ~ 600 °C).

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15:00 - 15:15

Integrated Thermoelectric Sensors based on Quantum Dots Superlattices for Thermal Management Applications

G. Savelli[1], J. Colonna[2], M. Keller[3], D. Wendler[3], P. Faucherand[1], A. Royer[2]

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[3]IMTEK / Univ. Freiburg, Germany

Due to technology scaling, temperature became one of the most important constraints in Integrated Circuit (IC) design, power consumption, and lifetime over the past years. This requires a pro-active approach to the thermal management of computational devices, in particular monitoring accurately their thermal state in real-time.

Considering IC, the temperature is usually monitored by embedded absolute temperature sensors, which continuously capture the surface temperature of an IC at specific locations. Their major drawbacks are the silicon area overhead and the limited approaches to their implementation. Moreover, the fabrication must comply with the technology process of the IC into which they are embedded and they need to be powered.

We developed planar micro-ThermoElectric Sensors (µTES) adapted to be directly manufactured on a silicon-based interposer. These µTESs use nanostructured thermoelectric (TE) materials, i.e., Quantum Dots Superlattices (QDSL), which consist of TiSi2 nanoparticles embedded in a doped SiGe matrix. These nanostructured materials achieve higher performances than their corresponding bulk SiGe counterparts as we showed previously1,2. However, this is the first time that such nanostructured materials were integrated in a TE device. The µTES were manufactured using a standard CMOS process and are thus very compact with a typical size of 500µm x 1mm. The performance of QDSL-based µTESs was compared to bulk SiGe-based µTESs. Up to 75% higher sensitivities were measured for QDSL-based µTESs compared to SiGe-based µTESs, which demonstrates the impact of the nanostructuring on the devices performance. Moreover, several µTESs were integrated on an interposer near thermal sources in order to perform a thermal mapping. For this purpose, a dedicated integrated Read-Out Interface was designed and implemented, which captures the µTES signals simultaneously. Measurements show that their output signals correspond to their distances to the heat sources and have a very fast response time of less than 4ms.

15:15 - 15:30

High power thermoelectric generators based on large arrays of silicon nanowires

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[3]Università di Pisa, Italy

Silicon nanostructures, such as nanowires, show a very low thermal conductivity together with a very high electrical conductivity if suitable doping values are used. Hence, Si nanowires (SiNWs) could allow the use of silicon, which is an unexpensive, biocompatible and technologically affordable material, for thermoelectric purposes. We developed a top-down and low cost process, based on the metal assisted etching technique, for the production of a large amount of vertical silicon nanowires (silicon nanowire forests): more than 10^7 nanowires/mm^2 as small as 50 nm and longer than 100 um can be simultaneously fabricated on surfaces of several cm^2. Si nanowire forests are perpendicular to a silicon substrate (bottom contact); the SiNW top ends can be contacted exploiting a procedure, previously developed, for the deposition of a copper layer. Therefore, it is possible to assemble a large amount of SiNWs electrically in series and thermally in parallel so that thermoelectric modules with surfaces of several cm^2, can be fabricated.

The thermal conductivity resulted as low as 1 W/(m K) for SiNW forests heavily p-doped. The Seebeck coefficient has been measured for several doping values, and resulted in line with that achieved on bulk silicon. The electrical resistance is very low (order of 10 mOhm cm^2) for heavily doped nanowire forests.

Our silicon nanowire-based thermoelectric modules generate an output power of several hundreds of uW/cm^2, with temperature differences of the order of 20 degrees. Even if this power value is promising for applications of energy scavenging, it can be improved of at least one order of magnitude because the electrical resistance, although low, is affected by the parasitic resistance of the contacts and of the silicon substrates. Strategies for decreasing the effect of these parasitic resistances, which could lead to a noticeable increasing of the output power, are under investigation.

Oxides I

14:15 - 15:30

Room: Megaron C

Chair: Emmanuel Guilmeau

14:15 - 14:30

Do the spins enhance the thermopower of both magnetic oxides and sulfides?

M. Antoine[1], B. David[1]

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In layered p-type cobalt oxides, magnetothermopower (MTEP) measurements revealed the spin entropy contribution to the Seebeck coefficient in the Ca3Co4O9 and BiCaCoO Curie-Weiss paramagnets [1, 2]. For the latters, when the magnetic moments are disordered (H=0), the magnetization being M~0, the entropy per carrier T is maximized. But when H increases, M= XH increasing (X= magnetic susceptibility), T decreases leading to the decrease of the Seebeck coefficient (S). In that respect, ruthenates are a model system to study the impact of the magnetic groundstate on S: SrRuO3, CaRuO3 and CaCu3Ru4O12 are ferromagnet, Curie- Weiss and Pauli paramagnets, respectively [3,4]. More recently, we have extended such MTEP measurements to the Sr2Fe1+xRe1-xO6 ferrimagnets [5]. Moreover, similar spins effect on S has been also discovered for the first time in a sulphide. CuCrTiS4 is a spinel showing a spin glass state with a negative MTEP effect of -26% in 9T at 20K [6]. This shows the interest of the MTEP measurements to study other magnetic sulfides.

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14:30 - 14:45

Investigation of the Electronic Transport Mechanism of La- and Y-doped $Ca_2M_nO_4$

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Improving electronic transport properties of thermoelectric materials is crucial for efficient conversion of heat to electricity. CaO(CaMnO3)m compounds are promising due to their intrinsically low thermal conductivity, e.g. 0.75 Wm-1K-1 at 900 K [1], which is associated to internal rock-salt CaO layers residing between adjacent CaMnO3 perovskite sub-cells. This study is aimed at increasing the electrical conductivity of Ca2-xRxMnO4 bulk materials, where R = La or Y, and 0.01 ≤ x ≤ 0.20. We prepare compounds with different doping levels of either Y or La applying standard solid state reaction routines [2]. The phase purity, chemical composition and microstructure are characterized, and electronic transport coefficients are measured in the range of 300-1000 K. It is found that Y-doping generally facilitates electronic transport compared to La-doping by up to two times. This trend is elucidated in terms of the small polaron hopping model, indicating that La-doping increases the conduction activation energy by 7-21 % in the range of 300-750 K, compared to Y-doping. Density functional theory (DFT) calculations corroborate this interpretation, showing that La substitution for Ca in Ca2MnO4 increases the transverse sound velocity by up to 33 % compared to Y substitution, implying that La-doping increases bond strength, thereby hindering lattice distortions. This is also manifested by higher shear moduli and Debye temperatures obtained for La-substituted compounds. Our results suggest that energy barriers for electronic transport in oxides may be tailored by point defect engineering.

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14:45 - 15:00

Near-broken gap junction for ohmic high temperature direct-junction thermoelectrics.

R. Schuler[1], F. Bianchini[1], H. Fjellvåg[1], T. Norby[1]

[1]University of Oslo, Norway

We present what appears to be the first broken-gap junction (BGJ) of transition metal oxides to the field of high-temperature direct-junction thermoelectric generators. Broken-gap junctions exhibit no rectification and thus are of special interest for direct-junction thermoelectric couples with omitted metal interconnects.

We introduce the concept using two different iron tungstates: n-type Fe2WO6 and p-type FeWO4. The two materials show high conductivity and thermopower, and are in equilibrium with each other over an immiscibility gap. In contrast to conventional n-p junctions, the I-V characteristics of the assembled junction exhibit fully ohmic behavior over the entire accessible temperature range (-196 to 1100C). This points towards a broken-gap junction alignment between the two semiconductor band structures, as commonly utilized in the field of tandem solar cells. X-ray photoemission spectroscopy confirms a band gap offset of 1.8 eV, consistent with the formation of a broken-gap junction. We simulated band structures by ab initio calculations using a hybrid functional to gain a deeper insight in the nature of the bands involved in the junction. The junction is thermochemically stable, and exhibits no sign of formation of other phases and a junction resistance of merely 1 Ωcm2. We propose the utilization of broken gap junctions as a key solution to the otherwise rectifying n-p junctions in direct-junction thermoelectrics.

15:00 - 15:15

Fully-inorganic p-type $Ca_3Co_4O_9$ and n-type ZnO thin films for flexible thermoelectrics

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The development of fully-inorganic flexible thin film materials is essential for flexible thermoelectric applications in a wide temperature range, e.g. harvesting power from the hot surfaces with varying geometries (e.g. hot pipe) and for near room temperature wearable applications. In particular, this is important for applications in hostile environments, e.g. wearable applications for fire workers. The organic materials are flexible, however, they cannot sustain high temperature and degrade over time. The inorganic materials are stable, however, the challenge is associated with their inherent rigidity, which restricts their use for flexible applications. Here, we report the growth of p-type Ca3Co4O9 and n-type ZnO thin films on flexible mica substrates. The films Ca3Co4O9-on-mica are grown by an interesting two-step sputtering/annealing method. The CaO-CoO films are first cosputtered in reactive atmosphere from the elemental targets of Ca and Co, followed by annealing at 700 ºC under O2 flow to obtain the final phase of Ca3Co4O9. The advantage of sputtering/annealing method is that it allows faster deposition and allows the tailoring of the films' structure at nanoscale. The nanostructuring in Ca3Co4O9 films depends on the pattern of structural evolution during thermally induced three-stage phase transformation, which is guided by the surface and strain energy and the distributions of CaO and CoO phases in the as-deposited films. For n-type component, the Ga-doped ZnO films are deposited by atmospheric pressure metalorganic chemical vapor deposition (APMOCVD). Both the Ca3Co4O9 and ZnO films are bendable to the bending radius of 14 mm, while sustaining the high power factor, above 0.1 mWm-1K-2 in a wide temperature range, from room temperature to 400 ºC. With this high power factor and mechanical flexibility, the grown Ca3Co4O9-on-mica and ZnO-on-mica films open a new opportunity for fully-inorganic flexible thermoelectric applications.

15:15 - 15:30

Control of Thermoelectric Properties of TiO2 Oxide Ceramics by Niobium Doping

X. Liu[1], F. Azough[1], R. Freer[1]

[1]The University of Manchester, United Kingdom

Oxide ceramic thermoelectric materials are based on earth-friendly elements and stable in high temperature environments. Donor-doped TiO2 ceramic materials are promising thermoelectrics. In this study, high density oxide ceramics in the (1-x)TiO2 - xNb2O5 (x=0.5, 1, 1.5, 3, 4.5 and 6 at%) system were prepared by the mixed oxide route; 0.5 wt% MnO2 was added to enable low temperature (1523 K) densification of the samples at in a single sintering step under reducing conditions.

Crystal structural characterization of the samples was carried out by X-ray diffraction and electron diffraction techniques. Results revealed that the samples are predominantly composed of a tetragonal (S.G. P42/mnm) TiO2 rutile phase. Microstructural analysis by SEM and EBSD indicates that sub-grain features, including twin boundaries and nano-domain structures, appears in compositions for X up to 0.5, and then disappear with increasing Nb content. Secondary phases rich in Mn segregate to grain boundaries, growing larger with increasing Nb content; they are believed to aid densification at lower temperature. Thermoelectric properties were determined using a ZEM facility. The investigation shows that Nb-doping is effective way to enhance carrier mobility and increase electrical conductivity. In optimised samples, a power factor of 5.3×10-4 W/mK2 was obtained at 823 K. This is a ~ 15% improvement over the highest values reported for Nb-doped TiO2 prepared under the same conditions. Most importantly, Nb-doping reduced thermal conductivity of the TiO2 ceramics, and temperature-stable thermal conductivity of 2.2 W/m.K was achieved for compositions with x=6. The highest ZT value of 0.20 at 873K was achieved for compositions with x=6.

Chalcogenides II

16:00 - 17:00

Room: Panorama

Chair: Marisol Martin Gonzalez

16:00 - 16:15

Template assisted electrodeposition of intricate Bi_2Te_3 structures

O. Caballero-Calero[1], R. Martinez-Moro[1], M.J. Ramírez-Peral[1], M. Martín-González[1]

[1]IMN-CNM, CSIC, Spain

Bismuth telluride is a semiconductor material which exhibits good thermoelectric properties around room temperature. In order to further increase its efficiency, in the last years many efforts have been done to fabricate different nano-structures that should reduce its thermal conductivity without affecting other properties, such as electrical conductivity and Seebeck coefficient. Within our group those efforts have been focused in preparing by template assisted electrodeposition in alumina templates bismuth telluride nanowire arrays [1] or 3D bismuth telluride nano-structures [2].

Here we explore the possibility of fabricating non-ordered micro and nano-structures by the same electrodeposition technique using polymeric foams as templates. In such a way, we can profit from the advantages of the fabrication technique (low cost, room temperature method, easily scalable to industry, etc.) along with using commercial polymeric foams, with a wide variety of intricate porous morphologies, which give us the possibility of exploring the influence of having an inverse replica of that porous structure made of of bismuth telluride. The properties of the different bismuth telluride intricate structures will be measured, from their actual morpohology, their structure, and transport properties.

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Nanomaterials 8 (5), 345 (2018).

16:15 - 16:30

Low-temperature synthesis of bismuth telluride-based materials and its characterization

D. Groeneveld[1], T. Dankwort[2], M. Poschmann[2], H. Groß[2], L. Kienle[2], W. Bensch[2], J. Woellenstein[1, 3], J. Koenig[1, 3]

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Bismuth telluride-based alloys are the most widely used thermoelectric materials around room temperature. Usually those thermoelectric materials are prepared by energy intensive synthesis methods e.g. melting or hot extrusion. Further, these industrialized batch-processes are time consuming when high quality materials are a prerequisite. For an economically and ecologically friendly large scale production a low temperature synthesis method is required.

In this work we report on the optimization of a low temperature synthesis of V2VI3 materials using mechanical alloying (MA) followed by field-assisted sintering technique (FAST)/spark plasma sintering. The reactants were pre-treated for a very short time during the MA. The final product is obtained during a low temperature sintering step. We have investigated the phase formation process and the microstructure using XRD, TEM and SEM. The dependence of the process parameters on the physical and thermoelectric transport properties were investigated in depth.

Samples of both n- and p-type bismuth telluride-based materials were synthetized. The structural analyses indicates an early formation of the corresponding phases during the MA. Beside the economically and ecologically friendly synthesis, this route leads to a low thermal conductivity due to the increase of the phonon scattering. The thermoelectric characterization of the materials demonstrate high ZT values. Through specific doping, the maximum value of ZT were shifted to higher temperatures that could be beneficial for waste heat recovery. The results clearly shows that this low-temperature synthesis method is advantageous for the industrial preparation of thermoelectric materials.

16:30 - 16:45

Binary and ternary chalcogenide thermoelectric thin films via single source low pressure chemical vapour deposition

K. de Groot[1], D. Newbrook[1], S. Richard[1], R. Huang[1], A. Hector[1], B. Levason[1], G. Reid[1]

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High performance thin film thermoelectric generators are a promising technique to produce sustainable power supply for the thriving IoTs sensor network while offering high reliability, long lifetimes, no maintenance and solid-state operation. We have recently developed a series of novel single source precursors, [BiCl3(EnBu2)3] (E = Se, Te), which enable chemical vapour deposition (CVD) growth of binary Bi2Te3, Bi2Se3, and ternary Bi2(Se1-xTex)3 thin films with very good compositional, structural and morphological control [1]. As well as binary Sb2Te3, and Sb2Se3 films from another single source precursor of [MeSb(EnBu)2] [2]. Not only do these reagents produce high quality thin films with competitive thermoelectric properties but, furthermore, they permit very highly selective deposition of the thin film semiconductor materials specifically onto the conductive TiN surfaces on lithographically patterned TiN/SiO2 substrates [2-3]. This highly and well-controlled selective deposition behaviour has enabled a novel processing method for the fabrication of integrated, material-efficient thin film thermoelectric micro-generators. In this work, we report on the measurements of Seebeck coefficient, electrical conductivity, and thermal conductivity of those films. Thermoelectric characterisation reveals that doping of bismuth telluride with selenium in thin films can optimise the carrier concentration and mobility to give a fourfold increase in power factor. And also the effect of structure and morphology on thermoelectric properties.

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16:45 - 17:00

Interplay between Structural and Thermoelectric Properties in Epitaxial $Sb_{2+x}Te_3$ Alloys

S. Cecchi[1], D. Dragoni[2], D. Kriegner[3, 4], E. Tisbi[5], E. Zallo[1], F. Arciprete[5], V. Holý[3, 6], M. Bernasconi[2], R. Calarco[1]

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Strain engineering in semiconductor heterostructures is a well known concept to shape their physical properties. Recently the peculiar behavior of epitaxial Sb2Te3/GeTe chalcogenide superlattices (SLs), in between covalently bonded and weakly bonded materials, was unveiled. [1] It allows for strain tuning of the GeTe layers in the heterostructures, with particular implications in the switching functionality for phase change memory applications. Here we present a study of the structural and thermoelectric (TE) properties of epitaxial Sb2+xTe3 films fabricated on silicon, [2] as they represent an intriguing option to expand the horizon of strain engineering in chalcogenide SLs.

Along with Sb2Te3 several Sb2nTe3 layered phases exist, formed by (Sb2Te3)m(Sb2)n ordered series of Sb2Te3 quintuple layers and Sb2 double layers. [3] Samples with composition between Sb2Te3 and Sb4Te3 were prepared by molecular beam epitaxy. We developed a combination of X-ray diffraction and Raman spectroscopy, supported by dedicated simulations, allowing a consistent evaluation of the structural properties and intrinsic disorder characterizing the material. Notably, the presence of both Sb2 and Sb4 slabs in the alloys is detected. Lateral electrical properties and Seebeck coefficient of films with composition close to Sb2Te3, SbTe and Sb4Te3 were measured at 300 K. We report improved TE properties linked to the higher structural quality achieved in these epitaxial samples. Strategies to further enhance the TE performances by engineering the intrinsic disorder will be discussed.

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Silicides I

16:00 - 17:00

Room: Megaron B

Chair: Johannes de Boor

16:00 - 16:15

Low-temperature thermal conductivity of $Co_{1-x}Fe_xSi$

Y. Ivanov[1], S. Novikov[1], A. Zyuzin[2], D. Pshenay-Severin[1], M. Volkov[1], A. Burkov[1], L. Schnatmann[3], N. Perez[3], H. Reith[3], G. Schierning[3], K. Nielsch[3]

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Cobalt monosilicide (CoSi) has attracted increased interest due to its unusual electronic topology. Its electronic structure contains the multifold band crossings with large topological charges ±4 and long Fermi arcs connecting the Γ and R points of the surface Brillouin zone. In addition, numerous bands with a nonparabolic dispersion near the Fermi level and semimetallic type of conductivity lead to appearance of some unusual features in transport properties of this compound and its alloys with other transition metal silicides.

In this work, we study the low-temperature electrical and thermal conductivity of CoSi and Co1-xFexSi alloys ($0 < x \leq 0.06$). Measurements reveal that the electrical conductivity of Co1-xFexSi alloys decreases at $x > 0.01$ by an order of magnitude compared with that of stoichiometric CoSi. To a first approximation, both, the lattice and the electronic contributions to thermal conductivity are expected to decrease in a metallic alloy. However, our experimental results revealed that at temperatures below 20 K the thermal conductivity of the alloys is by about 4 times larger than that of stoichiometric CoSi. We discuss possible mechanisms of the thermal conductivity enhancement. The most probable one related to the dominant scattering of phonons by charge carriers. This mechanism not only explains the increase of the lattice thermal conductivity with increasing disorder, but also qualitatively accounts for the linear temperature dependence of the thermal conductivity in the Co1-xFexSi alloys below 20 K.

16:15 - 16:30

Amorphous and crystalline Cr-Si thin films: thermoelectric properties and crystallization kinetics depending on the composition and film thickness

S. Novikov[1], A. Burkov[1], V. Kuznetsova[1], J. Schumann[2]

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[2]IFW Dresden, Germany

Thin Cr-Si films with different Cr/Si ratio and thickness were studied. Amorphous films with thickness from 11 nm to 100 nm were prepared by magnetron sputtering on unheated Si/SiO2 substrates. The initial amorphous structure was transformed into crystalline state by thermal annealing with in-situ measurements of the thermoelectric parameters. Thermoelectric properties of the amorphous and crystalline films were measured at temperatures from 100 K to 1000 K.

We found that onset of crystallization depends on thickness and composition of the films. The lowest crystallization temperature was observed for films with the smallest thickness and with a composition close to stoichiometric CrSi2. The initial, highly non-equilibrium amorphous state of the films persists up to about 400 K, at this temperature a modification of short-range order is observed. The crystallization starts at annealing temperatures above 560 K. With increasing film thickness and Cr/Si ratio the crystallization onset temperature increases. During crystallization the film samples start as the composites, consisting of nano-grains of CrSi2 in amorphous Cr-Si matrix. At sufficiently long annealing time or sufficiently high annealing temperature, the formation of percolating CrSi2 cluster is observed in the off-stoichiometric film nano-composites. Whereas the stoichiometric CrSi2 samples crystallize into single phase nano-crystalline thin film compound. At high temperature annealing, typically above 1000 K, the nano-composite films are transformed into conventional micro-crystalline composites. The best thermoelectric performance, as characterized by the power factor, have stoichiometric CrSi2 nano-crystalline films due to higher Seebeck coefficient.

16:30 - 16:45

Thermoelectric properties of modulation doped $Si_{1-x}(Si_{75}Ge_{25})_x$

V. Khovaylo[1], I. Serhiienko[1], A. Ivanova[1], A. Usenko[1], T. Mori[2]

[1]National University of Science and Technology "MISIS", Russia
[2]National Institute for Materials Science, Japan

Solid solutions of SiGe have been used for high temperature thermoelectric applications since 1970 [1]. These materials have usually been prepared by hot pressing of powder made from induction melted ingots [2]. However, it has been demonstrated recently that SiGe samples obtained by mechanical alloying exhibit lower thermal conductivity while electrical transport properties remain almost intact. In order to further improve thermoeletric properties, various approaches such as introduction of nanoscaled inclusions or modulation doping have been used [3]. Here we report on design of modulation doped Si1-x(Si75Ge25)x (x = 20 – 35) which has thermoelectric properties comparable with those of Si80Ge20 but is characterized by a lower content of the expensive Ge. The modulation doped samples were prepared as follow. First, powder of (Si75Ge25)0.98P0.02 was prepared by mechanochemical synthesis method. The obtained powder was then mixed with Si in concentrations Si1-x[(Si75Ge25)0.98P0.02]x where x = 20, 25, 30, and 35 by means of planetary ball mill. Finally, the samples were consolidated by Spark Plasma Sintering (SPS) method. Morphology and structural properties of the samples were studied by scanning electron microscopy (SEM). Obtained results revealed that three phases are presented in the modulation doped samples. Speaking about content of these phases, Si98Ge2 phase prevails in the samples, elemental Si is the second most abundant phase in the samples, and Si79Ge21 phase is the third one. Annealing at 1273 K during 170 h has virtually no effect on the stoichiometry and the relative content of the phases in the samples. Measurements of thermoelectric properties showed that electrical resistivity and Seebeck coefficient increase almost linearly with the increase of the doping phase x. Calculation of figure of merit ZT showed that the largest ZT = 0.65 was attained in x = 25 sample at T \le 1100 K.

16:45 - 17:00

Mechanical properties characterization of $Mg_2(Si,Sn)$ thermoelectric materials at room temperature and above

G. Castillo Hernandez[1, 2], M. Yasseri[1, 2], S. Ayachi[1], B. Klobes[3], J. de Boor[1], E. Müller[1, 2]

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[2]Justus Liebig Universität Giessen, Germany
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Light and inexpensive thermoelectric generators based on the solid solutions of Mg2Si and Mg2Sn could be implemented to harness waste heat. Their thermal and electric properties have been thoroughly studied in the past, unlike their mechanical properties. Mechanical studies are important because thermal stresses may arise from the coefficient of thermal expansion (CTE) mismatch or the material´s expansion within fixed supports, which may lead to a decrease in efficiency due to nucleation and propagation of cracks or even a failure. By having accurate understanding of the mechanical properties exhibited by thermoelectric materials, we can predict these effects and tailor the microstructure in the material to withstand the stress. In this work, we characterize the mechanical properties of the material and compare the obtained values with previous experimental and calculated data. Impulse Excitation Technique, Resonant Ultrasound Spectroscopy and Vickers Hardness were used to characterize Young´s modulus, hardness and fracture toughness. Using these methods, we obtained room temperature Young´s modulus values for the binary compounds (110 GPa for Mg2Si and 82 GPa for Mg2Sn) as well as their hardness. We also found a linear influence of tin content x in the solid solution Mg2Si1-xSnx (x=0, 0.4, 0.5, 0.6, 0.7, 1) for both properties characterized. Experimental deviation from the linear behavior can be attributed to a strengthening effect caused by Mg2(Si,Sn) secondary phases and indicate a path towards improvement of the mechanical properties. We analyze the softening of the material at high temperature by measuring the Young´s modulus between 25°C and 400°C which is crucial for the modelling of thermal stresses in different applications scenarios. Finally, we draw a link between mechanical and thermal properties by estimating the Debye temperatures using the elastic constants.

Theory and Modeling II

16:00 - 17:00

Room: Megaron C

Chair: Ole Martin Løvvik

16:00 - 16:15

Thermal transport in disordered nanoporous Si geometries from large-scale molecular dynamics

L. de Sousa Oliveira[1], V. Vargiamidis[1], N. Neophytou[1]

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The introduction of nanopores has been known to drastically reduce a material's thermal conductivity, in some cases even below its amorphous limit. A clear and complete understanding of the effect of pore configuration on thermal transport is key to engineering porosity to optimally reduce lattice thermal conductivity without significant detriment to electronic transport, as is needed to increase ZT. However, the effect of pore/void geometry and arrangement on thermal conductivity is complex, and a detailed understanding of the physical mechanisms that degrade the thermal conductivity in nanoporous materials has not yet been reached.

We report on a comprehensive atomistic-scale investigation of the effect of porosity on thermal transport in nanoporous bulk silicon, in what are some of the largest-scale (approximately 160,000 atoms) molecular dynamics (MD) simulations of nanoporous materials found in the literature. Upwards of 50 different geometries are considered, spanning a large number of geometrical degrees of freedom, such as (cylindrical) pores and (spherical) voids, different porosities, diameters, neck sizes, pore/void numbers, and surface-to-volume ratios, placed in ordered fashion, or fully disordered. We quantify and compare a number of important parameters that determine the thermal conductivity reductions in nanoporous materials. Ultimately, the most significant result from this study is that even at the nanoscale, the intuitive particle picture of a reduced phonon line-of-sight comes to be the most important feature in understanding thermal conductivity in nanoporous materials, beyond other metrics such as porosity, surface/boundary scattering or coherence effects. Interestingly, we also observed geometry-dependent anticorrelation effects that can contribute to further reduce thermal conductivity. Finally, we combine non-equilibrium Greens functions electron transport calculations with our MD results to estimate the effect of nanoporosity in ZT.

16:15 - 16:30

Numerical extraction of TE coefficients of complex bandstructure materials with full energy/momentum scattering dependences – the example of half-Heusler alloys

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[4]University of Warwick, United Kingdom

We present an approach for the numerical extraction of charge transport coefficients considering the full band energy/momentum dependence of the scattering rates and relaxation times in the framework of the Boltzmann Transport Equation.

We investigate the impact of different treatment of carrier scattering, specifically, the commonly employed constant relaxation time, versus energy dependent elastic and inelastic phonon scattering and ionized impurity scattering on the thermoelectric power factors of Co-based half-Heusler alloys. Typically, thermoelectric transport calculations employ the constant relaxation carrier scattering time to reduce computational complexity.[1,2] However, such simplifications fail to capture the details of bandstructure features such as band anisotropy and manifold band and valley degeneracies and therefore fail to give accurate results, especially for complex bandstructures.[3,4] In this work, we have developed an advanced simulator to go beyond this simple approximation and consider all the energy, momentum and band dependent details of the scattering process.

We show that depending on the scattering treatment, different material performance rankings, different optimal doping regimes, and different temperature dependent trends are found. We also give an indication of single relaxation time values that are valid for different Fermi levels/doping concentrations, which both experimentalists and theorists would find useful in interpreting measured/simulated data. We present simulation results of ranking the performance of number of half-Heuslers, as well as the possibility of further improving their thermoelectric powers factors by strain induced band alignment. The work points out the importance of detailed scattering physics in electronic transport, and provides understanding and optimization directions in the performance of complex bandstructure materials.

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16:30 - 16:45

First principle investigation of electronic and thermal properties of Stanene/h-BN hetrostructure

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In this manuscript, we reported Electronic and thermoelectric properties of Stanene/h-boron nitride (Sn/h-BN) hetrobilayer using first principle within the frame work of Density Functional Theory with inclusion of spin orbit coupling. Electronic band structure revels that Sn/h-BN hetrobilayer has a direct band gap at Dirac points and the meager effective mass leads to higher carrier mobility. From density of states and projected density of state we can also depict that the Stanene has unsaturated π-orbitals near valence and conduction band which suggest that charge carriers can transport only through Stanene layer thus h-BN proved to be a prime substrate for hetrostructure. Also seebeck coefficient, power factor and thermal conductivity are obtained in temperature range of 100-800 K. Positive value of seebeck coefficient shows p-type nature of hetrobilayer. Seebeck coefficient increases linearly within the temperature zone of 100-350 K, suggesting the diffusive thermo-power generation. Intensification in figure of merit is also expected, because of low thermal conductivity and high electrical conductivity. Other thermal properties such as free energy, entropy, specific heat and line width also calculated for Sn/h-BN hetrobilayer. Our result suggests that Sn/h-BN hetrostructure can be a potential candidate for Nano-electronics and thermo-electronic application.

16:45 - 17:00

Enhancement of the Seebeck coefficient in ferrofluid based thermoelectric materials

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Research into liquid-based thermo-electrochemical cells has increased significantly in recent years driven by their advantages of cost effectiveness and environmental sustainability [1]. Recently, it has been demonstrated [2] that thermocells containing ionically stabilized magnetic nanoparticles (ferrofluids) dispersed in aqueous electrolytes show enhanced Seebeck coefficient. Despite the growing experimental interest and the great potential of these novel systems there is virtually no theoretical study on how the intrinsic magnetic properties of nanoparticles contribute to the enhancement of the thermoelectric signal.

We have addressed this issue for first time by deriving an analytic expression relating Seebeck coefficient to the chemical potential and its temperature derivative taking into account the nanoparticle’s intrinsic characteristics, i.e. magnetization and magnetic anisotropy. Mesoscopic scale modelling with the implementation of the Monte Carlo Metropolis algorithm has been performed on diluted assemblies of γ-Fe2O3 and CoFe2O4 nanoparticles - commonly used ferrofluid materials with different magnetic anisotropies - to calculate the particle Seebeck coefficient at different temperatures and applied magnetic fields.

Importantly, our numerical results show enhancement of the Seebeck coefficient with the increase of the magnetic particle anisotropy and a maximum that shifts to higher temperatures as the anisotropy increases. Our findings suggest that by tailoring the magnetic particle anisotropy enhanced thermoelectric signal can be achieved in ferrofluid based thermoelectric materials.

This work supported by the H2020-FETPROACT-2016-2017, Project MAGENTA (GA No 731976).

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[2] Salez, T. J., Huang, B. T., Rietjens, M., Bonetti, M., Wiertel-Gasquet, C., Roger, M., Filomeno, C. L., Dubois, E., Perzynski, R., Nakamae, S. Can charged colloidal particles increase the thermoelectric energy conversion efficiency? Phys. Chem. Chem. Phys. 19, 9409–9416 (2017)

Materials: Chalcogenides I

17:00 - 18:30

Room: Panorama

Chairs: Marisol Martin Gonzalez, Luis Fonseca, Alexander Burkov

17:00 - 18:30

Mechanochemistry for Thermoelectrics : ternary Cu-Sb-S Sulphides Synthesized in an Industrial Mill

P. Baláž[1], E. Guilmeau[2], O. Dobrozhan[1, 3], M. Baláž[1], M. Hegedus[4], T. Barbier[2], N. Daneu[5], M. Achimovičová[1], M. Kaňuchová[6], Z. Lukáčová-Bujňáková[1]

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In this study we demonstrate the use of elemental precursors (Cu, Sb, S) to synthesize tetrahedrite Cu12Sb4S13 using an industrial excentric vibrational milling followed by spark plasma sintering. Mechanochemical synthesis of tetrahedrite leads also to the formation of covellite (CuS) and famatinite (Cu4SbS4). However, the composite product can be modified in favour of high purity tetrahedrite when the spark plasma sintering treatment is applied after milling. The as-synthesized product is composed of nanosized particles. The thermoelectric measurements performed for the optimal sample (milling time of 60 min) reveal a figure-of-merit value zT of 0.67@700K, as a consequence of relatively high power factor (1.07 mW K-2 m-1) and low thermal conductivity (1.12 W m-1 K-1). The obtained zT values for samples synthesized in an industrial mill are comparable to the ones obtained in laboratory mills. The synthesis of ternary sulfides by a scalable and industrializable milling process represents a prospective route for mass production of thermoelectric materials.

17:00 - 18:30

Solid-State Synthesis and Thermoelectric Properties of Permingeatite Cu_3SbSe_4

G. Lee[1], J. Pi[1], I. Kim[1]

[1]Korea National University of Transportation, South Korea

Recently, copper-based chalcogenides such as CuInTe2, Cu2CdSnSe4, Cu2ZnSn(S/Se)4 and Cu3Sb(S/Se)4 have received increasing attention as p-type semiconductors. Among them, the permingeatite Cu3SbSe4 is a promising thermoelectric material because it has relatively narrow band gap, large carrier effective mass, abundant and nontoxic components. Mechanical alloying, which is high-energy powder process, has various advantages compared with conventional melting techniques such as avoiding segregation from melting process and preparing nano-size powders in short time. In this study, Cu3SbSe4 was prepared by using mechanical alloying (MA) as a solid-state route and consolidated by using hot pressing (HP). Effects of MA-HP conditions on the phase synthesis (transformation) and thermoelectric properties were evaluated.

17:00 - 18:30

Synthesis and Thermoelectric Properties of Fe-Doped Tetrahedrites $Cu_{12-x}Fe_xSb_4S_{13}$

S. Kim[1], G. Lee[1], I. Kim[1]

[1]Korea National University of Transportation, South Korea

Tetrahedrite C12Sb4S13 has attracted attention as a p-type thermoeletric material with very low thermal conductivity by inducing anharmonic oscillation of Cu due to the lone-pair electrons of Sb. Many studies have been conducted to improve the thermoelectric performance by partially substituting the transition elements such as Co, Zn, Ni, Fe and Mn for the Cu sites. When Fe3+ and Fe2+ ions are doped at Cu+ sites, surplus electrons are supplied to decrease the electrical conductivity and electronic thermal conductivity due to reduction of the carrier (hole) concentration, and the power factor can be optimized and the thermoelectric performance can be expected to be improved. In this study, the Fe-doped Cu12-xFexSb4S13 were synthesized by mechanical alloying and sintered by hot pressing. Thermoelectric properties were evaluated in the temperature range from 323 to 723 K.

17:00 - 18:30

Effects of Se Doping on Thermoelectric Properties of Tetrahedrites $Cu_{12}Sb_4S_{13-z}Se_z$

S. Kwak[1], G. Lee[1], I. Kim[1]

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Tetrahedrite with a composition of Cu12Sb4S13 has attracted attention as a promising thermoelectric material in the mid-temperature range. Tetrahedrite has low lattice thermal conductivity because of the lone-pair electrons of Sb that cause the Cu atoms to vibrate at a low frequency and high amplitude. Although there have been several studies on the thermoelectric properties of synthetic tetrahedrite compounds by using substitutions for copper and antimony in the tetrahedrite, experimental investigations on the sulfur site substitution have been little reported. In this study, Se-doped Cu12Sb4S13-zSez were prepared by using mechanical alloying and hot pressing, and their thermoelectric properties were examined.

17:00 - 18:30

Thermoelectric Properties of Ge-Doped Famatinites $Cu_3Sb_{1-x}G_{ex}S_4$ Prepared by Mechanical Alloying and Hot Pressing

J. Pi[1], G. Lee[1], I. Kim[1]

[1]Korea National University of Transportation, South Korea

Cu-Sb-S systems have attracted much attention because of their good thermoelectric performance. Among these compounds, Cu3SbS4 exhibits excellent thermoelectric properties due to its low thermal conductivity and large Seebeck coefficient. Cu3SbS4 has a zinc-blende related structure (famatinite) with a moderate band gap of ~0.47 eV, and it shows a large effective mass derived from its degenerate bands, which is favorable for high thermoelectric performance. In this study, Ge-substituted famatinites Cu3Sb1-xGexS4 were synthesized by mechanical alloying and consolidated by hot pressing, and their thermoelectric properties were examined.

17:00 - 18:30

Structural, thermoelectric and stability studies of FE-DOPED copper sulfide

A. Mikula[1], P. Nieroda[1], K. Mars[1], A. Kolezynski[1]

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Copper sulfide (Cu2S) belongs to the binary chalcogenide structures, characterized by high thermoelectric performance. Although Cu2S and other copper-based chalcogenide materials indicate very good thermoelectric properties, there are still some key issues: the lack of n-type materials and very low stability under work conditions, that needs to be solved for these materials to be used in thermoelectric devices. One of the possible approaches is doping bulk copper sulfide with low-mobility ions which are at the same time electron-donors, e.g. Fe. Such an approach seems to be correct due to relatively high durability, n-type conductivity and low thermal conductivity of Cu-Fe-S materials. The aim of this study is an experimental verification of our earlier results obtained from ab initio calculations and thus an attempt to synthesize Fe-doped Cu2S or multi-component composite build from Cu2S and iron-rich phase and to analyze the structural, thermoelectric and stability properties of the resulting material. It has been shown that the synthesis of such materials leads to a two-phase composite consisting of Cu2S and Cu5FeS4. As a result of sintering processes, Cu5FeS4 initially dissolves in Cu2S, but during several thermoelectric measurements, iron is pushed out from the structure and finally oxidized at the surface. The studies concerning transport properties show that despite the degradation processes, a material with higher stability in comparison to bulk Cu2S with final ZT parameter at the level of 1.0 was obtained. Such results indicate that Fe-doped Cu2S has the potential as a thermoelectric material, but some optimization of the synthesis process (e.g. via melt-solidification method) or chemical composition is required.

Acknowledgments: This work was financially supported by The National Science Centre Poland under grant no. 2016/21/N/ST8/00184

17:00 - 18:30

Thermoelectical properties and Shubnikov – de Haas effect in single crystals $Sb_{2-x}Cu_xTe_3$

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In this work we report the results of the investigation of thermoelectric and oscillating properties of single crystals Sb2-xCuxTe3 (0≤x≤0.1) samples synthesized by the Bridgman method. The intercalation of bismuth and antimony tellurides and selenides is fairly easy, since they have a layered structure with weak van der Waals bonds between quintets. It has been found that Bi2Te3, Bi0.5Sb1.5Te3, and Bi2Te2.75Se0.25 can be intercalated by lithium and barium up to concentrations of 1021 cm-3 [1,2]. The Li and Ba atoms embedded in the van der Waals gaps act as donors and supply electrons to the matrix. In all investigated Sb2-xCuxTe3 samples, the Shubnikov - de Haas effect was observed in high magnetic fields at T=4.2 K. It was found that with increasing x, the frequency of oscillation monotonically increases. That is, the hole concentration increases strongly with doping of Sb2Te3 with Cu. Thus, the replacement of antimony by copper causes an acceptor effect in antimony telluride. At room temperature Seebeck coefficient S slightly decreases with copper doping of Sb2Te3 and S increases with temperature in the investigated temperature range T<330 K. Resistivity of investigated samples decreases with an increase of Cu content. Temperature dependence of resistivity obeys the power low ~Tm with m=1.2. The deviation from the value m=1.5, characteristic of scattering by phonons, is most likely due to the contribution of scattering by ionized impurities. The exponent is almost unchanged when doping by Cu to the maximum concentrations studied. Heat conductivity of the samples with Cu was slightly higher than of the pristine antimony telluride. As a result, the thermoelectric figure of merit ZT increases with increasing the Cu content at T>280 K. 1. N.B. Brandt, V.A. Kulbachinskii, Physica B: Cond. Mat. 173, 303 (1991). 2. V.A. Kulbachinskii, Z.D. Kovalyuk, M.N. Pyrlya, phys stat sol (b) 169, 157 (1992).

17:00 - 18:30

Thermoelectric properties of $Cu_{1-x}Pd_xFeS_2$ below room temperature

P. Levinsky[1], J. Hejtmanek[2], J. Navratil[1], C. Drasar[3], L. Kubickova[1]

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Sulfides are among the many materials which have recently been investigated with respect to their thermoelectric properties.[1] These include chalcopyrite, a compound with the chemical formula CuFeS2, which consists of low-cost, non-toxic and abundant elements. Chalcopyrite is an antiferromagnetic semiconductor with a tetragonal crystal structure. Charge carriers in optimally doped material exhibit enhanced effective mass and favorable power factor, nonetheless, the fairly high thermal conductivity results in values of ZT not exceeding 0.3.

In our previous study,[2] we investigated high-temperature thermoelectric properties of Pd-doped chalcopyrite Cu1-xPdxFeS2, x = 0–0.1. In the present study, we examine the properties of this system down to liquid helium temperatures. We present measurements and analyses of electrical, thermal and magnetic properties as well as Mössbauer spectra.

This work was supported by the Czech Science Foundation, grant No. 18-12761S, and SOLID21 CZ.02.1.01/0.0/0.0/16_019/0000760.

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[2] J. Navratil et al., J.Electron.Mater. 48, 1795 (2019).

17:00 - 18:30

Experimental and theoretical study of thermoelectric properties of Ge(Sn,Pb)Te alloys doped with bismuth and antimony.

D. Pshenay-Severin[1], A. Shabaldin[1], A. Samunin[1], S. Novikov[1], P. Konstantinov[1], A. Burkov[1]

[1]Ioffe Institute, Russia

GeTe based mid-temperature thermoelectrics gain an increase of interest in the recent years. While showing good potential for thermoelectric generation, germanium telluride posses large concentration of germanium vacancies leading to high hole concentration. In order to optimize it, different approaches were proposed in literature, including alloying with PbTe and Sb or Bi doping. In the present work we performed experimental and theoretical study of solid solutions based on Ge(Sn,Pb)Te alloys doped with bismuth and antimony. The temperature dependencies of thermopower, electrical and thermal conductivities were measured in the range from 77 to 800K. The optimization of alloy composition and doping level was made in order to increase thermoelectric efficiency. Using first principle calculations, electron and phonon transport properties of GeTe were analyzed and compared with experimental results, taking into account the effects of multiband electronic structure and energy dependence of relaxation time. The influence of point defects on the band structure and thermoelectric transport was also investigated.

17:00 - 18:30

Green Chemical and High-throughput Synthesis of Bi_2Te_3 and Sb_2Te_3 Nanostructures

B. Hamawandi[1], M. Orlovska[1, 2], S. Ballikaya[3], M. Toprak[1]

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A green chemical high-throughput synthesis process was developed for nanostructured Bi2Te3 and Sb2Te3 thermoelectric materials. The synthesis process uses water as the reaction medium and salts of bismuth, tellurium and antimony, thus minimising the use of nasty organic materials. Microwave assisted heating provides a homogenous volume heating, making it possible to form the final desired materials phase at the reaction temperature of 180˚C in a matter of 5 min reaction time. SPS sintering process has been used to consolidate these nano-powders into pellets. Powder samples and compacted pellets have been characterized in detail. X-ray powder diffraction (XRD), Transmission electron microscopy (TEM), and Fourier-transform infrared spectroscopy (FTIR) have been used to study the crystallinity, crystal structure, particle morphology, size and surface chemistry. Transport property of these materials was evaluated by measuring the thermal diffusivity, electrical conductivity and the thermal conductivity of sintered pellets, revealing promising characteristics for applications around ambient temperature.

The developed bottom-up synthetic route can produce large quantities of nanostructured thermoelectric within few minutes, enabling novel application opportunities where nano-powders as starting materials are desired. These materials could form a strong basis for the formulation of TE inks, without needing excessive ultrasound or other chemical treatments for downsizing (top-down), which is commonly used for commercial powders. The developed synthetic process and evaluation results are presented in detail.

17:00 - 18:30

Thermoelectric sulphides for a green and sustainable future

D. Moço[1], L. Filipe Santos[2], E. Branco Lopes[1], A. Pereira Gonçalves[1]

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The current thermoelectric materials with commercial applications are produced with expensive and/or toxic elements, such as the Bi, Pb and Te, among others. A potential alternative are the tetrahedrite (Cu12Sb4S13) materials, which are based on a mineral that is composed of earth-abundant elements with lower toxicity and displays good electrical and thermal properties that leads to a thermoelectric figure of merit, zT, of 0,6 at 700K in the pristine compound. This value is still small when compared with the materials used in current commercial thermoelectric devices (with zT> 1,0), but it can be increased by changing the composition. The present work focus on the detailed study of the effect in tetrahedrite properties of two simultaneous substitutions. In particular, compositions of the type Cu12-xMxSb4S13-ySey, where M=Ni or Co, were prepared by the classical solid-state method. Powder X-ray diffraction measurements show that all samples have as main phase tetrahedrite, with a very small presence of other phases after annealing at 723K for 7 days. Thermoelectric properties measurements are now under way.

17:00 - 18:30

Control of Electrical and Thermal Properties through Site-selective Codoping in n-type Bismuth Telluride Thermoelectric Material

J.K. Lee[1], B. Ryu[1], S. Park[1], J. PARK[1], S. Park[1]

[1]Korea Electrotechnology Research Institute, South Korea

Bismuth chalcogenides such as p-type (Bi,Sb)2Te3 and n-type Bi2(Te,Se)3 have been considered as potential thermoelectric materials near room temperature. We report the enhanced thermoelectric properties of the n-type Bi2Te2.7Se0.3 compounds via structural and point defect engineering and carrier concentration optimization. Codoping approach of I and Ag doped Bi2Te2.7Se0.3 system is introduced as a new approach to separately optimize the electrical and thermal properties. In Bi2(Te,Se)3, halogen atom prefers to replace the Te/Se atom acting as a donor, and thus the halogen doping increases the number of n-type carriers. The electrical conductivity of the I-doped Bi2Te2.7Se0.3 was nearly 2 times higher than the undoped sample. Meanwhile, Ag is known as a powerful source causing a staking fault defect, which accelerates the formation of the nano-twin structure in the Bi-Te based system. The nano-twin structures considerably influences to reduce the lattice thermal conductivity due to the phonon scatterings at the twin boundaries. By site-selective codoping strategy, the highest figure of merit ZT of 1.0 at 423 K was obtained in the bulk Bi2Te2.7Se0.3 material with simultaneous control of electrical and thermal properties.

Materials: Heuslers

17:00 - 18:30

Room: Panorama

Chairs: Marisol Martin Gonzalez, Luis Fonseca, Alexander Burkov

17:00 - 18:30

Effect of dual substitution for the thermoelectric properties of Fe_2VAl based Heusler alloys

A. Voronin[1], I. Serhiienko[1], A. Taranova[1], A. Novitskii[1], R. Umetsu[2], V. Khovaylo[1]

[1]National University of Science and Technology MISIS, Russia
[2]Institute for Materials Research, Tohoku University, Japan

Fe2VAl Heusler alloy possesses a high power factor in the temperature range from 300 K to 400 K, its thermoelectric performance is hindered due to its high thermal conductivity exceeding ~20 W m-1 K-1. To the best of our knowledge, no studies have been done so far on the effect of dual substitution of vanadium and aluminium sites on electrical transport properties of Fe2VAl based compounds. Through such a substitution, the power factor can be increased due to charge carrier mobility enhancement. Moreover, the dual substitution of V and Al sites may also lead to a valuable decrease in the lattice thermal conductivity due to increased phonon scattering by point defects.

In this work, the results of studying the electrical transport properties of Fe2V1-xNbxAl1-yGay ($0.1 \leq x \leq 0.2$ and $0.1 \leq y \leq 0.2$) are presented. On the one hand, the Ga doped samples exhibited negative values for the Seebeck coefficient as shown in Fig. 2, which indicates n-type transport behaviour. The maximum value of the Seebeck coefficient of –90 μV K-1 was reached at 270 K for Fe2VAl0.8Ga0.2 specimen. On the other hand, the Nb-doped samples exhibited p-type transport behaviour as evident from positive values of the Seebeck coefficient. The dually doped samples exhibited negative values of the Seebeck coefficient at low substitution level and negative values for higher substitution level, respectively. However, such evolution of the thermopower can be explained not only by the influence of V and Al substitution but by impurity phases existed in the main phase, which can contribute to the charge carrier concentration and mobility. The electrical resistivity of all the specimens displayed a semiconductor-like behaviour.

To check our experimental findings, we have used well-known density functional theory and Boltzmann transport equation to calculate the electrical transport properties of the studied samples.

17:00 - 18:30

Atomic scale characterization of Fe_2VAl Heusler alloy for thermoelectric applications

L. Gomell[1], S. Katnagallu[1], S. Maier[2], D. Raabe[1], C. Scheu[3], E. Alleno[4], B. Gault[1]

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The Heusler alloy Fe2VAl shows promise as a material for thermoelectric applications. It was shown to have a high power factor of approximately 5 mW m-1K-2, which can compete with the state of the art thermoelectric material Bi2Te3[1]. However, Fe2VAl exhibits a relatively high thermal conductivity of ~28 W m-1 K-1 at 300 K, leading to a low figure of merit of zT~0.1 [2]. Recently, it has been suggested that exploiting the order-disorder (L21 – B2/A2) transformations present in the system [1], nanostructuring can be achieved imparting a higher fraction of antiphase boundaries (APBs). APBs are efficient phonon scattering regions, which are known to reduce the lattice thermal conductivity [3].

To better understand the microstructure - property relationship, a qualitative and quantitative investigation of the structural and chemical information of the alloy is required. In the present study, we chose a meltspun Fe2VAl to estimate the number of ordered L21 antiphase domains (APD) and to study segregation of elements to APBs. Through a unique and highly correlative combination of field ion microscopy and atom probe tomography, we confirm the presence of ordered phases and also the presence of APBs. Also, we show the presence of nanoscale precipitates in the matrix and at the APBs. The APT measurement reveals that the precipitation consists of a combination of V, C, and N. From FIM we show that these precipitates have grown on an APB as no crystallographic misorientation is seen across the boundary. FIM also hints that these precipitates are possibly coherent. The presence of coherent precipitates and their role in phonon scattering is yet to be studied, but this unique analysis opens a doorway for further nanostructuring.

1. S. Maier et al. Acta Mater. 121 (2016) 126
2. E. Alleno, Metals, 8 (2018) 864
3. S. Maier et al, In preparation.

17:00 - 18:30

Enhanced thermoelectric properties of Fe_2VAl -based thin films

A. Riss[1], B. Hinterleitner[1], C. Eisenmenger-Sittner[1], E. Bauer[1]

[1]TU Wien, Austria

Thermoelectric properties of full Heusler compounds, such as Fe_2VAl, can be significantly enhanced when prepared as thin films. With suitable parameters in the deposition process, the power factor is increased with respect to the bulk material. High Seebeck coefficients, exceeding 2000 µV/K using certain (Fe,Cr)_2VAl alloys as thin films, were obtained in our studies, revealing substantially enhanced power factors. The thermoelectric properties show a strong dependence on the temperature and time of the annealing process. Most importantly, the crystal structure as obtained from x-ray diffraction becomes modified and changes from the classical Heusler type (fcc) to a bcc type, which also modifies the electronic structure and is attended from an entire disorder of all atoms in the unit cell. This structure is metastable in bulk form.

17:00 - 18:30

Fabrication of Half Heusler Solid Solutions: Mechanical Alloying vs. Arc Melting

G. Mesaritis[1], G. Breuer[2], Y. Gelbstein[2], T. Kyratsi[1]

[1]University of Cyprus, Cyprus
[2]Ben-Gurion University of the Negev, Israel

The half Heusler compounds have aroused the research community's interest to convert energy into medium temperature ranges. Due to their mechanical and thermal stability, half Heusler compounds find use in waste heat recovery applications such as automotive. The TiNiSn binary system has been extensively studied in terms of its thermoelectric properties with the ZT reaching up to 0.4. The high thermal conductivity of these compounds results in a reduction of the total thermoelectric performance. Thus, the need to reduce thermal conductivity has aroused the interest of the research community since 1990. An approach to reduce thermal conductivity is through the introduction of mass disorder in the Ti -site lattice which causes additional phonon scattering. However, the different melting points of the elements are the main obstacle to the direct synthesis of the compounds by mechanical alloying since they create second phases.

In this work, (Zr,Hf,Ti)NiSn solid solution powders were prepared following two different techniques; mechanical alloying as well as arc melting, both followed by sintering via hot pressing. The thermoelectric properties and figure of merit were evaluated in both cases and are discussed in terms of microstructural differences.

17:00 - 18:30

Thermoelectric properties of p-type Half-Heusler TiCoSb Solid Solutions fabricated by Mechanical Alloying and Arc-Melting

I. Ioannou[1], G. Breuer[2], Y. Gelbstein[2], T. Kyratsi[1]

[1]University of Cyprus, Cyprus
[2]Ben-Gurion University of the Negev, Israel

Global energy and enviromental crisis have significantly urged the search for highly efficient and cost effective thermoelectric materials. Half-Heusler (HH) and especially the n-type TiNiSn and the p-type TiCoSb based compounds were recently identified as highly potential, cost effective and environmentally friendly thermoelectric materials. Reasonably high ZTs of up to ~1, were achieved for both n- and p- type HH compounds which were mainly prepared by arc-melting method, at temperatures higher than 600K. While the results are very encouraging, there is much more work needed in order to develop higher-efficiency thermoelectric devices.

The aim of this work is to study the thermoelectric properties of p-type (HF,Ti)Co(Sb,Sn) based materials prepared by mechanical-alloying and arc-melting. The temperature dependence of all thermoelectric properties (electrical conductivity, thermal conductivity and Seebeck coefficient) was measured on hot pressed pellets and the thermoelectric power factor and dimensionless figure of merit (ZT) values were estimated. In this presentation, our recent results on different compositions of (HF,Ti)Co(Sb,Sn) based materials that were successfully prepared by mechanical alloying and arc-melting will be discussed.

17:00 - 18:30

Thermoelectric properties of self-substituted Fe_2VAl alloys

A. Diack Rasselio[1], E. Alleno[2], C. Barreteau[1], J. Joubert[1], J. Crivello[1]

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[2]CNRS, France

Bi2Te3 is currently the best thermoelectric material in the market, displaying a dimensionless figure of merit ZT = 1 at 300 K. The Heusler alloy Fe2VAl might be considered as a substitute since it is advantageously constituted by abundant, cheap and non-toxic chemical elements. Fe2VAl can either be doped as a n-type or a p-type conductor and its power factor is strongly improved to values which can be larger than that of Bi2Te3. Self-substitutions of V by Al, Al by V, Fe by Al and Al by Fe introduce anti-site defects, which modify the charge carrier concentration and allow optimizing the power factor (PF). These self-substitutions also give rise to atomic scale mass defects which scatter the phonons and secondarily lead to a decrease of the lattice thermal conductivity that is presently too high for applications of this material. We will thus present microstructural and thermoelectric properties in the alloy series Fe2V1-xAl1+x and Fe2+xVAl1-x ($-0.1 \leq x \leq 0.1$).

Materials: Nanomaterials

17:00 - 18:30

Room: Panorama

Chairs: Marisol Martin Gonzalez, Luis Fonseca, Alexander Burkov

17:00 - 18:30

Temperature dependent changes in the material properties of sputtered $Si_{80}Ge_{20}$ thin films in combination with ultra-thin Au films

A. Steigert[1], D. Kojda[1], K.A. Mazzio[1], R. Gunder[1], F. Ruske[1], J. Frisch[1], K. Habicht[1, 2], S. Raoux[1]

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[2]Institut für Physik und Astronomie, Universität Potsdam, Karl-Liebknecht-Straße 24-25, 14476 Potsdam, Germany

Nanostructured Silicon-germanium (Si1-xGex) alloys are of interest as thermoelectric materials because they promise high potential to improve the figure of merit ZT. To transform an amorphous Si1-xGex film into a poly-crystalline layer, metal-induced crystallization (MIC) can be applied. It has been shown that a 20 nm Au film drastically reduces the crystallization temperature of Ge and Si to 170°C [1] and 220°C [2], respectively. Nevertheless, the MIC process for Si1-xGex alloys on Au has not yet been investigated. We utilize a combination of several measurement methods including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) to investigate the fundamental processes that occur at the two layer system Au/Si1-xGex. We detail the composition, the structure and the morphology during MIC of Si1-xGex on Au as function of temperatures up to 600°C. The influence of the Au film thickness during the crystallization process of Si1-xGex is also discussed, as the electrical properties of the Si1-xGex films are strongly determined by the state of the Gold film. Finally, the temperature-dependent changes in the Seebeck coefficient and the electronic conductivity in Si1-xGex films are presented and related to different stages during the crystallization process.

17:00 - 18:30

Flexible thermoelectric materials by hybridizing PPy particles/PEDOT: PSS with nanoporous $Ca_3Co_4O_9$ thin films

B. Xin[1], E. Ekström[1], L. Wang[1], A. Febvrier[1], B. Paul[1], P. Eklund[1]

[1]Linköping University, Sweden

Inorganic/organic hybrids materials with good flexibility and fascinating interfacial transport properties are promising new candidate in flexible thermoelectrics, in particular, for wearable applications (e.g. harvesting power from body heat to power wearable electronics). Recently, poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT: PSS)-based polymeric materials have been widely used in organic flexible thermoelectric devices due to their flexibility, light weight and low thermal conductivity, however, with challenge with its sustainable performance. On the other hand, the Ca3Co4O9 not only offer the stable performance, but also promising for wide scale practical applications, as due to the low cost, nontoxicity, and earth abundance of the constituent raw materials. The challenge with Ca3Co4O9 is that it is inherently rigid material. Here, we develop the hybrid film, where the flexibility of organic material is integrated with high performance of inorganic materials. For the purpose, nanoporous Ca3Co4O9 thin films have been grown on mica substrates using rf-magnetron reactive cosputtering from metallic targets of Ca and Co followed by annealing at 700 ºC in air. Then, we take the advantage of the nanoporous structure to hybridize the Ca3Co4O9 thin films with polypyrrole (PPy) by filling the nanopores of the former with the nanoparticles of later. The nanopores of Ca3Co4O9 thin films is also filled with PEDOT: PSS to prepare the inorganic/organic hybrid films. The structural properties of the films are investigated by XRD, SEM and TEM. XRD and TEM results showed perfect layered structure of Ca3Co4O9. SEM results show that the nanoscale pores of Ca3Co4O9 thin films are completely filled by PPy nanoparticles in the hybrid

17:00 - 18:30

Phases study of the thermoelectric $NaPb_{10}SbS_{12}$ composite by Electron Microscopy Techniques

S. Kozakos[1], C.B. Lioutas[1], N. Vouroutzis[1], N. Frangis[1], T.J. Slade[2], M.G. Kanatzidis[2]

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Thermoelectric materials have attracted a growing interest over the last decades as promising alternative energy sources, due to their environmentally friendly heat-to-power generation combined with relatively low cost production. The key point of the growth of efficient thermoelectric materials involves reducing thermal conductivity by introducing a suitable nano-texture into a matrix material, which reduces the average free path of heat transfer phonons, acting as scattering centers.

In the present work, the structural characterization results of the thermoelectric composite NaPb10SbS12 (10PbS + NaSbS2) are presented. The study was performed by using conventional, high resolution transmission electron microscopy (CTEM, HRTEM) and Geometrical Phase Analysis (GPA) on HRTEM micrographs.

Selected Area Electron Diffraction (SAED) patterns showed additional weak spots, suggesting the existence of nanocrystals embedded in the matrix. Moreover, on HRTEM micrographs, the existence of boundaries was clearly noticeable between areas showing nearly the same structure, without any presence of extra distinct spots in SAED patterns. Fast Fourier Transform (FFT) of these areas revealed a slight splitting of the matrix material spots indicating the presence of another endotaxially grown phase. The stress field mapping using GPA allowed an estimation of the cell parameters of these nanocrystals. They were found slightly larger compared to those of the matrix PbS and clearly different in the <100> and <110> cubic directions. Thus, for the new phase, a tetragonal unit cell with parameters a=6.07 and c=6.21 nm is suggested. A possible explanation for the existence of this phase is the growth of a solid solution of (PbS)1-x(Na2S)x type.

Acknowledgments:

This work is supported by 1) the General Secretariat for Research and Technology (GSRT) and the Hellenic Foundation for Research and Innovation (HFRI) (Scholarship Code: 95077) and 2) the U.S Department of Energy, Office of Science and Office of Basic Energy Sciences under award number DE-SC001452 (Northwestern University).

17:00 - 18:30

Electron microscopy study of the thermoelectric $NaPb_2SbS_4$ composite

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The efficiency of a thermoelectric material is related to the figure of merit, ZT. Effective strategies for improving ZT involve decreasing the thermal conductivity by introducing substitutional alloying on specific crystallographic sites in the structure and at the same time inducing nanostructures in the matrix as scattering centers to reduce the mean free path of heat carrying phonons.

In the present work, the structural properties of the thermoelectric composite NaPb2SbS4 = 2PbS + NaSbS2 were investigated. The structural characterization was performed by using electron diffraction (ED) and high resolution transmission electron microscopy (HRTEM).

The combined study showed that the material consists of nanocrystals having cubic NaCl type of structures. The cubic lattice parameters were found to be close to those of PbS or NaSbS2 or with intermediate values, denoting the local alloying between the two compounds, only in some areas.

In other cases, the ED patterns showed the presence of extra weak spots at positions forbidden by the cubic symmetry (figure 1), denoting the presence of one or more modulated phases, besides the cubic one.

In HRTEM images taken along the same zone axis (e.g. [100] as in figure 2) three different types of projected unit cells were found in different areas. One is consistent to the cubic NaCl type of structure and the other two are modulated cases of it. The corresponding Fast Fourier Transforms (FFT) confirm the differences between the three areas.

Acknowledgments:

This work is supported by 1) the General Secretariat for Research and Technology (GSRT) and the Hellenic Foundation for Research and Innovation (HFRI) (Scholarship Code: 95077) and 2) the U.S Department of Energy, Office of Science and Office of Basic Energy Sciences under award number DE-SC001452 (Northwestern University).

17:00 - 18:30

Photoresponse manifestation in thermoelectric phenomena on thin films of bismuth and bismuth-antimony

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The paper presents data on the interaction of Tz-radiation and thin films of a semimetal. Since the band gap of semimetals, namely bismuth-antimony alloys, is comparable to the energy of Tz-radiation, charge carrier generation is observed. This leads to a change in the resistivity of the thin film and the Seebeck coefficient.

17:00 - 18:30

Design and Fabrication of Si-based multi-barrier structures using non-uniform doping distribution

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Energy filtering is a promising strategy to achieve high improvements of the power factor in thermoelectric (TE) materials. This mechanism, which eliminates low-energy carriers through energy barriers, increases the Seebeck coefficient and the mobility of charge carriers as well, thereby increasing simultaneously the electrical conductivity. Heavily boron-doped silicon nanocrystalline thin films annealed up to 1000 °C have been reported with a power factor ~30 times higher than that of the pristine material.[1] Here, we attempt to extend this approach and to validate the energy filtering model by fabricating Si structures with multiple barriers and wells using non-uniform doping distribution along the channel.

Si multi-barrier structures were fabricated with the top-down method, using high-resolution electron beam lithography, rapid thermal annealing and wet etching. Selective doping is carried out in alternate subsections using thermal diffusion of phosphorus atoms and SiO2 nano-strips as masks. Differential doping with n– – n+ junctions and variable inter-barrier spacing down to 30 nm allow us to build the energy barriers. At the final stage, heater, temperature sensors and metal contacts made of Au metal tracks are going to be constructed using metal evaporation to measure TE properties. We report the design of the integrated device, showing the strategies used to develop and improve the multi-barrier structures. This will enable to explore experimentally the potential of energy filtering for TE enhancement in Si and to investigate how critical parameters, such as the barrier height, the doping level and the inter-barrier distance, affect the TE properties.

Reference:

[1] N. Neophytou, X. Zianni, H. Kosina, S. Frabboni, B. Lorenzi and D. Narducci, Nanotechnology, 24, (2013), 205402.

17:00 - 18:30

MEMS integrable vertically aligned SiGe thermoelectric nanowires

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Among Chemical Vapor Depositions techniques, Vapour-Liquid-Solid (VLS) Gold-catalysed processes has been widely used for the production of bottom-up Si NWs. This 1D nanostructures improve the intrinsic thermoelectric (TE) properties of bulk Si and allows to integrate them into micromachined TE generators (μTEGs) [1].

However, NWs of SiGe alloys have been always more desirable thanks to their reduced thermal conductivity and therefore better TE figure of merit. Nevertheless, so far this grow processes require relatively low growth temperatures (over 650 K) and thus they are slow and do not suitable for integration of NWs into μTEGs. The correct doping of such NWs have resulted to be problematic too.

Here we present a novel VLS methodology to grow in-situ heavy boron doped up to 15 μm long SiGe NWs at a rate higher than 100 nm/min. This is the result of a combination of flows that include the use of borane, chloride acid, relatively low pressures (~ 300 Pa) and temperatures above 900 K. These NWs are easily integrated into μTEGs and the improvement in device performance from Si NWs to SiGe ones have been evaluated.

Additionally, the effect of boron impurities in the growth process has been assessed. X-ray fluorescence mapping of these NWs have revealed maximum thresholds in the boron content for this VLS process. Beyond them, the catalyst gold amount trapped into the SiGe lattice dramatically increases, degrading the electrical conductivity and thus the TE properties. Understanding this phenomenon is essential to overcome this limit in the future.

[1] G. Gadea et al., “Towards a full integration of vertically aligned silicon nanowires in MEMS using silane as a precursor,” Nanotechnology, vol. 26, no. 19, p. 195302, May 2015.

Materials: Organics

17:00 - 18:30

Room: Panorama

Chairs: Marisol Martin Gonzalez, Luis Fonseca, Alexander Burkov

17:00 - 18:30

Fabrication and characterization of Graphene nanoplatelets and ethyl cellulose composite as printable thermoelectric materials

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The interest in organic thermoelectrics materials is rapidly increasing because they have benefits such as light weight, low thermal conductivity, and high flexibility. Up to now, most of the attention was on conducting polymers, like P3HT, PEDOT, but these materials have limited stability, which has hindered their widespread applications. In other words, non-conducting polymers are more stable and processable and they are thermally insulator, however, their applications have been limited due to their high resistivity. Using conductive fillers is an approach for improving the conductivity. There are few studies on using non-conducting polymer as thermoelectric materials, like (PDMS)/CNT nanocomposites PVDF/MWCNT nanocomposites.

Ethyl cellulose is an insulator polymer which has been widely used as a binder for printing different types of films like Titania, and carbon. This polymer is soluble in variety of solvents and, it is green, inexpensive.

Here, the paste of Graphene nanoplatelets (GNs) and ethyl cellulose (EC) has been prepared in different ratios between GNs and EC. The films were deposited by blade coating with an automated machine employed to deposit the paste on the glass. Then the films were annealed at 120 °C for 30 minutes. Two stripes of silver for thermoelectric measurements were made by silver ink. The thicknesses were in the range of 9 to 13 μm. The resistance, Seebeck coefficients and output power of thermoelectric devices were measured by homemade system in vacuum chamber. The results confirm that conductivity has been improved by increasing the ratio between GNs and EC, the conductivities for ratio of 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 were 13, 15, 45, 157, 175, 279 S/m respectively. The seebeck coefficient for all ratios were in the range of 15 to 30 μV/K. Finally, these results show the applicability of this polymer for thermoelectric application.

Materials: Oxides

17:00 - 18:30

Room: Panorama

Chairs: Marisol Martin Gonzalez, Luis Fonseca, Alexander Burkov

17:00 - 18:30

Reactive sputtering of oxide thin films on sapphire and van der Waals epitaxial growth on flexible muscovite

E. Ekström[1], A.I. Febvrier[1], L. Landälv[1, 2], J. Palisaitis[1], F. Eriksson[1], B. Paul[1], P. Eklund[1]

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Oxides materials, due to their high thermal stability, environment-friendliness, low cost and availability of elements, are promising for thermoelectrics. Here, reactive magnetron sputtering was used to grow thin CaMnO3 and VxOy films on flexible mica substrates. Mica is flexible and allows for van der Waals epitaxial growth of the films. A two-step sputtering/annealing approach is used to grow CaMnO3, whereas VxOy thin films are grown by one-step direct sputtering approach. In the two-step approach, the Ca0.5Mn0.5O thin films are sputter deposited on sapphire substrates from elemental Ca and Mn targets followed by annealing at 700°C to form perovskite CaMnO3 phase. The Nb-doping up to 10 at.% is performed by co-sputtering from an additional Nb-target to enhance the electrical conductivity of the films. A change from 2.70 Ωcm to 0.09 Ωcm is observed at optimum Nb-doping of 5 at.%. The presence of Can+1MnnO3n+1 Ruddlesden-Popper phase is observed in the film, which might act as scattering center for both charge carriers and phonons. The Seebeck coefficient is measured to be

-270 μVK-1 and -145 μVK-1 for pure and doped CaMnO3, respectively.

The van der Waals epitaxy allows the growth of strain free films at large lattice mismatch. Furthermore, it allows for film transfer to other substrates, as the film is weakly bonded to the substrate. For proof-of-concept the vanadium oxides are investigated. The VxOy films are directly deposited by reactive pulsed DC magnetron sputtering. The V2O3, VO2 (in M1 and M2 phase) and V2O5 phases are grown on mica substrates. The films exhibited an electrical resistivity of 1 Ωcm, 0.05 Ωcm and 17 Ωcm for M1, M2, and V2O5, respectively. The M2 phase is stabilized by high residual stresses in the GPa range. VO2 is thermochromic and a phase transition was observed at 70°C by in situ annealing during XRD.

17:00 - 18:30

Substrate-induced modification of microstructure and thermoelectric properties in Sr-doped $Ca_3Co_4O_9$ thick films

M.A. Madre[1], M. Mora[1], H. Amaveda[1], M.A. Torres[1], A. Sotelo[1]

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Ca3Co4O9 ceramic material is one of the most promising p-type thermoelectric oxides. It can work at high temperatures without degradation or oxidation due to its high thermal and chemical stability. These properties allow the exploitation of high temperature waste heat sources. Moreover, the use in form of thick films is very promising in practical applications due to their low costs and relatively high performance.

In this work, thick films of Sr-doped Ca3Co4O9 thermoelectric ceramics have been prepared through the dip-coating technique. The effect of the amount of solid in the suspensions has been determined by using two different powders content (22, and 29 vol.%) to produce different coatings on Al2O3 polycrystalline substrates. The resulting coating thickness has been determined from [1] using the values of powder density, the surface tension, viscosity of the suspension at 100 s-1, as well as the withdrawal speed. Moreover, the effect of substrate has also been investigated using Al2O3 monocrystalline substrates. After drying the coatings they were sintered at 900 ºC for 24 h with a final furnace cooling, and characterized through surface XRD, and SEM observations in the transversal direction to evaluate microstructure and thickness of the sintered coating. These results will be related with the final thermoelectric performances determined through the power factor, PF (S2/□).

[1] T. Schneller, R. Waser, M. Kosec, D. Payne (Eds.), Chemical Solution Deposition of Functional Oxide Thin Films, Springer-Verlag, Wien, 2013.

17:00 - 18:30

Modifying $Ca_3Co_4O_9$ properties through CTi nanoparticles addition

A. Sotelo[1], H. Amaveda[1], M. Mora[1], S. Marinel[2], M.A. Torres[1], M.A. Madre[1]

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Energy produced from fossil fuels is increasing prices day by day and it creates many environmental problems, such global warming. Moreover, the efficiency of such production is very low, and most of the potential energy is lost in form of heat. In this regard, thermoelectric materials appear as a convenient solution to harvest the waste heat and transform it into useful energy. Among all the thermoelectric materials, Ca3Co4O9 ceramic is one of the most promising thermoelectric oxides for practical applications. It can work at high temperatures without degradation or oxidation provided by its high thermal and chemical stability. Moreover, in spite of their relatively low thermoelectric performance, the capability to work at high temperatures makes them very attractive for integration in thermoelectric modules for energy harvesting due to the enhanced efficiency when subjected to high temperature gradients. On the other hand, there are several other characteristics of these materials which should be evaluated to find the adequate n-type counterpart to build the module, as the mechanical properties, or their dilatation with temperature.

In this work, the effect of CTi nanoparticles addition, in very low concentration, to Ca3Co4O9 thermoelectric material prepared through the classical solid state method, will be studied. The structural and microstructural modifications will be studied and related to the variations in thermoelectric, mechanical, and dilatometric properties.

17:00 - 18:30

Structure/property relationships of the thermoelectric $Zn_{1-x}Al_xO$ obtained by chemical precipitation and spark plasma sintering

I. Serhiienko[1], E. Chernyshova[1], A. Novitskii[1], E. Kolesnikov[1], V. Khovaylo[1], T. Mori[2]

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Recently, ZnO-based thermoelectric materials have attracted significant attention due to a low price high thermal stability. ZnO is a n-type semiconductor with direct wide band gap of 3.37 eV and the hexagonal Wurtzite structure. Because of the simple crystal structure and light element composition ZnO exhibit high thermal conductivity hindering their widespread applications. However, the charge carrier mobility reaches over 200 cm2V-1s-1 at room temperature resulting in relatively high Seebeck coefficient in comparison with state-of-art thermoelectric materials. It was previously reported that doping ZnO with Ni, Al, Ti or Sb lead to a noticeable thermoelectric performance enhancement.

In this work, the nanostructured Zn1-xAlxO (x = 0.02; 0.04; 0.06) were fabricated using by means of two techniques followed by spark plasma sintering. On the one hand, ZnO and Al2O3 powders obtained by chemical precipitation were mixed by ball milling (a). On the other hand, Zn1-xAlxO powder was produced directly by chemical co-precipitation of Zn(NO3)2 and Al(NO3)2 as precursors (b). As a result, a disk-shaped pellets were fabricated with high relative density of 95 %.

X-ray phase analysis revealed that ZnAl2O spinel was formed for Zn1-xAlxO with x > 0.02 densified using ball milled mixture (a), while for (b) specimens no traces of secondary phases were observed. Moreover, a peak shift for XRD patterns of (b) samples indicated a successful formation of Zn1-xAlxO solid solution.

The thermal conductivity for all the samples steadily decreasing over the entire temperature range. It is worthy noted that, at low temperature, the κ values of Al-added ZnO samples are lower than for pure ZnO sample. This agrees with the theoretical prediction that at low temperature grain boundary and impurity scattering contribute in phonon transfer and determine the whole thermal conductivity. More details on electrical transport and structural properties will be presented.

17:00 - 18:30

Crystal Growth of Aurivillius phase Bi-V-O

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Aurivillius compounds are bismuth layered oxides and known as oxygen ion conductors. The Aurivillius compounds consist of Perovskite layers and Bi-O layers. It is expected that nano-layered structure shows high Seebeck coefficient due to the quantum confinement of carrier in Perovskite layers. It was reported that the Seebeck coefficient of hot-pressed specimen for Aurivillius phase Bi2VO5.5 was high value of -28.3 mVK-1 at 1010 K, and the electrical resistivity of the one was also high value of 0.033 Ωm at 1010 K. Therefore, thermoelectric properties of Bi2VO5.5 substituted with Cr, Mo or W were investigated. However, the electrical resistivity of the substituted sample was not clearly reduced. It was considered that high resistivity was caused by crystal orientations with high resistance were mixed in the measurement direction because the specimens were sintered bodies. Therefore, in this presentation, the crystal growth of Aurivillius phase Bi2VO5.5 was attempted by the horizontal gradient freezing method.

Bi2O3 and V2O5 as raw materials were put into Pt boat. The starting materials were melted at 1273 K. The crystal growth was carried out under the temperature gradient with 1 or 2 K/mm at a rate of 1 K/min or 1K/h.

From the results of XRD of the crystal plane parallel to the growth crystal surface, the main peak became weaker as the growth rate became slower, and the peak intensity derived from (0 2 0) increased. From the results of impedance parallel and perpendicular to the crystal surface grown at 2 K/mm and 1 K/h, insulating behavior was confirmed even at 900 K in the vertical direction. On the other hand, arcs were confirmed in the Nyquist plot of the parallel direction. From these results, highly oriented crystals were obtained under the conditions of 2 K / mm and 1 K / h.

Applications

17:00 - 18:30

Room: Panorama

Chairs: Marisol Martin Gonzalez, Luis Fonseca, Alexander Burkov

17:00 - 18:30

Thermoelectric generation as a part of the optimal solution in off-grid hybrid renewable system in places with low irradiation.

d. Champier[1], R. Dufo-López[2], S. GIBOUT[1], J.M. Lujano-Rojas[2], J.A. Domínguez-Navarro[2]

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Stand-alone (off-grid) electrical systems are usually powered by renewable energy; the most common system is composed of a photovoltaic generator with battery energy storage system. In windy places, wind turbines with battery energy storage system can be a good option, usually hybrid with photovoltaic panels. In some cases, the optimal system is hybrid renewable with fossil fuel generator commonly diesel or petrol. Thermoelectric generators could also be competitive in an off-grid application where there is a need for thermal energy for heating during many hours of the day, and where the PV generator during long periods cannot supply energy due to the low irradiation or the accumulation of snow and also where low wind speed is recorded like in some locations of Norway.

In order to promote the use of thermoelectric generators coupled to biomass boilers or stoves, it is desirable to be able to demonstrate that it is an economically viable solution. Minimization of the net present cost (including all the costs during the system lifetime) is a good argument for developing this type of system.

A new method has been developed for the optimisation (minimisation of the total net present cost) of hybrid power systems which can be composed of a photovoltaic generator, wind turbines, fossil fuel generator and thermoelectric generator biomass boilers with battery energy storage system. This method has been included in iHOGA (improved Hybrid Optimization by Genetic Algorithms) software.

The model has been applied in the optimization of the electricity supply of an off-grid household in the south of Norway with heating pellet stove and demonstrate the economic interest of thermoelectric generators

17:00 - 18:30

Study of different heat exchangers for geothermal thermoelectric generators for Timanfaya national park (Spain)

L. Catalan[1, 2], M. Araiz[1, 2], P. Aranguren[1, 2], D. Astrain[1, 2]

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[2]Institute of Smart Cities, Spain

Despite being one of the largest renewable sources, geothermal energy is not widely utilized for electricity generation due to the associated intrinsic difficulties: high initial investment, difficulties in modularizing and assessing the resource, as well as complexity in the implementation of cycles (the only installed technology nowadays). In this sense, thermoelectric generators can be considered an alternative in order to promote sustainable generation and contribute to the reduction of greenhouse gases. The present work presents the experimental development and the computational study of a project that aims to obtain electrical energy by means of thermoelectric generators in Lanzarote Island (Spain), where one of the most important hot dry rock fields in the world (with temperatures of 500°C at only 3 meters deep) is located. In particular, different heat exchangers for the cold side of the thermoelectric modules have been analyzed: fin dissipators assisted by a ventilator, heat exchangers with water as heat carrier and fancoils, and biphasic thermosyphons. The heat exchangers have been experimentally characterized and subsequently used in a prototype that simulates the favorable conditions of the island. As a result, it has been demonstrated that biphasic thermosyphons are the best alternative due to their low thermal resistance and, especially, due to their lack of auxiliary consumption that deteriorates net generation, leading to a 12.5% higher generation than fin dissipators. Experimental results have served for the validation of a computational model, based on which it has been estimated that in Lanzarote almost 100 kW can be generated thanks to thermoelectric generators that use biphasic thermosyphons as heat exchangers in the cold side.

17:00 - 18:30

Thermoelectric wearable devices

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[2]Dycotec Materials Ltd., United Kingdom
[3]Kymira Ltd., United Kingdom

A temperature difference often exists between the human body and the ambient air, offering an opportunity for thermal energy harvesting. However, there are significant thermal resistances represented by the body and the body to air interfaces, especially as the body has evolved to reduce heat losses. This typically results in the actual temperatures seen across wearable thermoelectric generators being significantly lower than the system level temperature difference, with heat flows typically only 10-100 μW/mm2 [1]. Some previous work has used solid metal heat sinks to try to improve upon this, but this is not easily incorporated or further scaled into a wearable energy harvesting solution.

These challenges result in previously reported prototype devices which have been tested on a person having fairly low power outputs, e.g. 0.04 nW/mm2 [2], ~0.01 nW/mm2 [3]. Using a solid heat sink and minor modifications to standard commercial thermoelectric devices to form a fairly thick (e.g. ~9mm) rigid device, can increase this up to 600 nW/mm2 [1] or 200 nW/mm2 [4] which can be maintained when the heat sink is replaced by a moderately flexible copper foil heat spreader [5].

We have developed a solution that aims to combine the benefits of both approaches. We use solid, inflexible thermoelectric material, enabling high performance, but incorporate this into a flexible, textile-based device. This enables a truly wearable device, without requiring an additional heat sink, but does not sacrifice too much performance to achieve this. We discuss finite element analysis modelling of the device architecture to fully optimize performance by using coupled electrical and thermal solutions in COMSOL Multiphysics. The modeling suggests that >30 nW/mm2 can be achieved with this approach. An initial device has been produced, demonstrating up to 8.8 nW/mm2 of electrical power production on a person.

17:00 - 18:30

Experimental study and modeling of thermoelectric energy harvesting in low temperature dynamic condition

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[1]ICMATE - CNR, Italy

Low power energy harvesting from low temperature sources usually features dynamic regime. Periodic and non-periodic temperature variations are due to transient heat sources, environmental conditions and load. Moreover, the time dependent behaviour of temperature difference, and thus output power depends on mass and thermal properties of thermoelectric module, heat sink and hot source. As a consequence, the evaluation of a thermoelectric generator under dynamic thermal load presents difficult tasks to solve. In particular, with natural convection cooling, the main issue is to evaluate the performance of a heat sink of given geometry and material with a varying heat source.

In this work, we present a transient numerical thermal model of simple thermoelectric generator, whose behaviour has been experimentally studied with a custom-built setup working at low temperature. The numerical model has been used to evaluate potential thermal storage effects due to the coupling of elements with different heat capacity. Particular attention has been focused on modeling the transient buoyancy-driven airflow to evaluate the evolution of heat transfer coefficient in natural convection. Moreover, we investigated with experimental measurements the minimal requirements of the thermoelectric generator to achieve increasing electrical power storage under temperature varying conditions.

Cooling Systems

17:00 - 18:30

Room: Panorama

Chairs: Marisol Martin Gonzalez, Luis Fonseca, Alexander Burkov

17:00 - 18:30

Influence of the Design Parameters of a Thermoelectric Subcooler on the COP of a Transcritical CO2 Refrigeration System

P. Aranguren[1, 2], D. Astrain[1, 2], M. Araiz[1, 2], L. Catalan[1, 2], Á. Casi[1], D. Sánchez[3], R. Llopis[3], R. Cabello[3]

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[2]Smart Cities Institute, Spain
[3]Jaume I University, Spain

Nowadays, due to the increasing climate change problem, the existing regulation in the refrigeration market is leading to intense research on systems that use CO2 as an efficient alternative to fluorinated substances. In these systems, whose operation implies high working pressures, it has been demonstrated that in transcritical conditions of the cycle, it exists a prominent improvement when an additional subcooling is introduced after the gas cooler.

This work presents a vapor compression refrigeration system that operates with transcritical CO2 and which utilizes thermoelectric technology in order to cause the subcooling. A computational model has been developed representing both, the vapor compression equipment and the subcooling system powered by thermoelectric modules. The thermoelectric subcooling includes different design parameters that have been modified in order to optimize the COP of the whole system. These parameters are the thermal resistances of the heat dissipation systems located on both sides of the thermoelectric modules, the voltage supplied to the modules and the number of modules used. Moreover, the discharge pressure has to be adjusted in order to optimize the operation of the global system.

The obtained results show that improvements up to 24% in the global COP of the system are possible, and increments of 33% in the cooling power can be achieved by means of thermoelectric subcooling.

17:00 - 18:30

Finite Element Modeling of a Thermoelectric Cooler

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In the last decades interest in thermoelectric (TE) technology has experienced a dramatic rise due to the growing concern about global warming, the depletion of fossil fuels and the discovery of new materials, with various synthesis and processing methods, which have high TE efficiency.

In this work we have adopted Finite Element analysis to model the performance of a TE cooler device. FEM is a computational technique used to obtain approximate solutions of boundary value problems in engineering. The basic concept of FEM is splitting the computational domain into individual small patches, finding local solutions in each patch and stitching the individual solutions on these patches back together into a global solution. Thus, FEM modeling allows a methodical variation of device features, often beyond the capacity of experimental methods.

Numerical simulations were carried out by using the thermal-electric coupled multiphysics analysis technique in ANSYS 19.2. A complex geometry realistic model which consists of p- and n-type legs with diffusion-barrier layers, metallization patches and solder to coated electric conductors was constructed between two ceramic plates. Design issues like the geometrical characteristics of the various elements in the geometry, the temperature dependence of their parameters (S, σ, κ), the electrical & thermal contact resistance and the role of the ceramic plate thickness were analyzed.

Modules

17:00 - 18:30

Room: Panorama

Chairs: Marisol Martin Gonzalez, Luis Fonseca, Alexander Burkov

17:00 - 18:30

Study of the degradation of different thermoelectric modules in acidic environment

L. Catalan[1, 2], G. Perez[1, 2], C. Berlanga[1, 3], A. Garacochea[1], D. Astrain[1, 2], P. Aranguren[1, 2], M. Araiz[1, 2]

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[2]Institute of Smart Cities, Spain
[3]Institute for Advanced Materials, Spain

Supplying power to volcanic monitoring stations constitutes a challenge due to both the access difficulties and the acidic environment associated with volcanos. In order to face this situation, one of the objectives of ELECTROVOLCAN project (RTC-2017-6628-3) consists in the development of thermoelectric generators that make use of the temperature of the fumaroles available to directly supply electricity to the stations in a robust, compact and reliable way. The main element of thermoelectric generators are the thermoelectric modules, devices made up of semiconductor materials that directly transform heat into electricity thanks to Seebeck effect. Nonetheless, before designing the generators, it is essential to study the behavior of the modules in acidic environments. In this sense, the present work analyzes the degradation in the generation of different thermoelectric modules after their exposure to the acidic environment of Teide National Park. The analyzed thermoelectric modules are Marlow TF12-8 (bismuth-telluride), European Thermodynamics GM200-127-14-16 (bismuth telluride) and TECTEG TEG1-PB-12690 (lead-tin-telluride), whose degradation has been studied with two different methodologies. On the one hand, thermoelectric modules have been exposed next to one of the fumaroles for eight months. On the other hand, an accelerated corrosion process with a similar gas composition has been replicated in a controlled atmosphere. In both cases, the variation in the generation capacity of the thermoelectric modules for different load resistances and similar heating conditions has been periodically analyzed. The results show an important degradation on the modules, mainly due to copper corrosion, that leads to a reduction in the power generation of more than 25% in case of bismuth-telluride modules. Nevertheless, even taking into account this reduction, the generation is still higher than the one of lead-tin-telluride modules for the temperature range considered.

17:00 - 18:30

Development of TE segmented (FGM) p-leg with contacts over a wide temperature range (50 - 600 °C)

Z. Dashevsky[1], R. Knura[1, 2], T. Parashchuk[1], K. Wojciechowski[1, 2]

[1]The Lukasiewicz Research Network - The Institute of Advanced Manufacturing Technology, Poland
[2]AGH University of Science and Technology, Poland

The efficiency of thermoelectric generators directly depends on the average value of the thermoelectric figure of merit Zave and temperature T. One of the successful concepts for obtaining high ZT value over wide temperature range is to develop segmented functionally graded (FGM) thermoelectric material with a maximal value of ZT, corresponding to respective operating temperature range.

The work is proposed to develop high efficient thermoelectric p-leg working in 50 – 600 °C temperature range with commutative contacts by one pulse electric current (PECS) process. We propose to use for 50 - 300 °C temperature range two segments of low-temperature thermoelectric material, based on Bi2-xSbxTe3, placed perpendicularly and parallelly to the pressing direction. The third stage is Pb1-xSnxTe solid solutions for a 300 - 600 °C temperature range. Optimization of the thermoelectric performance at different temperature ranges can be achieved by varying the doping level x in Pb1-xSnxTe. An alternative approach for controlling the carrier concentration can be attained by indium doping Pb1-xSnxTe at a fixed doping level. This second approach allows obtaining a controlled energy gap and a specific lattice thermal conductivity. The present research focuses on the development of Pb0.5Sn0.5Te alloys doped by different levels of indium concentration. The preparation techniques included preparation of master alloys with the optimized structure, comminuting to appropriate powder particles size, cold compaction, sintering, and annealing. The samples were examined by thermoelectric properties (Seebeck coefficient, electrical and thermal conductivity) over a wide temperature range (50 - 600 °C).

Authors thank the Foundation for Polish Science (TEAM-TECH/2016-2/14 Grant “New approach for the development of efficient materials for direct conversion of heat into electricity”), co-financed by the European Union under the European Regional Development Fund for financial support to The Lukasiewicz Research Network – The Institute of Advanced Manufacturing Technology.

17:00 - 18:30

Detachable Contacts for Simultaneous Thermoelectric Characterization of Half-Heusler Materials

A. Micallef[1], C. Stiewe[1], G. Oppitz[1], S. Tiedke[2], E. Müller[1, 3]

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The Combined Thermoelectric Measurement facility (CTEM) was developed to simultaneously determine the Seebeck coefficient (S), electrical conductivity (σ) and thermal conductivity (

17:00 - 18:30

Performance Evaluation and Stability of Silicide-based Thermoelectric Modules

A.d.P. Shyikira[1], G. Skomedal[1, 2], P. Hugh Middleton[1]

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[2]Elkem AS, Norway

This paper presents long-term studies on thermoelectric generator modules based on N-type magnesium silicide (Mg2.01Si0.49Sn0.5Sb0.01) and P-type higher manganese silicide (Mn0.98Mo0.02Si1.73Ge0.02) materials, in operation temperature range of 2000C-4000C. Emphasis is put on the performance and reliability of the current collector configuration, especially, on the hot side of the module and on the thermomechanical stresses that are created during operation and lifetime testing, as a result of large temperature gradients experienced across the thermoelectric legs. With silver (Ag) paste as contact material, the long term-stability of the unicouples were carried out on non-metalized legs and gold metalized legs under vacuum and ambient environments. The key aspect is to decrease the stresses in the unicouples assembly to prevent device failure and hence increase the operational lifetime. Under isothermal and thermocycling tests, the non-metalized legs showed gradual decrease in open circuit voltage (after a period of 300h) and increase in internal resistance (after 100 thermal cycles). In contrary, the metalized leg-based module was robust and stable for the same isothermal period and similar characteristics were observed on the contact layer after more than 300cycles. Post-operation analysis by SEM/EDS and mechanical testing were used to determine microstructure, mass transport changes and mechanical properties including hardness and compressive strength parameters. It was found that, oxidation and adherence of the contact material to the functionalized legs were essential to performance drawback of the modules.

17:00 - 18:30

Method for investigation of laser processing parameters on thermoelectric properties of dispenser printed bismuth telluride-based thermoelectric materials

M. Greifzu[1], R. Tkachov[1], L. Stepien[1], F. Lange[1], A. Marquardt[2], E. Lopez[1], F. Brückner[1, 3], C. Leyens[1, 2]

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[2]Technische Universität Dresden, Germany
[3]Luleå University of Technology, Sweden

Laser sintering is a promising alternative method to traditional heat treatment of printed functional materials in a furnace. The advantage of laser sintering is its high speed, precise control of energy, and the ability thus to significantly speed up and tailor the manufacturing process of a device.

A series of experiments for laser sintering of dispenser printed p- and n-type bismuth telluride-based thermoelectric materials was conducted. The laser process is compared to conventional thermal post processing of the printed individual layers in a tube furnace. The experiments were part of an additive manufacturing approach to produce thermoelectric generators/Peltier coolers with the possibility for automatized manufacturing.

A 600 W, 1064 nm continuous wave laser was used for the experiments in combination with a scanning system, together with a 160 mm collimation and a 340 mm F-Theta objective for focusing the beam. Laser treatment was done off the focal plane.

The role of sintering atmosphere and specific laser energy density on the electrical conductivity and Seebeck-coefficient was investigated. A design of experiment approach was chosen in order to analyze the specific influence of single laser process parameters on the electrical conductivity of the printed layers. It is shown that reducing the influence of the laser parameters of power, pitch, and scan velocity to the overall parameter specific surface energy density does not sufficiently describe the process. Further, experiments with p- and n-type materials gave different results. Problems concerning the exact determination of the conductivity of the layers are discussed. It is shown, that the electrical conductivity can be improved via laser processing with respect to the oven processed specimen. Nonetheless, the measured Seebeck coefficient decreased significantly which is attributed to the phase changes in the material or local depletion of elements. Cross sectional images and elemental distribution are presented and discussed.

17:00 - 18:30

Optimizing heat harvesting in a membrane based planar µTEG; modelling and fabrication

Z. Bougrioua[1], I. Bel-Hadj[1], K. Ziouche[1]

[1]IEMN, CNRS and Lille University, France

Micro-thermoelectric generators (µTEGs) are energy harvesting solutions to supply power for autonomous microsystems and other miniature applications. Based on a preliminary modeling we designed original all-Silicon µTEGs with a planar configuration in which the heat to harvest flows in-plane of a TE thin film. Such planar µTEGs were fabricated by CMOS compatible technology: they are ~1/3 cm² and are based on a polySi/Au thermopile periodically distributed onto dielectric membranes; a heat-collector permits to concentrate the energy to harvest onto half the junctions of the thermopile. This planar topology allows the implementation of thermocouples with a high aspect ratio compared to classical vertical TEGs. This results into modules with high thermal resistances (can be tuned from 10 to 112 K/W) and that generate an important open circuit voltage which varies linearly with input heat: for instance, 6 to 10 Volt for 1W heat injected in the devices. Those experimental values correspond to a gradient of temperature at each thermocouple of 113°K, 74°K or 27°K for µTEG with respectively 2, 5 or 10 membranes. However, the weak point of these µTEGs is their high internal electrical resistance, which result into maximum output powers (P_max) that are moderate: up to 62µW/cm², 164µW/cm², and 86 µW/cm², for respectively 2, 5 or 10 membranes µTEGs and 1W injected. To better clarify further improvement to be carried out, the µTEG structure is modelled using COMSOL 3D thermal simulation for different new situations: higher power factor, modified thermal conductance, elimination of parasitic heat losses. In particular, we show that: i/ considering a thermopile integrating a constantan layer can triple P_max, ii/ the optimum membrane number is 4 (not 5), iii/ a modified heat-collector with corner bosses made of porous Silicon permit to generate up to 64% more power.

Theory and Modeling

17:00 - 18:30

Room: Panorama

Chairs: Marisol Martin Gonzalez, Luis Fonseca, Alexander Burkov

17:00 - 18:30

Correction of Lattice Thermal Conductivity in Compounds with Electrically Resistive Grain Boundaries

M. Wood[1], J. Kuo[1], T. Slade[1], G.J. Snyder[1]

[1]Northwestern University, United States

Nano structuring thermoelectric materials has long been a technique to scatter phonons and lower a material's lattice thermal conductivity [1]. The lattice thermal conductivity of a material has historically been estimated by subtracting the electrical portion of thermal conductivity (calculated using the Weidman-Franz law) from the total thermal conductivity of a material ($\kappa_L=\kappa-L\sigma T$). This method treats heat conducted by phonons and heat conducted by electrons as two separate and independent transport channels. While nano-structuring is known to scatter phonons, in some materials shrinking the grain size can have a detrimental effect on the electronic properties through additional grain boundary scattering [2]. Herein we discuss how this grain-boundary scattering can lead to underestimating the experimentally obtained electronic thermal conductivity, which necessitates a correction term to our estimation of lattice thermal conductivity.

1. Minnich A. et al., Energy Environ. Sci., 2009, 2, 466

2. Kuo J. et al., Energy Environ. Sci., 2018, 11, 429

17:00 - 18:30

Modeling and uncertainty analysis of Seebeck coefficient measurements by Finite Element Method

K. Huang[1], F. Edler[1], S. Haupt[1], P. Ziolkowski[2], C. Stiewe[2], E. Mueller[2]

[1]PTB, Germany
[2]DLR, Germany

Precise and to SI units traceable measurements of the transport properties of thermoelectric materials, Seebeck coefficient (S), electrical conductivity (σ) and thermal conductivity (κ), are the basis for the performance characterization and comparison of different thermoelectric materials. Uniform measurement techniques or consistent measuring protocols have not yet been well established at metrology institutes around the world. Therefore, reference materials for the thermoelectric transport properties play a fundamental role to assess measurement devices and measuring procedures. Hence, the aim of our project “TEST-HT” (Thermoelectric Standardization for High Temperatures, funded by the German Ministry of Education and Science) is the development of the first semiconducting reference material for the power factor (PF = S2·σ) in the temperature range between 300 K and 1100 K [1].

The work presented here is focused on the determination of the measurement uncertainty of the Seebeck coefficient of semiconducting bulk materials. A reliable and precise Seebeck coefficient determination requires the measurements of the electric potential and the temperature difference at the same time and at the same position. Different simulations of Seebeck coefficient measurements are performed to quantitatively explore effects and measurement uncertainties. The following effects are studied by finite element method (FEM): different analytical data choices of the whole data set which lead to different results, the influence of minimal temporal shifts of voltage and temperature measurements, the “cold-finger” effect, the applications of quantitatively different temperature gradients, etc. FEM allows the exploration of the data space under ideal conditions, which are hardly obtainable in real experiments. The results of the simulations are used to establish a detailed uncertainty budget of the Seebeck coefficient measurement.

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17:00 - 18:30

First-principles evaluation of electron-phonon coupling factor and lattice thermal conductivity of L12 type alloys

S. Yabuuchi[1], Y. Kurosaki[1], N. Fukatani[1], J. Hayakawa[1]

[1]Hitachi Ltd. Research & Development Group, Japan

Recently, it has been reported that a nanoscale metal/nonmetal multilayer is a potential structure to reduce the thermal conductivities in spite of using metallic materials [1]. We have reported that a nanoscale meal/semiconductor multilayer enables to enhance the thermoelectric figure of merit by using metals with a weak electron-phonon coupling factor and a low lattice thermal conductiviy[2]. In this study, we focus on L12 type alloys as a typical metal. The electron-phonon coupling factor, the lattice thermal conductivity, and the interfacial thermal resistance originated from non-equilibrium state between electrons and phonons were theoretically investigated by using first-principles calculations.

We evaluated the properties of L12 type alloys (X3Y: X,Y = Cu, Ag, Au, Pt, Pd,). The electron-phonon coupling factors of Pd- and Pt-based alloys are much higher than that of Cu-, Ag-, and Au-based alloys because the density of states at Fermi level of Pd- and Pt-based alloys are much higher than that of Cu-, Ag-, and Au-based alloys. The lattice thermal conductivities of Au-based L12 type alloys are lower than other alloys because of the low force constant and the heavy atomic mass of Au. We also evaluated interfacial thermal resistance originated from non-equilibrium state between electrons and phonons. The interfacial thermal resistance regarding Au3Ag is the highest owing to the low electron-phonon coupling factor and the lattice thermal conductivity. Our results indicates that Au-based alloys are promising candidates for metallic materials enhanceing the ZT of meal/semiconductor multilayer.

This work is based on results obtained from the Future Pioneering Program “Research and Development of Thermal Management and Technology” commissioned by the New Energy and Industrial Technology Development Organization (NEDO). It is also supported by TherMAT.

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17:00 - 18:30

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

K. Shishov[1, 2], R. Poshekhonov[1, 2], A. Osipkov[1, 2], P. Shiriaev[1, 2], S. Sattar[1]

[1]RUDN, Russia
[2]BMSTU, Russia

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

17:00 - 18:30

In silico studies of chosen doped and co-doped type I silicon clathrates

W. Szczypka[1], A. Kolezynski[1]

[1]AGH University of Science and Technology, Poland

Establishment of silicon clathrates as convenient materials in thermoelectric applications is based on two important assumptions: high abundance of elements and good stability up to high temperatures. In this work several compositions of doped and co-doped type I silicon clathrates of general composition K8MxSi(46-x) were studied within full-potential DFT calculations carried out using WIEN2k software. Various configurations of dopants location in a system allowed to determine their most probable location. Electronic structure of analysed systems, described by total densities of states together with band structure was discussed from the point of view of thermoelectric performance. Local influence of dopants in a system - introduced distortions of structure and charge - was described based on the analysis of total electron density topology within Bader's approach. Detailed investigation of local and global properties of a system toghether allowed to indicate the most promising candidates for further analysis in a real experiment.

17:00 - 18:30

Thermodynamics of atom motion and metal deposition in mixed ionic electronic conductors

M. Agne[1], P. Qiu[2], X. Shi[2], G.J. Snyder[1]

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[2]Shanghai Institute of Ceramics, China

The possibility of decomposition in superionic mixed ionic-electronic conductors (MIEC) has limited their engineering applications. Specifically, high efficiency MIEC thermoelectric materials have not been utilized due to decomposition under large electronic currents and large temperature gradients. Herein, we derive the critical condition for decomposition, which corresponds to a critical chemical potential difference defined from linear non-equilibrium thermodynamics. This analysis leads to the conclusion that voltage, not current density, is the relevant design parameter. Consequently, the decomposition condition is independent of the geometry of the device; whereby, a strategy is presented for improving stability in devices subjected to electrical and temperature gradients.

By using a series of electronically conducting, but ion-blocking barriers to reset the chemical potential it is possible to keep the material below the threshold for decomposition. Experimentally, the thermodynamic theory is validated in copper chalcogenide MIEC systems.

17:00 - 18:30

FEM simulation of terahertz antenna based on Sb and BiSb12 thing films

A. Asach[1], M. Khodzitsky[1], E. Makarova[1], N. Kablukova[2, 3], A. Tukmakova[1], I. Tkhorzhevskiy[1], A. Novotelnova[1]

[1]ITMO University, Russia
[2]Herzen University, Russia
[3]SPbSUITD, Russia

Thermoelectric materials are perfectly suited for terahertz detectors. Electric potential due to the Seebeck effect in the contact of two semiconductors enhances the antenna's efficiency. This work presents the numerical modeling of terahertz antenna based on Sb/BiSb12 thin films taking into account the influence of thermoelectric effect. The thin layer of two semiconductors which was placed on mica, absorbs and dissipates the terahertz radiation energy. THz radiation power was 20 mW, the frequency was 0.7 THz. The influence of the antenna's layer thickness from 50 to 150 nm was considered. The contribution of the thermoelectric effect to the electric potential difference was analyzed.

This work was financially supported by the Russian Science Foundation (Grant №19-72-10141).

Invited II

8:45 - 10:15

Room: Panorama

Chair: Terry Hendricks

8:45 - 9:15

Advanced High Temperature Thermoelectric Converter Technologies: Resolving Development Challenges and Planning for a Successful Infusion into System Applications

J. Fleurial[1], T. Caillat[1]

[1]Jet Propulsion Laboratory, United States

Radioisotope Thermoelectric Generators (RTGs) have proven to be extremely reliable components of space power systems, enabling the scientific exploration of deep space, Mars, and the moon. These systems are based on technological advances completed in the 1960's and 1970's. RTGs have relied on thermoelectric couple technology based on materials identified and developed over 50 years ago. These "single point design" generators use a "simple but effective" converter array configuration with hundreds of discrete thermoelectric (TE) couples interconnected on the cold side in a series-parallel "laddering" pattern to achieve high redundancy and eliminate single point failures while meeting their output voltage requirement under maximum output power condition.

NASA constantly seeks the development of more capable and high-performing flight systems in support of future science and exploration missions, and it is desirable to identify and develop common energy converter technology "building blocks" that could span a wide range of potential next-generation system configurations and power levels.

An optimal approach for practical and efficient thermal and mechanical integration with the heat source and heat rejection system components is to develop robust modular TE device architectures. This provides maximum versatility for application to system concepts ranging from terrestrial high-grade waste heat recovery to space power. The research community has heavily focused on the development of more efficient thermoelectric materials, an important goal in terms of expanding the range of potentially relevant power generation applications, but it is unfortunately only addressing the first step along a number of scientific and engineering challenges in developing viable converter technologies capable of operating reliably for many years in harsh environments at an acceptable combination of cost and performance points.

We illustrate these challenges by discussing progress and setbacks in the development of high temperature multicouples based on skutterudites and Zintl phases for application to space power systems.

9:15 - 9:45

Thermoelectric generators with high power density: challenges and study case with skutterudites-based modules

I. Kogut[1], D. Kenfaui[1], P. Masschelein[1], S. El Oualid[1], C. Candolfi[1], B. Lenoir[1], M. Bartel[2], E. Geczi[2], M. Jaegle[2], J. König[2], A. Dauscher[1], A. Jacquot[2]

[1]Institut Jean Lamour, France
[2]Fraunhofer IPM, Germany

Thermoelectric power generators could be well suited to convert low-graded heat into useful electricity and to increase energy efficiency on a global scale. Nevertheless, power density and the scarcity (and thus price) of the elementary constituents of the thermoelectric materials are critical factors when it comes to applications on an industrial scale.

In this presentation, we will present the challenges and our strategy to reach higher power density by using quite thin thermoelectric converters that are able to produce more power in a compact design with less thermoelectric materials. Research and development effort focused on the production of thermoelectric legs made of efficient thermoelectric materials (n and p- type skutterudites) able to work in the mid temperature range (up to 850 K). Legs that encompassed diffusion barriers and electrodes on both sides of the thermoelectric material have been produced in one step by spark plasma sintering so that they can be directly used in the further building the thermoelectric converters. The thickness of the thermoelectric materials could be down-sized to 200 µm, but the output power was maximum for a thickness of 1 mm. Very compact thermoelectric converters have been fabricated, with a lower amount of thermoelectric material than in prior works. A power density as high as 7.3 W/cm2 could be achieved for a □T of 600 K, far above the current state of the art.

9:45 - 10:15

Understanding Detailed Crystal Structures to Further Improve Thermoelectric Properties of Silicide-based Materials

Y. Miyazaki[1], H. Nagai[1], W. Saito[1], K. Hayashi[1]

[1]Tohoku University, Japan

Silicide-based thermoelectric (TE) materials have recently attracted renewed interest as they consist of naturally abundant and less-toxic elements. Among the silicide TE materials, higher manganese silicides (HMSs), CrSi2 and Mg2Si-based materials are potential candidates to be used at a mid-temperature range 500-1000 K. In this contribution, we will focus on detailed crystal structures of the silicides to further improve TE properties.

HMSs had a serious problem to form MnSi (monosilicide) striations during the solidification. We have discovered that the partial substitution of transition elements, e.g., Cr, Co and V for Mn sites effectively dissipates such striations as well as a moderate hole-doping which raises the TE power factor almost doubled at 800 K. The Cr- or Ru-substitution induces a domain separation of Mn-rich and Mn-poor regions, with a micrometer-scale, which causes a significant reduction of lattice thermal conductivity. Unusual temperature evolution of lattice parameters, originates from the difference in the coefficient of thermal expansion of two sublattices, is another critical phenomenon to restrict the material for a wide use. We will discuss the solutions from the viewpoints of crystallographic knowledge.

CrSi2 allows partial substitutions on the Cr sites and lots of partial substitutions with V, Mn, Mo or Nb have been performed. We have discovered that some metal atoms can also occupy the Si sites as hole-dopants and may shift the maximum operating temperature towards higher, which ensures a wide usable temperature range from room temperature to ~800 K.

Interstitial Mg (MgI) plays a crucial role to dictate the conduction type in Mg2Si-based materials. We will demonstrate the effect of MgI and possible point defects on the TE properties in Mg2(Si1-xSnx) solid solutions.

This study is supported, in part, by New Energy and Industrial Technology Development Organization (NEDO) and JSPS KAKENHI (25289222, 17H03398 and 17H05207), Japan.

Power Generation

10:45 - 12:15

Room: Panorama

Chair: Dario Narducci

10:45 - 11:00

Thermoelectric System Economics: New Hot-Side Thermal Design Paradigm Drives Terrestrial Thermoelectric Power System Costs

T. Hendricks[1]

[1]Jet Propulsion Laboratory/California Institute of Technology, United States

Thermoelectric power technology can have key benefits and strengths in many terrestrial energy recovery applications. Thermoelectric system cost, G [$/W], and its dependency on TE converter fill factor, F, are key factors governing final decisions on using thermoelectric energy recovery systems in all terrestrial applications; thus cost being just as important as power density or efficiency in adopting of waste energy recovery (WER) thermoelectric generators (TEG). New integrated cost analysis / thermoelectric analysis approaches have now shown key optimum [Gopt, Fopt] relationships and interdependencies between overall TEG system costs, including TE material costs, manufacturing costs, and specifically heat exchanger costs, and the TE performance design metrics such as TE material properties, TE device design parameters, heat exchanger performance metrics such as hot-side and cold-side conductances and UA values, and hot side heat flux in achieving optimal WER TEG designs. New work now examines the key heat flux and heat exchanger cost sensitivities and interrelationships using the new optimum [Gopt, Fopt] relationships to show the dominating role TEG hot-side heat flux plays in new thermoelectric system economics (TSE) paradigms, generates quantitative data showing these sensitivities, and their serious implications on TEG system design in terrestrial WER applications. This work elucidates a new TSE paradigm that indicates hot-side heat flux plays a more influential role than TE material costs themselves or TE device geometry factors in reducing TEG system costs toward the elusive $1-$3/W range. Current results show a four-fold increase in hot-side heat flux can decrease TEG system costs by approximately four times, and has a more dramatic effect on TEG system costs than a five-fold decrease in TE material and manufacturing costs or a four-fold decrease in TE couple dimensions. Raw heat exchanger costs [$/(W/K)] to achieve the high- heat-flux conditions are also shown to have a dominating influence.

11:00 - 11:15

Industrially Scalable Thermoelectric System for Waste Heat Recovery using Heusler-based Modules and Heat Pipes

G. Roy[1], v. Marchal-Marchant[1], O. Poncelet[1], C. van der Rest[1], A. Schmitz[2], P.J. Jacques[1]

[1]UCLouvain, Belgium
[2]CRM Group, Belgium

Thermoelectricity has been proposed as a promising solution for waste heat to electrical power conversion for decades now. However, it has rarely passed the step from prototype to commercial product due to cost limitations. It is well established that thermoelectric materials and heat exchangers are the major parts of the cost [1]. We propose a solution to decrease these costs: (i) the use of low-cost modules based on the full Heusler Fe2VAl compound [2] and (ii) the use of water-filled carbon steel heat pipes [3].

In this work, a thermoelectric system for waste heat recovery is designed for an industrial case study. This design shows that costs could be decreased by a factor of two compared to a system using Bi-Te based modules and a copper finned heat exchanger. In order to validate this design, the combination of a heat pipe with TE modules has been experimentally characterised demonstrating the high heat transfer capability of heat pipes. Finally, a fully instrumented pilot thermoelectric heat exchanger based on 30 heat pipes has been developed and tested on a 450 kW hot gas test rig with gases up to 450°C. Experimental results will be presented and the next steps to reach the industrial scale will be discussed.

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11:15 - 11:30

Growth of a compact thermoelectric generator based on multi-disciplinary approach

C. Fanciulli[1], S. De Iuliis[2], A. Nespoli[1], H. Abedi[1], E. Bassani[1], N. Bennato[1], R. Dondè[2], F. Migliorini[2], S. Battiston[3], N. El Habra[3], F. Montagner[3], R. Gerbasi[3], F. Passaretti[1]

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Electrical power and device portability are two actual challenges of technological world. The capability of achieving a full connectivity and a smart interaction between environment and devices are two of the mainstream engines of actual technological development. Such a target requires a diffuse network of electrical power, able to support the battery needs related to mobile devices. This work wants to introduce the supply chain the ICMATE group is growing in the development of a novel device based on the combined action of thermoelectric effects, catalytic combustion, additive manufacturing and advanced coating technologies. The device aims to support a distributed electrical low power production in a compact and light design, taking profit from the advantages offered by the embedded technologies and the expertise in processes analysis of the team involved in the development. The preliminary results display an improved chemical efficiency of the combustor ranging between 85 and 90%. At the same time, the overall efficiency results to be almost independent of the operating regime. The electrical output of the TEG reaches 8.6W using 16g/h of propane, but the most promising characteristic is related to the matching load voltage, close to the 12V useful for battery backup applications.

11:30 - 11:45

Integration of the Lifetime Performance Prediction Model with SINDA for Improved Thermoelectric Generator Power Estimates

C. Matthes[1], T. Hendricks[1], E. Wood[1]

[1]NASA - JPL, United States

The Lifetime Performance Prediction Model (LPPM) developed at Jet Propulsion Laboratory is a generalized physics-based tool to model thermoelectric converter performance in Radioisotope Thermoelectric Generators (RTGs) for a variety of flight and storage operating conditions over long durations. LPPM was originally developed to employ a simple one-dimensional thermal-thermoelectric (TE) system model, with a set of physical equations to be solved iteratively. An input database of test data includes time- and temperature-dependent thermoelectric (TE) materials properties (Seebeck, thermal conductivity, and electrical resistivity) from TE coupon testing, and measured TE degradation mechanisms including time and temperature-dependent sublimation rates for coated and uncoated TE material elements.

Through the years, one-dimensional LPPM predictions have been verified and validated using flight mission power data as well as electrically-heated thermoelectric generator (ETG) power data. Until recently, LPPM's one-dimensional thermal approach assumed uniformity among the couples across the generator by using a single hot junction temperature node, which prevents insight into the effects of axial and circumferential thermal variations. In preparation for the Mars 2020 and future potential NASA missions, JPL is refining and upgrading its modeling capabilities for future RTG system configurations. Recent efforts to upgrade LPPM's capability using a system-level SINDA (Systems Improved Numerical Difference Analyzer) thermal model have significantly enhanced the model's ability to provide detailed three-dimensional performance estimates. This SINDA-LPPM analysis enhancement effort will be discussed, highlighting major modeling advances and refinements, and including initial comparisons to other RTG performance models as well as actual ETG data. This enhanced SINDA-LPPM tool has been shown to provide powerful insight into mission power resources over time. Three-dimensional power degradations and generator-level thermal environments can now be estimated for different time profiles, spacecraft configurations structures, and solar and planetary environments for current and planned missions, and beyond.

11:45 - 12:00

Assessment of a High Power Density Thermoelectric Generator Concept for Industrial Applications

F.P. Brito[1], R. Vieira[1], N. Pacheco[1], J. Martins[1], L.M. Goncalves[1], A. Goncalves[2], T. Kyratsi[3], J. Stockholm[4]

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Thermoelectric generators (TEGs) often display a high cost per unit power and a low power density. This has limited the interest of TEGs for large scale waste heat recovery applications. While the conversion efficiency of currently available thermoelectrics materials is still modest, it is also true that often TEG generators are not optimized geometrically: they are built with commercially available modules which have a design more suited for small scale cooling applications. Each module is comprised of dozens of tiny thermoelectric elements cut and assembled together with tight tolerances. A large scale TEG application needs dozens of these modules, so it is apparent that the cost per unit power produced with such intricate systems could hardly be low when compared with competing waste heat recovery technologies.

Until now, little attention has been given to custom-built systems displaying larger TEG elements arranged in series along smaller chains of n- and p-type elements. This configuration is much simpler in terms of construction. It has been previously demonstrated that it is possible to achieve a high theoretical power density using this arrangement, but challenges related to the customization and the lower voltages/higher currents achieved with such systems has prevented their development.

The present study assesses the potential of a TEG concept comprised of large (24-25mm diameter, 1mm thickness) bismuth telluride elements arranged along a column such that the electrical path is short and straight and allows for acceptable current density despite the high currents involved. Additionally, the use of novel high figure-of-merit and earth-abundant n-magnesium silicide and p-tetrahedrite elements was also assessed as it may allow an affordable solution for large-scale applications.

The geometry assessed will also allow to test the ultrafast conduction phenomenon conjectured by Apostol, which predicts even higher power density and system efficiency when operated under high frequency loading.

12:00 - 12:15

SiGe low density fibres mats as efficient thermoelectric generators

M. Pacios[1], J.M. Sojo[1], G. Gadea[1], A. Morata[1], A. Cabot[1, 2], A. Tarancon[1, 2]

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A cost-efficient and environment-friendly synthesis route for the fabrication of silicon thermoelectric (TE) material based on nanostructured fibres has recently been shown [1]. The p-silicon thermoelectric system displays high figure of merit and high power densities at middle and high operating temperatures. The methodology has proved to be reproducible and scalable.

Now we go one step forward and we show the versatility of the methodology by its the extension to other materials such as SiGe. We have achieved power densities of some tens of mill-watts per square centimetre when it is at 1000k. To demonstrate its potential, we have fabricated a proof of concept p-type mono-leg thermoelectric generator.

Self-powered sensors and sensing systems without an external power supply have become popular in recent years and have shown superior advantages. Therefore, we also propose the possibility of our system to be used as a thermoelectric sensor employing catalytic deposited thin films on the thermoelectric surface. The large surface area of our fibre-based TE could present an advantage for such applications.

[1] Morata et al. Large-area and adaptable electrospun silicon-based thermoelectric nanomaterials with high energy conversion efficiencies. Nature Comm. 9, 4759 (2018)

Chalcogenides III

10:45 - 12:15

Room: Megaron B

Chair: Janusz Tobola

10:45 - 11:00

Tl-doped SnSe single crystals

K. Šraitrová[1], P. Levinsky[2], J. Hejtmanek[2], V. Kucek[1], Č. Drasar[1]

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Tin selenide (SnSe) is a semiconducting material with an extraordinary thermoelectric (TE) performance especially in high temperature range. According to our observations, a stable and effective doping of this compound is still disputable. This is mainly due to the very low equilibrium solubility of dopants and formation of extraneous phases at elevated temperatures. Thus, a shift of optimal TE performance towards low temperatures is advisable. In the present contribution, we report on TE properties of Tl-doped SnSe single crystals. The single crystals were oriented using electron backscatter diffraction (EBSD). Examinations included X-ray diffraction (XRD), energy-dispersive spectroscopy (EDS), measurements of the Seebeck and Hall coefficient, and electrical and thermal conductivity. The experiments suggested rather low solubility of Tl (<0.5 %) however a reasonable doping efficiency. Slight Tl doping (≈0.1 %) resulted in a substantial improvement of TE performance. However, the dopant is distributed non-homogeneously in single crystals prepared by free melt crystalization. This in turn led to some fluctuation of TE properties of doped samples within one batch. Importantly, TE performance of some samples is largely superior to other samples indicating space for further improvements of preparation route. We found room temperature power factor above 4 mWK-1m-2 along crystallographic axes b.

11:00 - 11:15

Effect of the resonant In dopant on the electronic structure, effective mass and lifetimes in SnTe studied using Bloch spectral functions

B. Wiendlocha[1], S. Misra[2], A. Dauscher[2], B. Lenoir[2], C. Candolfi[2], J. Tobola[1]

[1]AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Poland
[2]Institut Jean Lamour, Université de Lorraine, Nancy Cedex, France

Indium doped SnTe has recently gained attention as an example of a lead-free classical thermoelectric material, whose performance may be improved due to the formation of a resonant state. Resonant In impurity strongly affects electronic structure of SnTe and at sufficiently low temperatures is probably even responsible for superconductivity in this material. From the thermoelectric point of view, the key problem whether such a resonant impurity state may improve thermoelectric properties is related to the (de)localization of electronic states associated with resonance, or in other words tendency to forming a narrow impurity band, which would not contribute much to the thermopower of the system. Such a tendency may be suggested by the fact, that resonant impurities form sharp peaks in electronic densities of states.

In this work we apply the KKR-CPA method to calculate Bloch spectral functions, which replace usual dispersion relations in a disordered system and allow to take into account effects of strong scattering of charge carriers on the resonant level and on Sn vacancies, always present in the material. We show that In does not create impurity band near the Fermi level in SnTe, but strongly affects the host band structure, leading to smearing of energy bands near the band edge. In return, additional electronic states, being of hybridized impurity and host character, appear between L and Sigma points in the Brillouin zone, increasing the number of carriers available for charge transport near the valence band edge. This shows, that In doped SnTe is much similar to the better known example of a resonant system, i.e. Tl doped PbTe. In addition, effective mass m* and carrier life times t are computed and increase in m* and reduction of t due to the presence of resonant state in SnTe:In are discussed.

11:15 - 11:30

Thermal conductivity of Bi_2Te_3 and SnSe using Debye-Callaway model and Boltzmann transport equation

P. Al Alam[1], D. Lacroix[1], G. Pernot[1], M. Isaiev[1], M. De Vos[2], N. Stein[2], D. Osenberg[3], L. Philippe[3]

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[2]Université de Lorraine, CNRS, IJL, France
[3]EMPA, Thun, Switzerland

Due to the various applications in power generation and waste heat harvesting, thermoelectric materials attract the attention of researchers for their ability to convert directly heat into electricity. The efficiency of energy conversion is strongly related to the lattice thermal conductivity which requires to be properly investigated. This work presents the assessment of thermal conductivity for Bi2Te3 and SnSe thermoelectric materials through the resolution of Boltzmann transport equation (BTE) for phonons. First, simplified dispersion properties combined to the Debye-Callaway model based on relaxation time approximation were used to evaluate phonon scattering lifetimes using experimentally measured input parameters (i.e.: the Grüneisen parameter γ, the Debye temperature θD, the mass disorder lifetime Γ and the group velocities vg). For both materials distinct crystalline directions are considered to evaluate phonon frequencies and group velocities (Γ- Z and Γ- X for Bi2Te3 and Γ- X, Γ- Y and Γ- Z for SnSe). On this basis, using our model, the bulk thermal conductivity of the latter compounds is computed for the first time with a Monte Carlo (MC) method to solve the BTE.

For Bi2Te3 and SnSe, the mass disorder Γ and the Grüneisen γ parameters were found to influence significantly the computed thermal conductivity in bulk at several temperatures. Thus, the latter quantities are adjusted to fit experimental data proposed in the literature. In the second part of this study, the thermal conductivity for these two thermoelectric compounds is computed in the case of thin films (cross-plane) and for nanowires. A significant reduction in thermal conductivity is observed for thin thicknesses due to boundary scattering and ballistic phonon transport. For both materials, MC results are successfully compared to experimental measurements reported on similar crystalline structures like nanowires.

11:30 - 11:45

Electronic mechanisms for optimizing the thermoelectric properties of SnTe alloys

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The demand for energy efficiency was motivated many researchers to seek for novel methods capable of enhancing the conversion efficiency of heat to electricity. Most of the recently published methods for thermoelectric (TE) enhancement are mainly attributed to the reduction of the lattice thermal conductivity, with a limited focus on efficiency enhancement due to an improved electronic optimization. This is attributed mainly to the fact that the electronic properties are correlated and opposing each other upon increasing the carrier concentration.

SnTe is receiving an extensive attention due to its eco-friendly nature and band structure which is very similar to the efficient Pb-based TE materials. SnTe has inherent Sn vacancies and a high hole concentration leading to degraded ZT. Nevertheless, with effective electronic approaches, such as co-doping of bismuth and another donor-type impurity, significant improvements can be achieved.

This research aims to investigate the approach of increasing the number of vacancies in the bismuth doped non-stoichiometric SnxTe1-x compound, in order to extend the solubility limit of another dopant and enhance its effect on the electronical properties. Indium/iodine were chosen as cationic/anionic impurity dopants, in an attempt to improve the TE performance.

11:45 - 12:00

Transition metal dichalcogenides: the influence of samples sintering on their thermoelectric properties

V. Kuznetsov[1, 2], G. Yakovleva[1], S. Artemkina[1], B. Kuchumov[1], A. Romanenko[1], V. Fedorov[1], M. Han[3], S. Kim[3]

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There are several ways to form polycrystalline ceramic samples. Here we investigate the influence of the sintering of the transition metal dichalcogenides samples formed with a laboratory hydraulic press on their thermoelectric properties by the example of TixNb1-xSySe2-y (x from 0.02 to 0.15, y from 0.7 to 1.5). Polycrystalline powder specimens of the dichalcogenides were obtained by high temperature synthesis in a sealed ampoule. Thermoelectric properties were studied on the bulk samples formed at a pressure of 2000 MPa at room temperature and on the samples sintered at 600, 850 and 950°C in evacuated quartz ampoules. Morphology of the samples was studied with scanning electron microscope TM-3000. It has been shown that the crystallites are predominantly oriented perpendicular to the pressing direction. The sintering resulted in an increase of the grain sizes, and first to an improvement of the properties and then to their degradation. The maximum value of figure of merit ZT at room temperature for measurements along the grains was about 0.22 for the composition of Ti0.98Nb0.02S1.3Se0.7.

The work was supported by the Russian Foundation for Basic Research (Grant No. 18-503-51017) and by the National Research Foundation of Korea (NRF) Grant funded by the Korean Government (NRF-2015R1A5A1036133 and NRF-2017K2A9A1A06051881).

12:00 - 12:15

The effect of samples texturing on thermoelectric properties of titanium dichalcogenides with double substitutions $Ti_{1-x}Nb_xS_{2-y}Se_y$

A. Romanenko[1], G. Yakovleva[2], A. Ledneva[1], S. Artemkina[1], V. Kuznetsov[3], K. Zhdanov[1, 4], V. Fedorov[1], M. Han[5], S. Kim[5]

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In thermoelectric materials, an increase in the electrical conductivity σ, which is necessary to increase the thermoelectric figure of merit ZT of the thermoelectric, is always accompanied by a decrease in the thermoelectric power S and an increase in the electronic part of the thermal conductivity kel. And this, in turn, leads to a decrease in thermoelectric figure of merit in accordance with the equation ZT=S2σT/k, where T is the temperature. Therefore, it is necessary to optimize the parameters of thermoelectrics. Anisotropy of transport properties adds an additional parameter affecting the relationship between the electrical conductivity and thermoelectric power in a thermoelectric. But in textured samples, usually, the electrical conductivity and thermal conductivity across the texture decrease equally and the thermopower is isotropic. As a result, the figure of merit ZT is almost independent of orientation in textured samples. In systems with quasi-two-dimensional electronic transport the quasi-two-dimensionality of the electron transport is added to the usual texturing. As a result, the ratio between thermoelectric parameters is changed.

We investigated the effect of texture on thermoelectric properties in quasi-two-dimensional transition metal dichalcogenides. We found that the electrical conductivity and thermal conductivity vary in different ways in titanium dichalcogenides with double substitutions Ti1-xNbxS2-ySey, which leads to an increase in the figure of merit ZT in textured samples on the base of Ti1-xNbxS2-ySey across the texture. Besides in systems with Fermi degeneration statistics, which include degenerate semiconductors and metals, the thermopower is inversely proportional to the Fermi energy EF. This leads to an increase compared to the three-dimensional case, since EF decreases when moving from three-dimensional systems to a lower dimensionality.

The work was supported by the Russian Foundation for Basic Research (Grant No. 18-503-51017) and by the National Research Foundation of Korea (NRF) Grant funded by the Korean Government (NRF-2015R1A5A1036133 and NRF-2017K2A9A1A06051881).

Oxides II

10:45 - 12:15

Room: Megaron C

Chair: Antoine Maignan

10:45 - 11:00

High Thermoelectric Performance of Reduced Nb-doped $SrTiO_3$ Containing Exsolved Ni nanoparticles

M. Ohtaki[1, 2], S. Hirata[1], K. Suekuni[1, 2]

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[2]Transdisciplinary Research and Education Center for Green Technologies, Kyushu University, Japan

Microstructure control has been a key to improve the thermoelectric performance of bulk thermoelectric materials, enabling a significant reduction of the thermal conductivity and a possible enhancement in the power factor. In this paper, we report a high thermoelectric performance of sintered SrTiO3 (STO) doped with Nb and Ni, containing Ni nanoparticles formed via an exsolution reaction caused by a reducing post-treatment.

Samples with the representative composition of Sr0.95(Ti0.8Nb0.2)0.95Ni0.05O3 were prepared by conventional solid state reaction. The samples were sintered at 1693 K for 10 h in air and subsequently reduced at 1623 K for 20 h under 5% or 20% H2 in N2. The XRD patterns of all the samples after sintering confirmed that the samples crystallize in the STO structure without any impurity phases. While the STO phase unchanged after the reducing post-treatment, SEM/EDS observation of the cross-section of the samples revealed discretely dispersed Ni particles of ca. 50 nm in diameter inside of the sintered bodies. While the electrical conductivity of the sample reduced in 20% H2 was significantly higher than that reduced in 5% H2, the Seebeck coefficient of the former was just slightly lower than the latter. Moreover, the lattice thermal conductivity was the lowest for the sample reduced in 20% H2, leading to ZT = 0.6 as the highest value among the STO-based oxides so far reported. These results imply that the reducing post-treatment caused the electron doping in STO and the exsolution of Ni nanoparticles simultaneously, resulting in the increase in the electrical conductivity and the suppression of the lattice thermal conductivity. The barely noticeable change in the Seebeck coefficient is probably due to the large effective mass of electrons in the Ti 3d orbitals.

11:00 - 11:15

Enhancement of Thermoelectric Response in A-site Deficient $Ln_2/3TiO_3$ (Ln=La and Nd) Perovskites by Nano Structuring

F. Azough[1], D. Ekren[1], D. Kepaptsoglou[2, 3], Q. Ramasse[3, 4], E. Guilmeau[5], M. Schaefer[5], R. Freer[1]

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[2]Jeol Nanocentre, University of York, United Kingdom
[3]SuperSTEM Laboratory, United Kingdom
[4]University of Leeds, United Kingdom
[5]Laboratoire CRISMAT, France

In the search for new oxides for thermoelectric applications, we have identified A-site deficient perovskites as systems with great potential [1, 2]. Here, we present a synthesis route for the fabrication of nano-structured A-site deficient perovskites.

We prepared A-site deficient Ln2/3TiO3 (Ln = La, and Nd) stabilized with additions of 10 mole% CaTiO3 or SrTiO3 and 1 mole% of MnO by the mixed oxide route. Ceramic samples were directly sintered in a reducing atmosphere or initially sintered in air followed by annealing in a reducing atmosphere. Crystallographic data from X-ray and electron diffraction showed Cmmm and Pban orthorhombic symmetry for Nd0.6Ca0.1TiO3 and (La0.6Ca0.1TiO3 / La0.6Sr0.1TiO3) respectively. Scanning electron microscopy (SEM) showed the presence of phase-transformation-induced twin boundaries and core-shell type structure within the grains of the annealed ceramics. The cores contain inclusions, which are rich in Ti, and include the other constituent elements of the main composition. Atomic-resolution, high-angle annular-dark-field imaging and electron energy loss spectroscopy in the scanning transmission electron microscopy (STEM-HAADF-EELS) showed atomic level structural features that are likely to contribute to the Glass-Phonon thermal conductivity behaviour of this family of perovskites. Nanostructured La0.6Ca0.1TiO3 and Nd0.6Ca0.1TiO3 ceramics exhibited high power factors of 580 and 500 μW/m.K2 and low thermal conductivities of 2.75 and 1.95 W/m.K at 1000 K leading to ZT values at 1000 K of 0.23 and 0.26 respectively.

1. D. M. Kepaptsoglou et al. Inorg. Chem. 2018, 57, 45−55.

2. F. Azough et al. ACS Appl. Mater. Interfaces 2017, 9, 41988−42000.

11:15 - 11:30

“Structural imperfections” in the transition metal oxides SPS synthesis and thermoelectricity.

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The modern requirements of “green” energy technology boosts the search for new “friendly-for-environment” materials and their energy-conserving synthesis. We focus our interest on the chemical insight of the transition metal oxides, using also alternative synthesis routes. Special interest is focused on the spark plasma sintering as a modern and technologically applicable synthesis route for an obtaining the different class of the transition metal oxides. The lager class of the oxides having extended or “structural” defects have a great scientific and industrial demand. Structurally all these oxides are closely related and can be derived from a basic structure, usually highest oxides in the respective metal – oxygen binary systems. In the investigating systems containing ordered planar defects, which include the higher oxides of Ti, Mo, W, oxygen atoms assembled in a three-dimensional framework of close-packed arrangement and metal atoms occupy the octahedral positions. Crystallographic or microstructural features of these oxides are in 0.3–2 nm size range, so that oxide phonons can efficiently interact with them.

The reactivity of solid oxides is a wide and complex topic. A detailed mechanism of SPS reactions between and non-conductive oxide and respective conductive oxide or metal is established. The advantages of our proposed SPS route compared to the classical synthetic techniques for the preparation of the solid oxides are: simultaneous synthesis, compaction and shaping of the final materials, short reaction times, better control of the homogeneity of the final products.

We report the SPS-assisted investigation of a part M – O (M – Ti, V, Mo, W) binary systems in regions TiO2 – TiO and MO3 – MO2 (M – Mo, W) phases. We will show how the formation of the different types of the “structural imperfections” influences on the crystal structure, electrical and transport properties of the synthesized sub-oxides.

11:30 - 11:45

Improved thermoelectric performance of calcium cobaltite by controlling composition and processing conditions

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Calcium cobaltite (Ca3Co4O9) has been identified as a promising p-type thermoelectric oxide material [1]. Here, we present an approach to optimize thermoelectric performance of Ca3Co4O9 by controlling chemical composition and fabrication processes. Ca2.7Bi0.3CoxO9+δ (x=3.92, 3.96, 4) and Ca3-yBiyCo3.92O9+δ (y= 0.1, 0.2, 0.3) ceramics were prepared by the mixed oxide route (MO) and spark plasma sintering (SPS). Stoichiometric mixtures of raw materials were combined and then calcined at 930 °C for 12 hours, followed by pressure-less sintering at 930 °C for 12 hours or SPS at 750 °C for 5 minutes (pressure of 50 MPa). The SPS samples were annealed at 750 °C and 930 °C for 12 hours in air atmosphere.

XRD analysis showed formation of the cobaltite misfit phase with minor amount of secondary phase. Combining data with SEM-EDS results, confirmed the presence of Bi-rich and Co-rich secondary phases in both the initial and annealed SPS samples. However, the amount of the secondary phases decreased significantly or disappeared after annealing at 930 °C for 12 hours. HRTEM images showed that high-quality layer-structured calcium cobaltite based ceramics were successfully prepared; the layers of CoO2 and Rock Salt were stacked along the c axis. Transport properties showed that by controlling the cobalt deficiency and bismuth content the electrical conductivity could be enhanced without significant changes to Seebeck coefficients. As a result, about 15% enhancement in power factor for Ca2.7Bi0.3Co3.92O9+δ, ceramics was achieved (3.23×10-4 Wm-1K-2 at 550 °C) compared with previous studies [2, 3].

[1] N.V. Nong et al., Adv. Mater., vol. 23, no. 21, pp. 2484-2490, 2011.

[2] D. Moser et al., Solid State Sci., vol. 13, no. 12, pp. 2160-2164, 2011.

[3] F. Delorme et al., Ceram. Int., vol. 41, no. 8, pp. 10038-10043, 2015.

11:45 - 12:00

BiCuSeO phase formation mechanism during reactive spark plasma sintering

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In this work, we examined the phase formation mechanism of BiCuSeO oxyselenides fabricated via reactive spark plasma sintering (RSPS) using (a) Bi2O3, Bi, Se and Cu or (b) Bi, Se and CuO as starting materials. The BiCuSeO phase was directly formed in bulk from mechanically activated precursor's stoichiometric mixture during RSPS. It was observed, that single phase bulk BiCuSeO oxyselenides can be obtained for both (a) and (b) precursors. While for samples obtained by conventional solid-state route (SSR) followed by SPS there was no significant difference in the phase composition and density of the final BiCuSeO bulk samples, the relative density of the samples obtained using one-step RSPS process was strongly affected by the used reaction. Thus, the density of the RSPSed samples did not exceed 90% and was not less than 97%, for (a) and (b) reactions, respectively. Our thermodynamic calculations revealed that the formation of BiCuSeO using CuO, Bi and Se (b) requires lower activation energy and has larger thermodynamic driving force compared to than that for the reaction through the Bi2O3, Bi, Se and Cu (a) as precursors. Moreover, according to X-ray phase analysis, the BiCuSeO phase formation mechanism through the reaction (a) was more complicated with complex intermediate phase formed before the main BiCuSeO phase, while for the reaction (b) BiSe and CuO directly formed BiCuSeO. Additionally, it was revealed that phase formation mechanism in bulk during RSPS was similar to that for samples fabricated by mechanical alloying and self-propagating high-temperature synthesis in powder form [1,2].

References:

1. J. Wu, F. Li, T.-R. Wei, Z. Ge, F. Kang, J. He, and J.-F. Li, J. Am. Ceram. Soc. 99, 507 (2016).

2. D. Yang, X. Su, Y. Yan, T. Hu, H. Xie, J. He, C. Uher, M. G. Kanatzidis, and X. Tang, Chem. Mater. 28, 4628 (2016).

12:00 - 12:15

Experimental study of the structure and thermoelectric properties in the Bi_2PdO_4 system

H.H. Nguyen[1, 2], J. Hoffmann[1], K. Habicht[1, 2], K. Fritsch[1]

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Recent computational work has predicted high thermoelectric performance in materials exhibiting a pudding-mold band structure that appears to be realized in compounds containing Pd2+ ions in a square planar configuration [1]. In this respect, the oxide material Bi2PdO4 has theoretically been put forward as an example that combines such favorable electronic band structure with the additional presence of stereo-chemically active Bi3+ lone pair electrons responsible for a low lattice thermal conductivity [2].

In this contribution, we will present the successful synthesis of pure polycrystalline and bulk samples of Bi2PdO4 and Li-substituted Bi2Pd1−xLixO4. We will report on the results of X-ray and high-resolution neutron diffraction measurements to reveal the influence of Li substitution on the crystal structure of Bi2PdO4. Further, we will discuss the results of our thermoelectric characterization performed over a wide temperature range. We will show that the incorporation of Li in Bi2Pd1-xLixO4 leads to an increase in electrical conductivity by two orders of magnitude over un-substituted Bi2PdO4 while maintaining a remarkably low thermal conductivity close to the amorphous limit for both Bi2PdO4 and Bi2Pd1−xLixO4 at high temperatures. We will conclude by comparing our experimental findings to the theoretically proposed involved scattering mechanisms and show that the experimental validation of theoretical predictions is still a crucial step towards the design of future thermoelectrics.

[1] J. He et al., Chem. Mater. 2017, 29, 2529-2534

[2] E.B. Isaacs and C. Wolverton, Chem. Mater. 2018, 30, 1540-1546

Chalcogenides IV

13:30 - 14:45

Room: Panorama

Chair: Euripides Hatzikraniotis

13:30 - 13:45

Power Factor Improvements in Thermoelectric PbTe under Stress

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Lead telluride is one of the most efficient thermoelectric materials known, and previous experiments [1] indicated that hydrostatic pressure can greatly improve the power factor of lead telluride, but the origin of this change has remained unknown.

We have conducted ab initio electronic structure and transport calculations in the framework of density functional theory (DFT) and Boltzmann Transport Theory in order to model how hydrostatic pressure and uniaxial stress can tune the direction-dependent electrical transport properties and enhance the power factor of PbTe.

The electronic band structure and thermoelectric properties of p- and n-doped PbTe were calculated as a function of hydrostatic pressure as well as uniaxial stress along several crystal directions. We found that significant enhancements of the thermoelectric power factor can be obtained, and we analysed the underlying changes in the electronic band structure. We identified the key effects in PbTe, which allowed us to deduce a few more general rules for identifying stress conditions that may improve other thermoelectric materials. These will be presented along with the specific results for PbTe.

Acknowledgments: This work was supported by EPSRC under grant no. EP/L015110/1.

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13:45 - 14:00

Inflection Point for Phonon Thermal Conductivity in Submicron Scale Grained Undoped PbTe by Mechanical Grinding-Hot Pressing

M. Bumrungpon[1], I. Morioka[1], T. Hirai[1], R. Yasufuku[1], K. Hanasaku[1], K. Hasezaki[1]

[1]Tokushima University, Japan

PbTe thermoelectric materials perform well in the intermediate temperature range 450–850 K. It is a narrow band gap semiconductor, of which conduction type and carriers can be controlled by impurity doping or controlling the deviation from stoichiometry. PbTe-based alloys are promising thermoelectric materials because of their low thermal conductivities and large power factors. Considering their limited mechanical strengths, mechanical grinding (MG) is useful for preparing homogeneous and reinforced materials. The improvement in thermoelectric performance can be attained by reduced thermal conductivity due to grain boundary scattering. Undoped PbTe samples were prepared at various planetary ball milling rotational speeds by mechanical grinding (MG) followed by hot pressing (HP). Two kinds of samples were; (i) One by melting at 1123 K and then HP at 147 MPa and 650 K. (ii) MG–HP ones melting at 1123 K and ball milling at rotational speeds from 90 to 180 rpm, followed by HP at 147 MPa and 650 K. The Melting–HP and MG–HP disks had relative densities more than 99% and average grain sizes were estimated to be 660 nm to 22.62 μm with κphonon 1.29-2.21 W m−1K−1. The minimum κphonon of 1.29 W m−1K−1, was obtained for a PbTe disk produced by milling at 120 rpm, with an average grain size of 800 nm. The κphonon for the PbTe disks was constant up to an average grain size of 1 μm, and then decreased in that of less than 1 μm, which shows a threshold for κphonon of a PbTe disks. These results show that there is a grain size inflection point for the threshold value for κphonon of a PbTe disks. The relationship between the average grain size and κphonon corresponds to theoretical calculations and the rotational speed is found dependent upon the thermoelectric properties.

14:00 - 14:15

Enhancement of thermoelectric performance in $Pb_{1-x}In_xTe_{1-y}I_y$ semiconductor by Fermi level tuning and optimization of carrier concentration

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[3]The Łukasiewicz Research Network - The Institute of Advanced Manufacturing Technology, Poland

Thermoelectric properties (Seebeck coefficient S, electrical σ and thermal κ conductivity) of stoichiometric and In-doped PbTe were studied over 25 - 500 °C temperature range and different indium concentrations (0.05, 0.1, and 1.0 at. %, respectively). It was demonstrated that measured values for the Seebeck coefficient at room temperature do not change significantly for different In contents. It confirms the pinning effect, i.e., the close localization of Fermi level EF and indium doping level EIn. The indium doping level is located close to the bottom of conduction band EC, which is optimal to get the maximum value of power factor S2σ over a wide temperature range.

PbTe semiconductor doped by In and I is an excellent candidate for middle-temperature thermoelectric application. Such a combination of dopants gives the possibility for both attuning Fermi level at an optimal position and keeping the required concentration of carriers at high temperatures. High electron concentration caused by indium and iodine dopants at high temperature minimizes the influence of minority carriers at n-PbTe, which drastically decreases their thermoelectric efficiency.

14:15 - 14:30

The effect of exceptionally high Cd addition on room-temperature thermoelectric properties of monocrystalline PbTe-CdTe solid solution

M. Szot[1], P. Pfeffer[1], K. Dybko[1, 2], A. Szczerbakow[1], L. Kowalczyk[1], P. Dziawa[1], R. Minikayev[1], T. Zayarnyuk[1], K. Piotrowski[1], M. Gutowska[1], A. Szewczyk[1], W. Zawadzki[1], T. Story[1, 2]

[1]Institute of Physics, Polish Academy of Sciences, Poland
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The unremitting interest in the investigation of PbTe-CdTe materials combination originates from the expectation, that addition of cadmium, similarly like thallium, can improve widely known good thermoelectric properties of PbTe. Additionally, limited mutual solubility of both semiconductors resulting from the difference in their crystal structure (rock-salt for PbTe and zinc-blende for CdTe) favors this heterosystem for realization of the idea of phonon-glass electron-crystal material for thermoelectric applications in the form of PbTe-CdTe nanocomposite. However, for the same reason, so far only polycrystalline Pb1-xCdxTe bulk samples with low Cd content x=0.01 were examined. Here we present experimental and theoretical studies of thermoelectric properties of unique, high quality, p-type Pb1-xCdxTe monocrystals with Cd content up to 10 at. % obtained by self-selecting vapor growth method. We have found, that increasing addition of Cd leads to significantly enhanced Seebeck coefficient (up to 500 microV/K for x=0.1) with respect to the reference p-PbTe crystals. Simultaneously, the total thermal conductivity of investigated samples decreases from 2 W/m/K for pure PbTe to 0.9 W/m/K for x= 0.09 crystal. This experimental finding we analyze theoretically within the two-band k•p model, in which the increase of light-holes effective mass resulting from experimentally confirmed widening of energy gap in Pb1-xCdxTe crystals, as well as increasing contribution of heavy holes in sigma-subband were taken into account. Following the relaxation time approximation, the carrier scattering modes bonded with alloy disorder, interactions with optical and acoustic phonons (expected to be dominant in the case of our Pb1-xCdxTe mixed crystal) as well as scattering by charged dislocations and ionized defects were included to the analysis. The decrease of thermal conductivity with increasing x we described within the Callaway's approximation assuming the alloy scattering of phonons responsible for observed behavior.

This research has been supported by NCBiR (Poland) through the TechMatStrateg2 project TERMOD (2019-2022)

14:30 - 14:45

Enhancement of the ZT parameter in PbTe by Bandgap and Fermi Level Tuning

R. Knura[1, 2], T. Parashchuk[2], A. Yoshiasa[3], Z. Dashevsky[2], K. Wojciechowski[1, 2]

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[3]Kumamoto University, Poland

Segmented thermoelectric legs with dimensionless figure of merit ZT parameter adjusted to local working temperature are known to be more efficient than homogenous materials. Present work shows method of controlling band gap energy Eg and Fermi level EF to achieve the best thermoelectric performance. Change of Eg was achieved in PbTe based compounds through isoelectronic substitution of Pb with Sn. This resulted in shifting the maximum value of ZT parameter on a temperature scale. Addition of electrons through substitution of Te with I alters EF and influences the type and concentration of carriers as well as modifies the Seebeck coefficient S.

Substitution of Pb with Sn at a level of 10, 25 and 50 % resulted in obtaining samples with maximum value of ZT parameter at temperatures 373, 523 and 773 K respectively. The highest average values of ZT parameter were found for undoped Pb0.75Sn0.25Te.

Increase of iodine concentration in Pb0.75Sn0.25Te1-xIxresults firstly in strong decrease of electrical conductivity due to decreasing number of holes. Further increase of I concentration leads to change of sign of Seebeck coefficient from positive to negative and strong increase of electrical conductivity. Power factor P = S2σ (σ is electrical conductivity) of Pb0.75Sn0.25Te0.999I0.001 (n-type conductivity) reaches values above 1.6 mW/(m·K) in temperature range of 323 - 623 K as opposed to undoped Pb0.75Sn0.25Te, where P is less than 0.6 mW/(m·K).

Modules II

13:30 - 14:45

Room: Megaron B

Chair: Luis Fonseca

13:30 - 13:45

Combined spray-coating and laser structuring as unique fabrication method for thermoelectric generators

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[2]Institute of Integrated Production, Hannover, Germany
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Utilization of waste energy with thermoelectric energy conversion has become an important topic in energy research. Due to the toxicity of the commonly used bismuth telluride, investigation of telluride-free alternatives have gained much attention in recent years. For example, thermoelectric oxide materials represent a group of low-cost, non-toxic and highly stable materials with attractive properties for thermoelectric energy conversion.

In addition to the material research, the production of conventional thermoelectric generators is a complex process that needs to be improved. Therefore, research also focuses on the investigation of alternative additive and subtractive manufacturing methods for processing various thermoelectric materials and generators.

In this context, a thermoelectric generator based on thermoelectric oxide Ca3Co4O9 was prepared by combined spray-coating and laser structuring technique. With this combination of additive and subtractive process design, the resulting layer thickness as well as the structuring and the final design can be easily controlled. As a flexible substrate, which can be adapted to different needs, a low-temperature co-fired ceramic (LTCC) was used. In the process, a subsequent sintering step ensures the thermoelectric properties of the porous Ca3Co4O9 layer and leads to a rigid thermoelectric generator. The universal production method can be further extended to different kinds of thermoelectric materials and generator designs.

13:45 - 14:00

Assembly of liquid-based thermoelectric generator modules based on amine bonding

L. Jeandupeux[1], E. Laux[1], C. Prieur[1], P. Potty[1], H. Keppner[1]

[1]University of Applied Sciences Western Switzerland (HES-SO), Switzerland

In the previous years, it has been shown ionic liquids (IL) are good candidates as base material for thermoelectric generators (TEG). Having identified potential IL, the next step is building a module integrating those liquids. To keep the flexibility given by a liquid TEG, the involved materials should also be flexible.

A TEG is composed of three different layers: 1) the bottom electrode foil, 2) the body, containing cavities with p- and n-type liquids and 3) the top electrode foil. The body must be flexible, tight, and easily shaped. Inspired by microfluidics, polydimethylsiloxane (PDMS) was chosen. The electrode foils have to withstand metal coating and patterning, must be flexible while retaining electrical conductivity, and must not react with the liquids.

Unfortunately, PDMS is not easily bonded to another polymer. Moreover, sealing the liquid in a cavity and keeping the contact with the electrode is complex.

In this paper, we will demonstrate a way to create the module first using amine bonding, and then filling the body cavities with liquid using a customized vacuum chamber. With this technique, only four steps are required: 1) coating the electrode foils with an amine, 2) activate both the amine-treated surface and PDMS with oxygen plasma and put the two in contact, 3) put the assembly in a vacuum chamber, 4) pour the liquid to fill the cavities. This ensures perfect contact between IL and electrodes. Electrical and mechanical characterization was performed on a module. The results will be shown in this paper.

14:00 - 14:15

Selection of tetrahedrite compositions for application on thermoelectric modules.

E.B. Lopes[1], R. Coelho[2], E. Symeou[3], T. Kyratsi[3], A. Pereira Gonçalves[4]

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[2]IST, Portugal
[3]University of Cyprus, Cyprus
[4]Instituto Superior Técnico, Universidade de Lisboa, Portugal

Tetrahedrites are mineral sulfosalts with Cu12Sb4S13 pristine composition. They are considered as very promising materials for thermoelectric applications due to the low toxicity of the elements, their earth abundancy, low cost, and the achievement of high thermoelectric figures of merit (zT), between 0.6 and 1 at ~700K, by composition adjustments [1]. These materials have already very low intrinsic thermal conductivities, to increase zT being necessary to prepare dense samples and focus on improving the Seebeck coefficient and having the highest electrical conductivity. Here we present the preparation of dense tetrahedrite materials through the solid-state method, followed by hot-pressing, and their structural, microstructural and thermoelectric characterization. The optimization of the hot-press parameters and the correlation with the final sample density are discussed. Results of the transport properties of several tetrahedrites, namely Cu11MnSb4S13, Cu11ZnSb4S13, Cu11.5Mn0.5Sb4S13, Cu10.5Ni1.5Sb4S13, Cu11.25Cd0.75Sb4S13, are presented, as well as the best compositions selected for use in the p-type leg of the thermoelectric module.

References

[1] Xu Lu and Donald T. Morelli, in Chapter 16:Tetrahedrites: Earth-Abundant Thermoelectric Materials with Intrinsically Low Thermal Conductivity, in Materials Aspect of Thermoelectricity, Ctirad Uher ed., (CRC 2016)

14:15 - 14:30

Modern developments in microTEC production

A. Nazarenko[1]

[1]RMT Ltd, Russia

Modern developments of the RMT LTD company for production of microTEC were considered. The last developments are focused at increasing the reliability, heat resistance and interference solution. All last development have been tested and put into production. These production solutions found applications in the market like sensors and detectors, photonics. Recently, the direction of Lidar is actively developing which also requires special technological solutions on cooling.

14:30 - 14:45

Thin Film TEG with Controlled Heat Flow

M. Uenuma[1], Y. Uraoka[2]

[1]NAIST, Japan
[2]Nara Institute of Science and Technology, Japan

In bulk thermoelectric materials, pi-type structures are usually used. But in thin film materials, it is difficult to obtain temperature differences in the film thickness direction. Therefore, many studies have been made on the use of transverse types in which temperature differences are obtained in the in-plane direction. Of course, the power generation output is lower than bulk material. But, there are also significant advantages to using thin film technology.

First, it is possible to form a flexible TEG or a transparent TEG. Many deposition techniques in low temperature processes are already studied in semiconductor processes, and it is possible to use those techniques. In addition, a transparent element can be realized by using an oxide semiconductor material. The second is that the thermal conductivity does not have to be an important parameter. In the case of bulk materials, the Seebeck coefficient, electrical conductivity and thermal conductivity are three key parameters that determine the characteristics of TEG. However, in thin film TEG, the thermal conduction is mainly limited by the substrate. Therefore, in the thin film element, the Seebeck coefficient and the electrical conductivity become important parameters. Therefore, unlike the conventional bulk materials, it is possible to use a material having a higher thermal conductivity, such as metals, Si, Ge, etc.

We have demonstrated transparent TEG and flexible TEG using oxide semiconductor thin films. Although output and heat flow still need improvement, thin film thermoelectric elements can be expected for materials and applications different from bulk materials.

Other Materials I

13:30 - 14:45

Room: Megaron C

Chair: Anthony Powell

13:30 - 13:45

Exploration of Thermoelectric properties of Nuclear Based Materials

J. Griveau[1], E. Colineau[1], R. Caciuffo[1]

[1]European Commission, DG Joint Research Centre (JRC), Germany

The last years have seen an increase of interest of thermoelectricity in a broad range of materials, techniques and processes for industrial applications but also from a theoretical point of view. Recent breakthroughs have taken place on “designed” materials in the case of textured or nanostructured materials tuning the ZT figure of merit by modifying on purpose electrical or thermal transport properties. Some of these compounds present interesting anisotropic structures with controlled inserted elements in the crystallographic cell with specific electronic features and/or semiconducting behavior (chalcogenides, half Heusler, clathrates, silicides).

Here we report studies on actinides based compounds presenting the aspect of itinerancy and localization in the 5f series which acts as an interesting way to control DOS at Fermi level, replacing at once doping effect. Few data are reported on thermopower of uranium materials and even less on transuranium based compounds where 5f electronic features are playing a definitive role in ground state and drastically tune electronic and thermal transport properties and thermopower.

Accessing these properties (electrical resistivity, thermal conductivity and thermopower) requires devoted apparatus to handle actinides (Th,U, Np, Pu, Am) materials specifically in the case of radioactive transuranium compounds. A comparison with their Rare Earths counterparts is given in some cases. We will present a versatile home made Seebeck set-up adapted to a standard PPMS Quantum Design equipment in the 2-350 K range under magnetic field up to 14 T.

13:45 - 14:00

$Yb_{14}M_nSb_{11}$ and Co: a Zintl-transition metal composite for enhanced thermoelectric performance

G. Cerretti[1], S. Bux[1], J. Fleurial[1]

[1]NASA Jet Propulsion Laboratory, United States

Composite materials are conceptualized with the intent of obtaining a final material with improved characteristics. In thermoelectrics this has been achieved for organic-inorganic composites where conducting materials embedded in polymeric matrixes improved the thermoelectric properties. A completely different situation is the combination of two inorganic compounds. Although according to several studies a thermoelectric composite cannot have better properties than its constituents, a study from Bergman and Fel (1999) proved that the enhancement of the figure of merit of a composite material is possible under specific conditions. The purpose of this work is to show the effect of Co inclusions on the electronic and thermal property of Yb14MnSb11. Yb14MnSb11, with a zT of about 1.2 at 1200 K, is already the most performing p-type material for high temperature thermoelectric applications. Our intent is to further increase its thermoelectric performance by decoupling the electronic transport properties (σ, S). Even though cobalt is characterized by a metallic electrical conductivity, it shows a relatively high Seebeck coefficient (S ≈ -25 μV/K at 1100 K). Therefore, cobalt inclusions are expected to provide a boost to the electrical conductivity, while affecting only marginally S. At the same time, if the inclusion size can be kept in the nm-μm range, inclusions can act as active phonon scattering centers and hence reduce the lattice thermal conductivity. To verify the validity of our assumptions, we synthesized four samples with different inclusion density (0, 2, 5, 10 vol%). The samples have been chemically, electrically, and thermally characterized and the obtained results will be shown and compared with the baseline of the Jet Propulsion Laboratory for the Yb14MnSb11 ATEC (Advanced ThermoElectric Converter). In the end, the sample with 5vol% cobalt inclusions is the one that showed the best thermoelectric properties achieving a peak zT of 1.6 at 1250K.

14:00 - 14:15

Modeling, Characterizing, and Engineering of Grain Boundaries in N-type Mg_3Sb_2-based Compounds

J. Kuo[1], M. Wood[1], K. Imasato[1], G.J. Snyder[1]

[1]Northwestern University, United States

Recently n-type Mg3Sb2-based compounds were discovered with a promising peak zT at 700 K spurring great interests in related compounds. However, near room temperature the zT is compromised due to a low electrical mobility. As practical applications require a zT that is high throughout a large temperature range, the low temperature performance is a problem that must be tackled. In this work we demonstrate how the low mobility near room temperature can be attributed to the electrical resistive grain boundaries, and how the boundaries can be mitigated through processing.

We verified that theoretically, the temperature dependency of the mobility can be modeled by simply treating the grain boundaries as a secondary phase (also called a grain boundary complexion) electrically connected in series with the bulk grains[1]. The model predicts >60% of zT improvement can be achieved if the boundary resistance can be minimized. Therefore, understanding the reason of the high boundary resistance is crucial to engineer this material.

The physical origin of the resistive grain boundaries can be associated with a local off-stoichiometry near the boundaries. In our recent work, a Mg-deficient concentration profile across the boundaries was discovered in Te-doped Mg3Sb2 using atom probe tomography[2]. This local off-stoichiometry can foster the formation of Mg vacancies, lowering the local concentration of n-type charge carriers and the local conductivity. Enhancement of the mobility after annealing the compounds in Mg vapor not only is consistent with our previous observation of Mg-poor boundaries, but also provides a potential treatment for other polycrystalline thermoelectric materials that are potentially suffering from an electrical grain boundary effect (e.g. SnSe, half-heuslers, La3Te4).

[1] J. J. Kuo, G. J. Snyder, et. al., Energy Environ. Sci., 11, 429-434, (2018)

[2] J. J. Kuo, G. J. Snyder, et. al., Adv. Mater. Interfaces, 1900429, (2019)

14:15 - 14:30

Improvement of Low-Temperature zT in Mg_3Sb_2-Mg_3Bi_2 Solid Solution via Mg-Vapor Annealing

M. Wood[1], J. Kuo[1], K. Imasato[1], G.J. Snyder[1]

[1]Northwestern University, United States

The thermoelectric community strives to find new materials with better performance by looking for higher peak zTs. However, in real devices it is often more important to have a high average zT over a broad range of temperatures in order to maximize the devices Carnot efficiency. Mg3Sb2-Mg3Bi2 alloys have recently garnered renewed attention due their high performance at mid-range temperatures (zT =1.5 at 700K). While having a relatively high performance at 700K, these materials suffer from grain boundary resistance at lower temperatures leading to an overall lousy performance at room temperature[1]. Synthesis and optimization process to mitigate these grain boundary effects have been limited due to the loss of Mg, which hinders a samples n-type dopability[2]. Herein we demonstrate that a Mg vapor anneal can preserve a samples n-type dopability, while allowing us to grow the grains within our material. We show that with different processing steps we can change the room temp performance of Mg3Sb1.49Bi0.5Te0.01 from zT = 0.2 to zT = 0.8.

Keywords: Mg3Sb2, grain boundary, vapor anneal, dopability

(1) Kuo J. et al., Energy Environ. Sci., 2018, 11, 429

(2) Ohno S. et al., Joule, 2018, 2, 141–154

14:30 - 14:45

Controlled doping and strategies for ZT optimisation in halide perovskites

O. Fenwick[1], T. Liu[1]

[1]Queen Mary University of London, United Kingdom

Halide perovskites have emerged as promising candidates for photovoltaics and light-emitting diodes. Recently, promising thermoelectric performance has been reported for single nanocrystals of a halide perovskite, but there is not yet a good understanding of how thermoelectric performance can be optimised, especially in thin films where a diverse range of structures and morphologies are accessible. This work will report a record thermoelectric figure of merit (ZT) for halide perovskites, using the example of CsSnI3 thin films. This result is in part due to the ultralow thermal conductivity of our films (0.38 W/mK at room temperature), as well as high electrical conductivity enabled by self-doping of the films through controlled Sn oxidation. The oxidation process can be modulated by incorporation of a mixed halide surface layer, which acts as an additional optimisation parameter for ZT whilst also making the material more stable. We quantify both the Lorenz number and the thermal boundary resistance in these materials.

Skutterudites

15:15 - 16:15

Room: Panorama

Chair: Olga Caballero-Calero

15:15 - 15:30

A review of rapid fabrication methods of skutterudite materials

M.J. Kruszewski[1], Ł. Ciupiński[1], R. Zybała[1]

[1]Warsaw University of Technology, Poland

Skutterudite materials are one of the most promising thermoelectric materials for middle temperature range (400-850 K) applications since they offer one of the highest efficiencies of energy conversion in this temperature range. It is well proven that skutterudite-based thermoelectric materials can be successfully synthesized using combination of processing techniques which in general consist of two stages: a) synthesis of the alloy (mechanical alloying, melting-quenching/annealing-grounding, solid-state reaction etc.) and b) final consolidation by means of various powder metallurgy techniques (hot pressing, spark plasma sintering, pulse plasma sintering etc.). However, due to complex and multi-stage nature of such fabrication routes they are time- and energy-consuming. The aim of this work is to review recent rapid fabrication methods of skutterudite thermoelectric materials. Advantages and disadvantages of selected fabrication routes such as gas atomization, selective laser melting, self-propagating high-temperature synthesis, melt-spinning and hydrothermal synthesis were discussed and compared to those of conventional synthesis of skutterudite alloys. All of the presented fabrication routes offer great potential for large-scale scalability because of their time and energy efficiency which may enable fast, low cost and mass production of thermoelectric materials.

15:30 - 15:45

ZTmax = 1.4 in non-nanostructured single filled $Yb_{0.15}Co_4Sb_{12}$

M.S. Benyahia[1], J. Vaney[2], K. Provost[3], V. Paul-Boncourt[1], J. Monnier[3], A. Dauscher[2], B. Lenoir[2], E. Alleno[1]

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[2]Institut Jean Lamour, France
[3]Université Paris-Est Créteil, France

Among the single-filled and non-nanostructured n-type AyCo4Sb12 skutterudites, Yb0.25 0.30Co4Sb12 (nominal composition) displays up to now the highest dimensionless figure of merit ZT = 1.3 at 750K [1-3]. The reasons for this superior performance is not yet fully understood. The heavy atomic mass of the Yb atoms indeed leads to low values of lattice thermal conductivity. However the filling concentration limit (FCL) of Yb in YbyCo4Sb12, which value is not consensual, also influences the thermal conductivity. The power factor varies like the electronic mobility which has been noticed to depend on the nature of the filler atom A in the AyCo4Sb12. But up to now, no systematics has been established on this point.

We thus decided to reinvestigate in details the properties of YbyCo4Sb12. We showed that the FCL of Yb in YbyCo4Sb12 synthesized at 800° is y = 0.4. From X-ray Absorption Spectroscopy, we demonstrated that the valence of Yb is equal to 2 and is intimately related to its electronic mobility. We also uncovered a spurious chemical instability of YbyCo4Sb12 which affects the filling concentration of Yb and thus its thermoelectric properties. By carefully taking this effect into account, we revealed that a high power factor as well as a large figure of merit (ZT = 1.4 at 750K) can be reached in single-filled and non-nanostructured Yb0.15Co4Sb12.

[1] Z. Xiong, et al., Acta Materialia 58 (2010) 3995.

[2] Y. Tang, et al., Journal of Materiomics 1 (2015) 75.

[3] S. Wang, et al., NPG Asia Mater 8 (2016) e285.

15:45 - 16:00

Structural evolution and correlation with thermoelectric properties in filled $CoSb_3$ skutterudites

N. Nemes[1, 2], J. Gainza[1, 2], F. Serrano-Sanchez[2], J. Prado-Gonjal[1, 2], O. Juan Dura[3], N. Biskup[1], J.L. Martinez[2], F. Fauth[4], M.T. Fernández-Díaz[5], J.A. Alonso[2]

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[4]Cells ALBA, Spain
[5]Institut Laue-Langevin, France

We used high pressure synthesis (to stabilize compositions and morphologies out of balance in ambient conditions) to obtain filled CoSb3 skutterudite–type thermoelectric materials with promising properties. We characterized the static and dynamic structure with synchrotron X-rays diffraction, with Rietveld refinement analysis to obtain both the crystalline structure and the dynamics of the constituent atoms through thermal factors (atomic displacement parameters). We correlate this structure with the thermoelectric properties, in particular with the contribution of the crystalline network to the thermal conductivity in skutterudites of CoSb3 filled with rare-earth atoms. We establish a strong correlation between low lattice thermal conductivity and phase-segregation of the rare-earth filler.

An exhaustive structural characterization of different M-filled CoSb3 (M=Y, K, Sr, La, Ce, Yb) skutterudites has allowed us to gain better understanding of the crystallographic effects of filling. This analysis focuses on the enhanced thermoelectric properties displayed by the family of filled-CoSb3 skutterudites, and their correlation with the chemical concepts behind the structural changes. These are mainly determined by Sb positional parameters, yielding an Oftedal plot that depends on the filling fraction, ionic state and atomic radius of the filler. Together with the distortion of Sb4 rings and CoSb6 octahedra, it is linked to the band converge concept and its influence on the thermoelectric transport properties.

16:00 - 16:15

Thermoelectric properties of bulk $CoSb_3$-PbTe composite and the effect of phase boundary on the transport parameters

A. Kosonowski[1, 2], T. Parashchuk[2], L. Chaput[3], K.T. Wojciechowski[1, 2]

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[2]The Lukasiewicz Research Network - The Institute of Advanced Manufacturing Technology, Poland
[3]Universite de Lorraine, LEMTA, Centre National de la Recherche Scientifique, France

The objective of this work is a basic study on the properties of the interface between two phases in thermoelectric composite and on the influence of this boundary on properties of the whole material.

Thermoelectric properties of bulk composites made of n-type CoSb3 and n-type PbTe polycrystalline materials sintered by PECS technique were investigated. A set of samples was prepared with fixed grain size distribution (5-50μm) but varying in volume fractions of the components. The phase composition was characterized by XRD coupled with Rietveld refinement method, microstructure, and chemical composition were investigated by SEM/EDS analysis. Thermoelectric properties were measured in the temperature range of 50-400°C. Sound wave velocities were measured for prepared materials for the determination of the acoustic impedance value. Moreover, an in-depth investigation of the interface between the two materials was conducted. For this purpose, a special layered sample was prepared for measurement of the transport of heat and electricity through the interface.

Total and lattice thermal conductivity of composite samples does not decrease for any composition and follows the rule of the mixtures. This could be explained by calculated values of acoustic impedance which suggest that the probability of phonon reflection at phase boundary is very small (~4%). Additionally, the measured value of Rint between PbTe and CoSb3 is also relatively small and the contribution of this resistance in regard to the resistivity of the whole sample is minimal (~0.5%). Electrical conductivity, however, does not follow the rule of mixtures.

This research provides interesting conclusions about the thermal and electrical properties of composite made from two bulk thermoelectric materials. A better understanding of the influence of phase boundary on the transport properties may support the development of thermoelectric composites with larger thermal resistance at the phase interface and more efficient transfer of the electrons through the boundary.

Silicides II

15:15 - 16:15

Room: Megaron B

Chair: Yuzuru Miyazaki

15:15 - 15:30

Beyond the rigid band model: thermoelectric transport in p-type Mg2Ge

J. de Boor[1], H. Kamila[1], A. Sankhla[1], M. Yasseri[1], E. Müller[1, 2]

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For the temperature range of 500K to 800K – where a large fraction of the waste heat is available – magnesium silicide based solid solutions Mg2X (X = Si, Ge, Sn) are among the most promising thermoelectric materials for large scale waste heat recovery applications. They combine very good thermoelectric properties with a high material availability, environmental compatibility and low cost of the raw materials Si, Sn and Mg. While the n-type has been improved to a level that makes practical application attractive, the p-type shows clearly inferior performance and requires further research. Previous research has mainly focused on solid solutions of Mg2Si and Mg2Sn, omitting Ge.

We have synthesized Li- and Ga-doped p-type Mg2Ge using high energy ball milling and current assisted sintering. The samples show a number of unusual features compared to p-type Mg2(Si,Sn):

Li-doped samples don’t exhibit the typical behavior of a degenerate semiconductor. Instead the electrical conductivity increases above 450K while the Seebeck coefficient remains almost constant.

The effective mass from the Hall measurements varies with carrier concentration and differs between Li- and Ga-doped samples.

The power factor can reach 2.2×10^(-3) W/mK^2, superior to Mg2Sn and the figure of merit can surpass 0.5 at 700K, significantly improved in comparison to Mg2Sn and Mg2Si, and comparable to the best solid solutions.

Modelling shows that the measured thermoelectric transport properties cannot be understood assuming a single or several degenerate valence bands. Instead, the behavior can be represented well by two parabolic bands having very dissimilar curvatures and shift against each other with temperature. And, while both Ga and Li don’t act like “standard” dopants, we can also show that they influence the thermoelectric properties of Mg2Ge distinctly different. In summary we find clear indications for non-rigid bands in Mg2Ge that lead to an unexpected improved thermoelectric performance.

15:30 - 15:45

Low resistance contacts for reliable $Mg_2(Si,Sn)$ based thermoelectric modules

E. Stefanaki[1], C. Koz[1], R.S. Tuley[1], K. Simpson[1]

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Thermoelectric materials based on non-toxic Magnesium silicide stannides, Mg2(Si,Sn) have attracted considerable attention for applications in the temperature range of 200- 500 °C as thermoelectric generators. They consist of elements that are abundant in the earth crust, low-cost, light-weight and with high ZT values (1.1-1.5) for n-type material. The major research in silicides has been focused on optimizing the materials properties and increase the ZT. However, for reliable and high performance thermoelectric modules working at temperatures at least as high as 400 °C, the development of very low resistance contacts with thermal stability and lifetime is mandatory.

In this work, the contacts for n-type Mg2(Si,Sn) pellets and the contact for p-type higher manganese silicide(HMS) pellets is presented. The test assembly consists of two pellets (n- or p- type) that are joined end to end with a joining material and a metallic contact in the middle. This uni-junction design is representative of the junction that would be made when upscaling into the module. The contact resistance is derived from four-point probe resistance measurements along the central axis of a sample. The average contact resistance measured for as built n-type samples is 2x10-5 Ω·cm2, while for p-type is 1.4x10-5 Ω·cm2. The long- term reliability of the contacts is evaluated through isothermal annealing in air at 400 °C. The impact of the contact resistance on module performance is illustrated by finite element analysis using COMSOL Multiphysics.

15:45 - 16:00

Thermal stability under air of $Mg_2Si_{0.6}Sn_{0.4}$ thermoelectric materials

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Several technological locks must be raised to make mature thermoelectric generators containing emergent materials for a reliable long-term use. Recurrent problems arise out of the thermal, chemical and mechanical stability of the elements included in the thermoelectric legs.

Innovative solutions must be brought to make low cost, eco-friendly (N-type: Mg2Si0.6Sn0.4 / P-type: MnSi1.77) based thermoelectric modules reliable for a long term use, in particularly thanks to the understanding of the mechanisms leading to their oxidation and their embrittlement. A recent work on the high temperature oxidation behavior of Mg2Si1-xSnx was published in 2016, when the effect of Sn content was highlighted [1]. In our study, we focused on the stability of Mg2Si0.6Sn0.4 under air at temperatures range 400-600°C. The effect of time and temperature on oxidation mechanisms was studied by carrying out thermogravimetric analyses followed by a characterization of the microstructure of the alloys by SEM. The study of material behavior was completed by following its decomposition under air by XRD in the same range of temperature.

16:00 - 16:15

Microstructural investigations of Bi-doped magnesium silicides: effects of the synthesis method

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Thermoelectric (TE) materials based on the magnesium silicide system have recently gained special interest due to their improved performance and impending applications in the 500–900 K temperature range, especially for their ternary Mg2Si1-xSnx counterparts. Previous band structure engineering approaches and attempts to alter their nanostructure lead to high figure of merit (ZT) values, reaching up to 1.4 in materials doped with Bi.

In this contribution, a thorough microstructural characterization of improved performance Bi-doped Mg2Si1-x-ySnxGey materials is presented, using predominately conventional (TEM) and high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDS)-based techniques, as well as post-experimental HRTEM image processing and analysis. The doped Mg2Si1-x-ySnxGey materials have been grown either by two-step synthesis or mechanical alloying, followed by hot pressing.

Microscopy experiments revealed considerable morphological differences between the two syntheses, i.e. four distinct phases in two-step, spanning the range from Si-, Ge-, to Sn-rich ones, compared to single phase existence in mechanical alloying. This has been confirmed both by more average selected area diffraction (SAD) patterns, as well as by atomic level imaging analysis. The variations in lattice constants, compared to nominal values, are up to 1.3% for the sample prepared with two step synthesis -depending on phase stoichiometry- and 0.6% for the one synthesized by mechanical alloying. EDS analysis by the electron channeling method provided complementary information regarding the site preference of host (Si, Sn) and doping (Bi) ions. These electron microscopy findings of the TE materials are consequently discussed in relation to their thermoelectric measurements, where both Mg2Si1-x-ySnxGey materials exhibit excellent ZT values for their Si-rich counterparts, albeit their distinct synthesis approaches and nanostructure.

Acknowledgements: Contributions by Vidar Hansen (University of Stavanger -UiS) and Johan Taftø (University of Oslo -UiO) are gratefully acknowledged.

Sponsors Session/Projects

15:15 - 16:15

Room: Megaron C

Chair: Jan Koenig

15:15 - 15:30

Thermoelectric Figure of Merit – Characterization by a Powerful Combination of Laser Flash Method and Seebeck Analyzer

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In recent years, the conversion of waste heat into electrical power has become increasingly important. So-called thermoelectric generators (TEGs) have been developed, which can be applied anywhere that a useable temperature difference is available. TEGs are used, for example, in vehicle exhaust systems in order to reduce fuel consumption. However, their use is also feasible for large-scale applications in the future, such as waste heat recovery in power plants. To realize such applications, thermoelectric materials with high working temperatures and optimized efficiency must be developed. The thermoelectric figure of merit (ZT) is used to assess performance. To achieve as high a figure of merit as possible requires high electrical conductivity (σ), a high Seebeck coefficient S and low thermal conductivity λ.

The laser flash method allows the quick and straightforward determination of any required information with regard to thermophysical properties. The specific heat, cp(T), and the thermal diffusivity, a(T), are measured directly. Once these figures are known along with the density, ρ(T), the thermal conductivity can be calculated.

The thermoelectric properties σ and S can be determined to a high level of accuracy with the Netzsch SBA 458 Nemesis. The Seebeck analyzer has a variety of special features with regard to ease-of-operation and high measurement precision. Different sample geometries can be used (round, square, also films) and therefore an ideal combination with LFA is given.

Presented in this work are the analysis methods and test results (ZT values) for thermoelectrical materials such as Half Heusler, Silicides and Skutterudite.

15:30 - 15:45

10 years of thermoelectric testing at TCS Ltd

J. Siviter[1], A. Knox[1]

[1]Thermoelectric Conversion Systems Ltd, United Kingdom

For over 10 years the staff at Thermoelectric Conversion Systems Limited have focused research efforts in understanding how thermoelectric generators and coolers interact at the system level and specifically how to maximise both electrical and thermal efficiency in the accompanying electronics. This presentation will show how the company has evolved its measurement techniques to enable rapid optimisation of the thermal and electrical performance of the TE device, whether for power generation or cooling applications.

The company has recently finished the development of a new completely customisable and bespoke measurement equipment for thermoelectric modules. Given the large variety in available devices (size, as well as materials used in their fabrication) and the specific nature of the end-use applications, it was important to ensure any measurement system not only maintained high levels of accuracy and precision but also retained flexibility for optimum mounting of TE devices, varying thermal limits and electrical parameters. In this presentation, the functionality and flexibility of the test system is described in more detail and a comparison with performance from TEG manufacturer datasheet results is also provided.

The function of the test system enables detailed characterisation of both TEG and TEC devices of different geometries and different materials, This is vital from a scientific standpoint and it is also invaluable when assessing the electrical performance for industrial applications. This presentation will detail the advantages in electrical performance attainable when TEG operates in a constant heat system and assess the performance against other off-the-shelf I-V tracers and MPP tracking systems.

TCS has developed a high efficiency cooling system exploiting the large coefficients of performance attainable from TECs when operating in constant current mode. This presentation will detail these new units, their performance and various other IOT applications.

15:45 - 16:00

Heatsink optimization with thermoelectric modules

N. Katenbrink[1]

[1]Quick-Ohm Küpper & Co. GmbH, Germany

Shrinking installation space for thermal systems is an often-desired demand for thermal engineers. In addition to that the market is looking for simple, quiet and robust solutions. Heat sink working on the principle of natural convection are the easiest way to realize water and dust proof devices. Given that the natural convection is strongly depending on heat sink surface the conflict of goals is inevitable. The presentation will show how the size of heat sinks can be reduced without losing cooling performance by enhancing the natural convection using thermoelectric modules. Thermoelectric modules or more precisely peltier coolers can be considered as thermal heat pumps, pumping thermal energy via electric energy from one side of the module to the other. While in thermoelectric cooling systems the waste heat dissipation is the bottle neck of the whole system, we found a way to utilize the effect and improve natural convection heat sinks. The fundamentals will be shown as well as Simulation results. Also, the experimental validation will be presented.

16:00 - 16:15

The H2020 INTEGRAL project: upscaling production of thermoelectric GEN2 TE materials and demonstrating waste heat harvesting

J. Escabasse[1, 2], L. Aixala[1, 2], C. Navone[1, 2], K. Romanjek[1, 2], J. Dufourq[3], D. Zuckermann[4], M. den Heijer[5], C. Lhomme[6], E. Hanrot[7]

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[6]TitanX, Sweden
[7]Valeo Systèmes Thermiques, France

Thanks to decades of academic and industrial R&D, improved TE materials have emerged as the so-called second-generation thermoelectric (GEN2 TE) materials: silicides and half-Heusler alloys. Based on mostly affordable, earth-abundant and eco-friendly elements, these materials are expected to allow for thermoelectric waste-heat harvesting to at last break through mass markets. Key elements for success are low cost of production for materials and thermoelectric modules, stable thermal and electric performance, reliability of generators over time in harsh conditions and fitness for purpose.

The three industrial pilot lines in INTEGRAL have upscaled different GEN2 TE materials to TRL 7 and have built four different demonstrators of thermoelectric generators for the transport and energy-intensive industry sectors: automotive, heavy duty trucks, autonomous temperature control and industry waste heat recovery.

Demonstrations in real or representative end-use conditions will open the way to commercialisation of thermoelectric generators in mass markets.

Materials: Chalcogenides II

16:15 - 17:45

Room: Panorama

Chairs: Marison Martin Gonzalez, Luis Fonseca, Alexander Burkov

16:15 - 17:45

The influence of synthesis methods on structural and transport properties of copper sulfide

A. Kolezynski[1], P. Nieroda[1], A. Mikula[1], K. Mars[1], J. Leszczynski[1]

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Copper sulphide, due to its interesting properties, gained significant research attention in recent years. In the past, this material has been found to be efficient photon absorber for solar cells and gained renewed interests in last years, due to a growing demand for earth-abundant and environmentally friendly photovoltaic materials. Recently, very good thermoelectric properties of non-stoichiometric binary copper sulphide were also reported, with the highest ZT value of 1.9 at 970K for Cu1.97S (J. Mater. Chem. A, 2015, 3, 9432). The uniqueness of these materials stems from their structural and electronic properties driven by composition and specific structure – superionic behavior of highly mobile Cu ions intercalated with a rigid anionic sublattice leading to highly disordered copper distribution in these compounds. Although the latter properties result in simultaneous ultralow lattice thermal conductivities and high electric conductivity and thus potentially very promising thermoelectric properties, they cause also many problems with chemical stability of these compounds, due to enhanced diffusion of copper ions at elevated temperatures, which in turn influences their transport properties. One of the important factors in terms of their structural and transport properties is the synthesis method used and thus the aim of this work was the comprehensive study of this problem. The materials obtained by synthesis from pure elements carried out in quartz ampoules under various conditions and then densified by RHP (Rapid Hot Pressing) method and by melting the sample were subjected to structural and thermoelectric properties measurements in order to assess the influence of the preparation method on those properties and the obtained results are analyzed and presented here in detail.

Acknowledgments: This work was financially supported by The National Science Centre Poland under grant no. 2016/21/B/ST8/00409.

16:15 - 17:45

Effect of changes in chemical composition on thermoelectric efficiency in $W_{1-x}Nb_xSe_{2-y}S_y$ solid solutions

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[2]Ioffe Physical -Technical Institute of the Russian Academy of Sciences, Russia
[3]Ewha Womans University, South Korea

Transition metal dichalcogenides are mostly layered compounds formed as MX2, where M is a transition metal atom, X is a chalcogen atom. The layer of metal atoms is between two layers of chalcogen atoms. Strong covalent bonds act between the metals and the chalcogen atoms, and the X – M – X layers are bound by a weak Van der Waals interaction. One of the representatives of this class of compounds is tungsten diselenide. The charge carrier concentration in tungsten diselenide is 1015-1016cm-3. As a result, this material has low thermoelectric efficiency. Based on experimental data it has been shown that the highest concentration of charge carriers in this compound can be obtained by doping with elements of the V group of the Mendeleev's periodic table, such as Nb, V and Ta. In the same time isovalent substitution Se on S does not significantly change the concentration of charge carriers. But, the addition of sulfur leads to the influence of light holes from the zone formed by the p-states of the chalcogen atoms on electron transport properties of solid solutions. Such modification of the chemical composition improved the thermoelectric efficiency of the studied compounds compared with pure tungsten diselenide from 0.002 (WSe2) to 0.26 (W0.98Nb0.02Se1.7S0.3).

The work was supported by the Russian Foundation for Basic Research (Grant No. 18-503-51017) and by the National Research Foundation of Korea (NRF) Grant funded by the Korean Government (NRF-2015R1A5A1036133 and NRF-2017K2A9A1A06051881).

16:15 - 17:45

Comparative study: transport properties of natural and high-purity synthetic pyrites (FeS2).

E. Zuñiga-Puelles[1, 2], R. Cardoso-Gil[3], M. Bobnar[3], I. Veremchuk[3], C. Himcinschi[1], C. Hennig[4], J. Kortus[1], G. Heide[1], R. Gumeniuk[1]

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Comparative study: transport properties of natural and high-purity synthetic pyrites (FeS2).

Synthetic polycrystalline and natural pyrite from the hydrothermal mine in Schönbrunn (Saxony, Germany) are stoichiometric FeS2 compounds and stable (for thermoelectric applications) up to ~600 K which was evidenced by combined thermal, chemical, spectroscopic and X-ray diffraction studies. Natural pyrite showed characteristics of a nondegenerate semiconductor and is suitable as a model system for investigation of thermoelectric performance. In the temperature range 50-600 K the electrical resistivity and Seebeck coefficient of polycrystalline samples became closer to Schönbrunn sample properties by longer annealing times under sulphur atmosphere. The large thermal conductivity in FeS2 (~40 W m-1K-1 at 300 K) is exclusively due to lattice contribution. A well pronounced maximum in κ(T) is observed only for natural pyrite at ~75 K. This maximum becomes almost completely suppressed in the sintered samples (grain size ≤ 100 μm) due to additional scattering (i.e. point defect and/or grain boundaries).1

The thermoelectric performance of a highly-pure pyrite is not enough for the TE applications, however it seems to be a promising TE material due to the enhanced electrical transport properties observed in the studied natural samples.

16:15 - 17:45

Chromium resonant impurity effect on the thermoelectric properties of $Pb_{1-x}Sn_xTe$

A. Królicka[1], K. Dybko[1, 2], R. Minikayev[1], A. Reszka[1], J. Więckowski[1], A. Szewczyk[1], A. Grochot[1], H. Przybylińska[1], W. Knoff[1], K. Gas[1], M. Sawicki[1], A. Mirowska[3], A. Materna[3], M. Piersa[3], T. Story[1]

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[3]Institute of Electronic Materials Technology, Poland

The aim of this study is to experimentally demonstrate the influence of chromium doping on thermoelectric properties relevant to heat – to – energy conversion in thermoelectric material Pb1-xSnxTe. Chromium forms in Pb1-xSnxTe a mixed valence Cr2+/3+ donor center resonant with conduction band in PbTe but with valence band in SnTe. The energetic position of Cr2+/3+ level can be tuned with Sn content, thus permitting the density of states enhancement in both n-type and p-type materials (after band inversion) required in thermoelectric converters. In this investigation we put particular attention into crystal growth as well as structural, chemical, magnetic, and thermoelectric characterization of Pb1-xSnxTe:Cr crystals grown by the Bridgman method.

This research has been partially supported by the Foundation for Polish Science through the IRA Programme co-financed by EU within SG OP and by NCBiR TechMatStrateg 2 project TERMOD (2019-2022)

16:15 - 17:45

Thermoelectric and Transport Properties of n-type Mn-Doped Chalcopyrite $Cu_{(1-x)}Mn_{(x)}FeS_{(2)}$ Compounds

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Semiconducting diamond-like CuFeS2 compound has recently attracted attention of the thermoelectric community [1-3] thanks to its attractiveness from environmental and economical point of views. In our recent study [3] we have showed that partial replacement Cu atoms by Pd ones in Cu(1-x)Pd(x)FeS2 compounds leads to enhancement of both power factor (~1x10-3 Wm-1K-2) and ZT-value (0.18 at 573 K). In present study we have investigated similar replacement on the copper sites by manganese atoms. A series of Cu1–xMnxFeS2 (x = 0 - 0.1) samples were synthesized and their hot-pressed pellets were characterized as for their thermoelectric and transport properties. The replacement of Cu by Mn has donor-like effect. Unlike the Cu(1-x)Pd(x)FeS2 system, where a formation of the secondary phase (PdS) was observed above the solubility limit of Pd in CuFeS2, no similar binary phase is detected in the studied samples. Instead, a formation of a cubic chalcopyrite phase is observed in x-ray diffractograms (for x≥0.02). The co-existence of the tetragonal and cubic phase in the studied samples leads to effective lowering of their thermal conductivity with the increasing nominal concentration of Mn in Cu(1-x)Mn(x)FeS2. Mainly due to the lowering of the thermal conductivity, ZT-value of 0.2 at 573 K is achieved at Cu(0.97)Mn(0.03)FeS(2) sample.

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16:15 - 17:45

Synthesis, Crystal Structure and Thermoelectric Properties of Cu-Sn-S Compounds

T. Xing[1, 2], I. Veremchuk[1], Y. Prots[1], P. Qiu[2], L. Chen[2], Y. Grin[1]

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Owing to the growing concern of energy sustainability, thermoelectric (TE) technology has drawn increasing attention from both academic and industrial communities. It can be potentially used to convert the waste heat directly into useful electricity, providing an alternative way to more efficiently utilize fossil energy. Industry application requires large-scale low cost, environmental, and non-toxic high performance thermoelectric materials. However, current state-of-the-art thermoelectric materials are usually composed of expensive, scarce, or toxic heavy elements such as Pb, Te, Bi, Co, Sb etc. In this work, ternary copper tin sulfide (Cu–Sn–S) compounds with non-toxic and earth-abundant elements were synthesized by the solid reaction and mechanical alloying (MA), combined with spark plasma sintering (SPS). Their crystal structures, thermoelectric performance and electronic transport mechanism were systematically investigated. It is found that there exists two single-phase samples with the same crystal structure but totally different behavior within a tiny variation of composition. XRD patterns are analyzed with Rietveld refinement method using the WinCSD program, and both of them are monoclinic structure (Cc). One of them shows a typical intrinsic semiconductor transport behavior with a high Seebeck coefficient (~400 □VK-1) and low electrical conductivity (~102 Sm-1). But another one shows a metallic transport behavior with a lower Seebeck coefficient (~70 □VK-1) and low electrical conductivity (~104 Sm-1). The huge difference between the two compounds is attributed to the internal electronic transport properties, including the carrier density and mobility. It revealed that ternary copper tin sulfide (Cu–Sn–S) compound is extremely sensitive to the composition, which provides a new thoughts for further improving the thermoelectric performance.

16:15 - 17:45

Percolation effects and self-organization processes in $Bi_2(Te_{1-x}Se_x)_3$ solid solutions

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One of the basic methods of increasing thermoelectric (TE) figure of merit that determines to a large extent the efficiency of a TE device, is “the solid solution method”, which has proved its fruitfulness. It is usually assumed that an increase in the impurity concentration leads to a monotonic change in properties. However, in a number of solid solutions, in the region of low impurity content, we detected concentration-dependent anomalies in the behavior of TE and mechanical properties and attributed them to the manifestation of percolation effects that occur during the transition from dilute to concentrated solid solutions [1]. For practical applications it is very important to know how properties change in the range of low impurity concentrations.

The objects of this study are Bi2(Te1-xSex)3 solid solutions, which are promising TE materials for cooling devices. The goal of the work was to study the room-temperature dependences of microhardness, electrical conductivity, the Seebeck coefficient, and TE power factor on composition in the concentration range x = 0–0.07. In the intervals x = 0.0075–0.0175 and x = 0.025–0.035, we observed an anomalous decrease in microhardness and the Seebeck coefficient and increase in electrical conductivity with increasing x. The first anomaly was attributed to critical phenomena, accompanying a percolation-type phase transition. The percolation threshold xc and the radius of deformation spheres R0 around Se impurity atoms were estimated. The second anomaly is assumed to be connected with a short-range ordering in the solid solution. The non-monotonic character of the dependences of microhardness on the load on an indenter, whose behavior depended on the impurity concentration, was attributed to the interaction of the deformation fields created by dislocations and impurity atoms.

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16:15 - 17:45

Synthesis, crystal structure, and thermoelectric properties of $PbGa_6Te_{10}$

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Due to its low thermal conductivity and high values of Seebeck coefficient, PbGa6Te10 may be an interesting potential candidate for a thermoelectric material. According to the phase diagram PbTe-Ga2Te3 [1], PbGa6Te10 forms congruently (melting point at 1003 K) and shows a wide homogeneity range between 73 and 81 mol. % of Ga2Te3. PbGa6Te10 crystalizes in the space group P3221, with a = 14.466(2) Å, c = 17.718(4) Å [2]. A disordered variant (R32) of this complex crystal structure was also observed [3].

Aiming to check the homogeneity range of PbGa6Te10 and to explain the nature of the disorder in the crystal structure we prepared samples with 71-83 mol. % of Ga2Te3 in the PbTe-Ga2Te3 system. The systematic characterization of all samples was made by X-ray diffraction, thermal analysis, metallography. Thermoelectric properties were measured.

The powder XRD pattern of sample with composition 75 mol. % of Ga2Te3 after annealing at 873 K, was indexed according to rhombohedral symmetry (R32). Single crystal structure refinement reveals rhombohedral symmetry and defect occupancy for lead sites. Whereas the X-ray powder pattern of the same sample after heat treatment (compaction SPS and thermal diffusivity measurements) was indexed in the trigonal symmetry (P3121).

Transport property measurements on synthesized samples show very low thermal conductivity, high Seebeck coefficient, however high electrical resistivity.

Acknowledgments

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16:15 - 17:45

Effect of strain on thermoelectricity of textured GeTe films and Bi_2Te_3/GeTe superlattices

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Thermoelectric (TE) materials, utilizing waste heat to harvest electric, are promising candidates for clean and sustainable energy technology. Over the past two decades, nanostructures, such as nanograins, nanowires and superlattices have been widely studied in minimizing the lattice thermal conductivity to enhance the TE performance [1,2]. It is well known that strain engineering plays a vital role in tuning band gap and carrier mobility [3]. To the best of our knowledge, however, the effect of strain on TE films has hardly been studied. Recently, we succeeded using Reflective High Energy Electron Diffraction (RHEED), to proof that strain persists in Bi2Te3-Sb2Te3 and Bi2Te3-GeTe multilayered films [4]. In this work, we have grown Bi2Te3, GeTe and Bi2Te3/GeTe layers with different thickness. The in-plane and out-of-plane lattice parameters were measured by RHEED and X-ray diffraction (XRD), respectively. The GeTe(006) XRD peaks showed clear asymmetry, which is related to a persistent strain relaxation profile in the GeTe layer as measured by RHEED. For practical applications, it is highly desirable that the maximum ZT values span a wide temperature range. To this end, the Seebeck coefficient and the electrical conductivity were measured by Linseis LSR-Platform and van-der-Pauw Method from 300K to 523K, respectively. In this way we aim to find a relation between the persistent strain and the thermopower of the layers studied.

16:15 - 17:45

Initial stages of formation, growth and thermoelectrical performance of bismuth selenide thin films deposited on different substrates by physical vapour deposition technique

E. Kauranens[1], L. Britala[1], J. Andzane[1], D. Erts[1]

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Thermoelectric generators are attractive devices for heat-to-power conversion applications. Absence of moving parts and low maintenance requirements make these devices attractive for applications in extreme environments as, for instance, polar regions of the Earth, space and ocean bed. However, the relatively low efficiency of thermoelectric devices, commonly referred as thermoelectric figure of merit (ZT) hampers their commercialization.

ZT of the thermoelectric material can be improved by downscaling and nanostructuring of the material. Recent theoretical predictions show that reducing of the thickness of thermoelectric material below 10 nm and simultaneous doping for tuning of Fermi level may result in significant enhancement of the existing ZT of the material.

Obtaining of high-quality ultrathin films on different substrates is very challenging. At laboratory scale, this can be done by expensive molecular beam epitaxy (MBE) technique. However for the commercial applications, an alternative cost-effective method should be developed. Physical vapor deposition method as a very good candidate for this role, but for the use of this method for thin films deposition, the knowledge of initial stages of nucleation and growth of common thermoelectric materials is crucial.

This work is devoted to investigation of nucleation and growth of bismuth selenide on different substrates, deposition of pristine and doped nanostructured bismuth selenide thin films of different moprhologies, as well as investigation and comparison of their thermoelectrical performance.

The initial nanostructures and thin films are deposited on different substrates as mica, quartz, annealed and not annealed monolayer graphene, using physical vapor deposition technique. The investigation methods include scanning and atomic force microscopy, energy-dispersive x-ray diffrection, physical property measurement system (PPMS) and home-made device for determination of Seebeck coefficient. The mechanisms of thin film deposition on different structures, their further structure and morphology, and their influence to thermoelectric performance to these thin films are discussed.

16:15 - 17:45

Fabrication and characterization of bismuth and antimony chalcogenide and CNT heterostructures

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In recent years carbon nanotubes (CNTs) have provoked a great interest due to their excellent mechanical, optical and electrical properties. Recently, the integration of graphene and CNTs with the narrow band gap semiconductors with topological insulator (TI) properties as, for example, bismuth or antimony chalcogenides, has gained interest due to its potential to be used as a platform for the experimental realization of new room-temperature applications of 2D TI structures. For instance, these include thermoelectric devices, as it has been shown recently that despite the good thermal conductivity of individual CNTs, a reduction of thermal conductivity can be observed in networks of CNTs. Since low thermal conductivity is an essential requirement for enhancing the TE efficiency, combined CNT-bismuth chalcogenide networks could have promising applications in building novel TE devices. Another important application is in active elements in high-performance optoelectronic devices, as it has recently been shown that photoconductivity of graphene may be significantly improved by its combination with bismuth telluride.

This work is devoted to fabrication of CNT-bismuth selenide and antimony telluride heterostructures. The bismuth and antimony chalcogenide nanostructures were synthesised on CNTs via catalyst-free vapour-solid deposition technique. The morphology of the prepared heterostructures was investigated using scanning electron microscopy as well as energy-dispersive X-ray analysis. The electrical, opto- and thermoelectric properties of the heterostructures were studied using a home-made experimental setup, physical property measurement system (PPMS) and electrochemical impedance spectroscopy (EIS) methods. Properties of CNT-bismuth and antimony chalcogenide heterostructures were compared with the properties of bare CNTs. Thermoelectric performance of the studied heterostructures and the possible charge carrier mechanisms are discussed.

16:15 - 17:45

Thermoelectric properties of gallium doped copper(I) selenide

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Copper(I) selenide doped with gallium (GaxCu1-x)2Se with x=0 – 3% is prepared by an oxide reduction method. Due to limited solubility of Ga in the structure, a CuGaSe2 phase is formed at low temperatures. The measured values of the Seebeck coefficient and electrical conductivity indicate, that a stoichiometric or near-stoichiometric (without copper deficiency) compound was obtained. Measurements of samples' properties performed up to a temperature of 873 K are repeatable. Moreover, the mass of the samples is not changing during the thermal cycles. Measurements of the samples' stability were performed for 24 h at 773 K with a 40 A/cm2 current density. Materials show stability under these conditions. Doping with gallium seems to have an influence on the α→β phase transition, manifesting itself by different changes of the properties during the α→β phase transition.

Materials: Silicides

16:15 - 17:45

Room: Panorama

Chairs: Marison Martin Gonzalez, Luis Fonseca, Alexander Burkov

16:15 - 17:45

Thermoelectric properties of hot-pressed p-$Mg_2Si_{0.3}Sn_{0.7}$ with SiO_2 inclusions.

G. Isachenko[1, 2], A. Samunin[1], K. Samusevich[1, 2], P. Konstantinov[1]

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The study of p-type Mg2Si0.3Sn0.7 samples produced from nanopowder by hot-pressing showed an increase in thermal conductivity and reduce the figure of merit. In order to reduce thermal conductivity, we considered “nanoparticle-in-alloy” approach as one of a way to decrease it. The study of thermoelectric properties of Mg2Si0.3Sn0.7 doped with lithium and with the addition of SiO2 particles was carried out in this work. Thermoelectric properties of samples contained different quantity and size of SiO2 were measured in the temperature range from 300 to 700K. It was shown decreasing of thermal conductivity when samples contain silicon dioxide. Because of that ZT increased up to 0.42 at 730K in samples with 1% SiO2 versus ZT=0.35 of hot-pressed samples without inclusion.

16:15 - 17:45

Co-pressed contact layers in $Mg_2Si_{0.8}Sn_{0.2}$ composition for silicide based thermoelectric generators.

G. Isachenko[1], D. Dolgintsev[2], A. Samunin[1]

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High figure of merit of Mg2Si-Mg2Sn solid solution has been demonstrated by many research groups. But commercial implementation demands complex technology to combine the material in an end-use thermoelectric device. One of the problems is to create effective electric and thermal contacts. Only a few researchers consider the problem of produces reliable and strong electrical contact with low contact resistance in this material. In this work, the samples by pressing Mg2Si0.8Sn0.2 powder with grain size 100 nm and simultaneously on top it with powder of contact layers material such as Cr, NiSn, FeSi were prepared. There have been studies of the contact resistance and durability over time.

16:15 - 17:45

Dependence of thermoelectric performance on Re amount in MnSiγ co-substituted by Re and Ge

Y. Kurosaki[1], N. Fukatani[1], S. Yabuuchi[1], A. Nishide[1], Y. Miyazaki[2], T. Takamatsu[2], J. Hayakawa[1]

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Enhancing thermoelectric figure of merit ZT of cost effective materials is essential towards practical applications and higher manganese silicide MnSiγ is one of the promising materials. Proper element substitutions such as Re and Ge have been known to enhance ZT [1,2]. In this study, we fabricated MnSiγ substituted by both Re and Ge, and investigated the dependence of thermoelectric properties on the Re amount.

The samples were prepared from powders of Mn, Re, Si, and Ge, whose composition ratio is 1.0-a : a : 1.74 : 0.03 (a = 0.0, 0.05, 0.1, and 0.15), respectively. Mechanical alloying was carried out with a rotation speed of 400 rpm for 20 hours, following sintering process at 850ºC for 10 minutes. The crystal structures were evaluated by X-ray diffraction. The Seebeck coefficient (S), electrical resistivity (ρ), and thermal conductivity (κ) were measured by 2-probe method, 4-probe method, and laser flash method, respectively.

The lattice constant linearly increases with Re amount indicating the succesful substitution of Mn by Re with that of Si by Ge. The ratio between sublattices of MnSiγ, γ, was also investigated and clarified to be reduced with Re amount. Both S and ρ decreases with Re substitution resulting in increasing the power factor in spite of the substitution with the same valence electron number between Mn and Re, owing to the generated carriers by the reduced γ. On the other hand, the κ decreases with Re amount because of the heavy-element-doping. As a consequence, ZT increases up to 0.70 at 506°C when a is 0.10. This work is based on results obtained from the Future Pioneering Program “Research and Development of Thermal Management and Technology” commissioned by the New Energy and Industrial Technology Development Organization (NEDO). This work is also supported by TherMAT.

16:15 - 17:45

Amorphous protective coatings for Mg2si and Cu2s thermoelectric materials

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Magnesium silicide and copper (I) sulfide are very promising, environmental friendly and relatively cheap thermoelectric materials. These attributes distinguish them from other well-known thermoelectric materials and therefore they are currently intensively studied.

In this work, the novel promising protective coatings for Mg2Si and Cu2S, based on amorphous silicon oxycarbide SiOC, (so called black glass), exhibiting very good mechanical properties and chemical stability were studied.

High purity Mg2Si and Cu2S samples were prepared and densified by rapid hot-pressing method. The structural and phase composition of the samples were examined by means of the X-ray diffraction (XRD) method and chemical composition analysis by SEM-EDX. Magnesium silicide and copper sulfide samples were covered with amorphous layers by dip-coating method and then annealed in various gas atmospheres (O2, Ar), at different temperature and for different time periods. The obtained layers were characterized using scanning electron microscopy (SEM) and Raman spectroscopy.

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16:15 - 17:45

Enhancement of Thermoelectric Performance of N-type Mg2Si by Chemical Pressure of Impurity Dopants

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[3]Tokyo University of Science, Japan

Mg2Si, which is a narrow gap semiconductor, has attracted considerable attention as an environmentally friendly thermoelectric material. In this study, we investigated the possibility of thermoelectric performance improvement by utilizing the chemical pressure of impurity dopants. First, we theoretically examined the dependences of the electronic and thermoelectric properties of Mg2Si on the lattice constant by performing first-principles calculations. A larger power factor was obtained when the lattice constant increased, which is consistent with previous theoretical work. This structural effect on the thermoelectric properties is attributable to the convergence of two conduction bands that is caused by the increase in the lattice constant. Next, we examined the systems doped with impurity atoms that cause cell expansion; such as, Sb (for Si site) and Y (for Mg site). As a result, the convergence of conduction bands occurs for Y doping, but not for Sb; in the only former case, an enhancement of the Seebeck coefficient was obtained. The difference between Y and Sb doping should be related to the structural properties; i.e., the shift of atomic positions induced by impurity doping. The present study provides a new strategy for material development based on Mg2Si utilizing the chemical pressure of impurity atoms.

16:15 - 17:45

Simultaneous enhancement of electrical and thermal transport properties of higher manganese silicide nanocomposites

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A nanostructuring approach were effective to enhance thermoelectric performance by manipulating electronic and thermal transport properties. Especially, correlation between intrinsic properties of the matrix and nanophases is an important design factor due to the complicated relationship. Here, we prepared nanocomposites of MnSi1.787A0.01 with soft-magnet transition-metal (Fe, Co, and Ni) nanoparticles and measured their thermoelectric properties to clarify the effect of magnetic nanoparticles on thermoelectric properties. The introduction of magnetic nanoparticles (50 – 100 nm) at grain boundaries caused the improved power factor due to the energy filtering effect and carrier transfer effect. We found that the effect of magnetic nanoparticles on electronic transport properties is more effective than thermal transport properties in higher manganese silicide. Resultantly, 0.6 vol. % Fe nanoparticle-embedded nanocomposite exhibited the maximum ZT value (0.53 at 773 K), an increase of 25% compared to that of pristine samples.

16:15 - 17:45

Structural and thermoelectric properties of higher manganese silicides synthesized by pack cementation

A. Teknetzi[1], E. Symeou[2], E. Pavlidou[1], T. Kyratsi[2], E. Hatzikraniotis[1], G. Vourlias[1]

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[2]University of Cyprus, Cyprus

Higher manganese silicides (HMS), with the general formula MnSix with x between 1.67 and 1.7, are of great interest for mid to high temperature thermoelectric application. They demonstrate good thermoelectric performance, mechanical and chemical stability, and oxidation resistance at high temperatures. A figure of merit ZT up to 0.7 has been reported for the undoped material, enhanced further to ZT=1.05 for the doped one [1-2]. In addition, HMSs consist of low cost and non-toxic raw materials. So far numerous methods have been applied for the preparation of HMSs, such as solid-state reaction, ion beam synthesis, mechanical alloying and spark plasma sintering [3-5]. The current study is an investigation of structural and thermoelectric properties of HMS powder synthesized by Pack Cementation, an in situ chemical vapor deposition (CVD) batch process. Pack cementation is a simple, economic and ecological approach, which has been used for corrosion-resistant coatings, and has been recently applied to thermoelectric silicide preparation [6]. HMS powders were synthesized using Mn & Si powders (-325 mesh) and NH4Cl as activator at different experimental conditions (synthesis temperature, holding time, concentrations of initial powder mixture) were structurally characterized and identified by X-ray diffraction analysis. Their morphology and the chemical composition are determined by scanning electron microscope equipped with EDS analyzer. HMS powder was successfully formed by pack cementation, free of oxides and with only negligible traces of the secondary phase MnSi. Selected powders were subsequently hot-pressed and their thermoelectric properties (Seebeck coefficient, electrical and thermal conductivity) were examined, exhibiting good thermoelectric performance.

16:15 - 17:45

Application of a two-band model to evaluate local thermoelectric properties

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Thermoelectric ingots are far from being considered “homogeneous”, in terms of doping distribution and carrier concentration. In-homogeneities occur either deliberately, as in materials with concentration gradients or modulation doping, or unintentionally due to local variation of the doping composition during growth, or different spatial concentration of secondary phases in multi-phase materials. These in-homogeneities result in differences in local free carrier concentration and therefore, different (local) thermoelectric properties.

In this work, analysis of local thermoelectric properties is conducted, using a two-band model. Experimental data were collected using IR-reflectivity measurements. Conventional IR reflectivity measurements are usually carried out with an iris of about 2 mm to 4 mm in diameter. In our work, microscope-equipped IR setup was employed, where the iris is reduced to 100 μm, which enables mapping of the sample for local in-homogeneities throughout a pre-selected area of the sample’s surface. Analysis of each of the IR spectra collected, allows the determination of the plasma frequency (ωP) which is related to the local free carrier concentration and the conductivity effective mass, and the dumping factor (γP) which is directly related to the carrier relaxation time. Applying the two-band model, we were able to determine the contribution of each band in each point of measurement, the evolution of the apparent effective mass and the total conductivity. Measured local Seebeck coefficient was found in good agreement with the estimated one by the two-band model.

Materials: Skutterudites

16:15 - 17:45

Room: Panorama

Chairs: Marison Martin Gonzalez, Luis Fonseca, Alexander Burkov

16:15 - 17:45

Thermoelectric Properties of Partially Double Filled Skutterudites (La/Ce/Yb)$_y$Fe$_{4-x}$Co$_x$Sb$_{12}$

Y. Cha[1], D. Choi[1], J. Pi[1], I. Kim[1]

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Filled skutterudite has a chemical formula RM4X12 (M: Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt and X: P, As, Sb) and is a good thermoelectric material which improves the thermoelectric performance by filling the void and reducing the lattice thermal conductivity by the rattling effect of the filler (R). Rare-earth elements with larger atomic masses can induce a lower lattice thermal conductivity due to low-frequency phonon scattering, and double or multiple filling can further decrease the lattice thermal conductivity owing to the broader spectrum of phonon frequencies. In this study, partially double filled and Co-substituted skutterudites (La1-zCez)yFe4-xCoxSb12, (La1-zYbz)yFe4-xCoxSb12, and (Ce1-zYbz)yFe4-xCoxSb12 were synthesized by using encapsulated melting and hot pressing. Thermoelectric and transport properties were examined and discussed.

16:15 - 17:45

Enhancement of thermoelectric properties by Zn and Cd substitution in p-type $Co_2Ge_3S_3$ skutterudite-related material

M. Han[1], S. Kim[1]

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Skutterudites have been of great interest for thermoelectric applications over the last years due to their unique transport properties. It is well known that optimization via doping and “void filling” will lead to improved thermoelectric properties. Here, focusing on the substitution of Ge sites by other atoms, Skutterudite-related material Co2Ge3S3 was studied as a potential thermoelectric material. The nominal composition of Co2Ge3-xMxS3 (M = Zn, Cd, In, Sb ; x = 0, 0.15, 0.3, 0.5) have been successfully prepared by the traditional solid-state reaction method, and subsequent hot-pressing for densification. Electron and thermal transport properties, i.e., electrical conductivity, carrier concentration, Hall mobility, Seebeck coefficient, thermal conductivity, of substituted Co2Ge3S3 samples are measured at the temperature range of 300–800 K to clarify the influence of substitution upon the thermoelectric performance of Co2Ge3S3. The microstructure and morphologies of substituted Co2Ge3S3 samples were investigated by powder X-ray diffraction and high resolution transmission electron microscopy. The substitution have a significant effect on the transport properties of these ternary Skutterudites. Zn, In and Cd act as an p-type dopants, whereas Sb acts as n-type dopant. Their composition and properties upon substitution will be discussed.

16:15 - 17:45

Composite Si-O-C amorphous coatings for protection against high temperature oxidation of antimonide skutterudites

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High temperature oxidation is one of the most important problems in use of antimonide skutterudites in thermoelectric generators. Protective coatings can effectively suppress the degradation process without huge deterioration of thermoelectric module performance. We have shown that Si-O-C coatings obtained from organo-silicon precursors can be used for this purpose on magnesium silicide and skutterudites. However, in our previous work we have observed an issue connected with cracking for thicker layers of the coating.

The aim of this work was modification of the Si-O-C coating deposited on skutterudite by using different types of filler (ceramic, metallic) in order to improve its protective performance and solve the cracking issue. The layers were studied using SEM observations combined with EDS analysis and by FTIR and Raman spectroscopy. Influence of composition, deposition conditions and heat treatment on deposited layers are shown. Protective properties of the composite Si-O-C layers were studied by comparison of electrical conductivity and Seebeck coefficient of coated and uncoated sample, before and after isothermal oxidation in air showing significant improvement over unmodified Si-O-C layers.

Measuring Techniques

16:15 - 17:45

Room: Panorama

Chairs: Marison Martin Gonzalez, Luis Fonseca, Alexander Burkov

16:15 - 17:45

3D X-ray diffraction computed tomography as a tool for elucidating the decomposition of PLEC thermoelectric materials

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X-ray diffraction tomography (XRDCT) yields 3D resolved powder diffraction data thatallow the mapping of all information present in diffraction patterns. Layer by layer, samples are rotated and scanned at each rotation angle, collecting diffraction patterns at each step, which allows 3D reconstruction.[1] Microfocused, extremely brilliant high-energy synchrotron beams (a few icrons in size) and modern X-ray detectors have brought significant advances to high-resolution XRDCT. This is extremely valuable for the investigation of mixed ionic and electronic conductors (MIECs) such as Cu2-xSe,[2] which have attracted much interest as phonon-liquid electron-crystal (PLEC) thermoelectrics. However, electrical currents and thermal gradients lead to electromigration. Temperatures of “superionic” phase transitions change as a consequence, affecting the phase composition and thermoelectric performance. In-situ-experiments passing currents through a sample under a temperature gradient while collecting data for 3D-XRDCT at beamline ID15A (ESRF, Grenoble) enable stress tests with detailed spatial information on the phases present with a resolution of ca. 25 µm. Such measurements can be complemented by ex-situ SEM and EDX measurements. These experiments reveal Cu migration in Cu2Se at low temperatures, which may be associated with the formation of cubic Cu1.8Se at the cold side. Its phase fraction increases as elemental copper is formed. The order-disorder phase transition of Cu2-xSe affords cubic Cu2-xSe also at the hot side, next to deposited copper. The phase boundaries between the two phases can be observed as a function of time, they moves towards regions of lower temperatures when Cu2Se decomposes, which leads to lower thermoelectric performance.

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Projects

16:15 - 17:45

Room: Panorama

Chairs: Marison Martin Gonzalez, Luis Fonseca, Alexander Burkov

16:15 - 17:45

MAGENTA: Magnetic nanoparticle based liquid energy materials for thermoelectric applications (EU-H2020-FET-Proactive project)

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MAGENTA is a 4-year research & innovation project supported by European Union's Horizon 2020 FET-Proactive programme. Our goal is to bring a paradigm change in TE-technology by exploiting the magneto-thermoelectric (MTE) property of ionic-liquid (IL) based ferrofluids (FF), i.e;, colloidal dispersions consisting of magnetic nanoparticles (MNPs) in non-magnetic ionic liquids. Magnetic nanoparticles are, as the name suggests, a class of nanoparticles made of magnetic elements such as iron and nickel and their alloys and chemical compounds. They are used in a plethora of technological fields from biomedicine to data storage. However, their use in energy applications remains quite limited so far. Ionic liquids (IL), on the other hand, are enjoying substantial attention in several areas of energy research including thermoelectricity in recent decades [1, 2]. As a thermoelectric material, ILs present many promising features such as high electrical conductivity, large temperature and electrochemical windows, low vapour pressure and toxicity, and raw material abundance [3].

In this presentation, MAGENTA's scientific motivations (how to produce thermoelectric voltage and current using IL based ferrofluids) will be first presented, followed by the methodologies and the project objectives; i.e., 1) to provide founding knowledge of novel MTE phenomena in IL based ferrofluids, and 2) to build application-specific MTE prototypes with tailor-made IL-FFs for their use in targeted industrial sectors (cars and portable electronics). Some encouraging preliminary results on liquid thermoelectric materials obtained by the project partners will also be presented.

MAGENTA project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 731976.

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16:15 - 17:45

THERMOSS Project: Sustainable Thermoelectric Modules based on Non-toxic Silicides and Sulphides for Recovery of Waste Heat to Power Generation

E. Symeou[1], L. Louca[1], I. Giapintzakis[1], T. Kyratsi[1], N. Vlachos[2], R. Coelho[3], E.B. Lopes[3], A.P. Gonçalves[3], F.P. Brito[4], J. Martins[4], L.M. Goncalves[4], R. Vieira[4]

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[4]Minho University, Portugal

Research activities within THERMOSS Project involve the development of n-type Mg2X (X: Si, Sn) and p-type Cu12-x (Co, Ni, Zn) xSb4S13-zSez materials and the development of thermoelectric modules for medium range temperatures. These materials have attracted increasing attention as environmentally friendly thermoelectric materials with promising properties for power generation. Moreover, potential applications are explored with emphasis on cement and automotive industries.

More specifically, the research objectives of THERMOSS Project are

a) optimizing scalable synthesis of cost-effective highly efficient thermoelectric materials with ZT≥ 1 at 350oC.

b) modelling of thermoelectric modules and development of a silicide-tetrahedrite-based prototype.

c) explore potential applications via simulations for cement industry and automotive.

THERMOSS Project is funded by EU network M-ERA.NET (KOINA/M-ERA.NET/0316/03). Cement industries (CIMPOR– INDÚSTRIA DE CIMENTOS, S.A. -Portugal and Vassiliko Cement Works Public Company Ltd – Cyprus) also participate and provide technical information regarding the applications.

16:15 - 17:45

MarTEnergy Project: Sustainable and Affordable Half-Heusler based Thermoelectric Converters for Utilization of Waste Heat into Electrical Power in Maritime Applications

I. Ioannou[1], G. Mesaritis[1], G. Breuer[2], N. Vlachos[3], L. Louca[1], Y. Gelbstein[4], T. Kyratsi[1]

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[2]Ben-Gurion University of the Negev, Israel
[3]ALTER ECO SOLUTIONS LTD, Cyprus
[4]Ben-Gurion University, Israel

MarTEnergy project concerns the development of new energy-harvesting thermoelectric materials and converters, based on bulk n- and p- type Half-Heusler materials with controlled structure and properties. Half-Heusler, and especially the n-type TiNiSn and the p-type TiCoSb, based compounds were recently identified as highly potential, cost effective and environmentally friendly TE compositions.

The research objectives of MarTEnergy Project are:

a. Synthesis of cost-effective, highly efficient Half-Heusler based thermoelectric compositions.

b. Development of compatible and stable joining techniques between the thermoelectric semiconductors and the metallic joints.

c. Integration of the components into practical devices exhibiting the maximal possible device efficiencies.

d. Verification of the long-term stability under practical operation temperatures.

e. Finite element analysis on the Half-Heusler prototype converter performance prediction in the maritime shipping industry.

16:15 - 17:45

H2020 European project EnABLES: free of charge characterization of thermoelectric materials

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EnABLES is a €5.2M EU research infrastructure project that started in Januray 2018 with the mission to create access to research infrastructure to allow ‘self-sustaining’ energy solutions to ‘power the internet of things’ based on energy harvesting, storage, micro-power management and system integration activities. Simulations, data libraries, equipment and expertise access, along with feasibility studies, can all be accessed in a fast-track manner via a Transnational Access (TA) and Virtual Access (VA) program.

The mission of EnABLES is to open up key research infrastructure in powering the Internet of Things (IoT) to all European researchers, from both academia and industry. Six research Institutes together with five knowledge hubs are providing access to researchers to enable them to create ‘self-sustaining’ energy solutions to ‘power the IoT’ based on energy harvesting, storage, micro-power management and system integration activities.

In this context, CEA-Liten acts as an access provider for the characterization of thermoelectric materials. We offer the access to our thermoelectric energy harvesting facilities and expertise, including test structures, processing and characterization infrastructure. Our technical offering includes thermoelectric materials microstructure analysis (X-ray diffraction and Scanning Electronic Microscopy), bulk and thin films thermoelectric materials characterization (cross-plane and in-plane properties), characterization of thermoelectric devices (measurement of electrical resistance, output voltage, power, devices failure analysis) in controlled atmosphere (air, inert gas or vacuum). The access is free-of charge for the applicants, funded by the EU. Thus, all companies, SME and research team developing new materials or devices for thermoelectric applications and needing access to characterization equipment to measure their properties can apply to our offer.

We will present in this poster the fast, easy and simple process for free-of-charge access to equipment, tools and expertise, as well as our detailed technical offering and available tools.

Power Generation

16:15 - 17:45

Room: Panorama

Chairs: Marison Martin Gonzalez, Luis Fonseca, Alexander Burkov

16:15 - 17:45

Effects of a Module Array on Electrical Power of a Thermoelectric Generator system

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Electrical power generation using thermoelectric generator (TEG) systems could be effective technology that can improve system efficiencies of automobiles. The increased efficiency could reduce CO2 emissions because CO2 emission regulations are getting more stringent and stringent. Most of TEGs installed in the automobiles are characterized by multiple thermoelectric modules in a proper arrangement. The TEG systems convert exhaust heat into electrical power based on heat exchanges. In the present study, arrays of thermoelectric module (20mm × 20mm) using skutterudite materials are used and can be applied up to 600°C. 12 modules in total are mounted on the heat exchanger; 6 are on the top of the heat exchanger and 6 on the bottom. Externally-powered hot gases to simulate the actual exhaust gases flow within the heat exchanger. The electrical power generated from the modules was measured. At the gas temperature of 610°C, the surface temperature of the heat exchanger was about 480°C. Under this condition, the maximum output of 30 W was obtained and the overall system efficiency was about 4%. The TEG modules can relieve the conventional automobile generation system.

16:15 - 17:45

Telluride-based Two-Stage Segmented Thermoelectric Module for High Power Generation in Mid-Temperature Application

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Thermoelectric effects enable waste heat recovery by direct energy conversion from heat into electricity. Many high peak-zT materials have been developed for high thermoelectric conversion efficiency. However, a single thermoelectric material is difficult to give high power performance in a wide temperature application due to the incompatibility issue arising through the legs. As thermoelectric materials have different optimal working temperatures for high thermoelectric performance, the leg segmentation can be a solution to overcome the incompatibility issue in material properties.

Here, we report a segmented module working at mid-temperature range (hot side temperature up to 500℃) with maximum power density up to 1.15 W/cm2. The segmented power module, so called PtoP module, was designed with segmented legs consisted of Bi2Te3 and PbTe-based telluride materials. Among 43,264 possible two-stage configurations (26 p-type materials and 8 n-type materials), we chose feasible configurations of high-power module considering material synthesis and module fabrication process. The high-throughput thermoelectric performance computations were performed using the KERI's own efficiency computation algorithm [1] and python-based efficiency computation code (pykeri). Then, we synthesized the 3x3x3 mm3 legs by one-step hot-press sintering process with Ni-based diffusion barriers. And we fabricated the 2-pair power module working at the temperature difference up to 410℃. The power characteristics of ourmodule was measured using mini-PEM system [2]. The PtoP power module shows relatively high output power of 0.75 W, which corresponds to high power density of 1.15 W/cm2.

16:15 - 17:45

Thermoelectric Properties in Thin Film with pn Junction

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Seebeck effect is generally used in thermoelectric power generation, but its performance enhancement is limited. As another method, a power generation by thermal excitation using a pn junction has been reported [1][2][3]. In this study, we fabricated pn junctions with InGaZnO and CuI film and evaluated thermal voltage.

RF magnetron sputtering method was used as a thin film deposition, and synthetic quartz was used as a substrate. We fabricated three types of samples, InGaZnO single film and CuI single film, film with pn junction using InGaZnO and CuI. The conductivity and the thermal voltage were measured in a dark room.

Current-voltage measurement showed that the ohmic characteristics were observed in the single films, but it changed to the nonlinear characteristics in the sample with the pn junction. This result suggests that the energy barrier at the pn junction affects the characteristics. Furthermore, in pn junction sample, the thermal voltage was different when the direction of the temperature difference was reversed. It was confirmed that a thermal voltage was generated without temperature difference. That is suggesting the possibility of thermal excitation between pn junctions.

16:15 - 17:45

Investigation of thermoelectrics generators use for waste heat recovery - power generation system and techno-economic feasibility analysis of different plant configuration in cement industry: A case study

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Energy consumption by a cement industry is estimated at about 2% of the worldwide primary energy consumption. The process is characterized by a significant amount of heat loss mainly by the flue gases and the air stream used for cooling down the clinker. At the range of temperature of 200 to 300°C, almost 40% of total input of heat is emitted from the exit gases of pre-heater and clinker cooler. A heat recovery system could increase the efficiency of the cement plant as well as reduce the amount of CO2 emissions to the environment by lowering the temperature of the exhaust gases. Thermoelectric (TE) generators convert heat directly into electricity when a temperature gradient is applied across the junctions of two dissimilar metals. Due to the low conversion efficiency (up to 5%) of commercial thermoelectric modules, the aim of the integration shall not be the electricity production for external power supply, but the energy self-consumption of cement industry electric auxiliaries.

Interest in thermoelectric for waste-heat recovery has flourished in recent years, but questions about cost and scalability remain unanswered. The major barrier to economical thermoelectric power generation results from costs for heat exchangers. In this work, we applyied the cost-performance metric to determine how thermoelectric generators can be designed and implemented for cement industry. The paper describes and analyses two different options for the integration of thermoelectric modules within a cement industry: a) heat recovery from drying processes, and b) waste heat recovery from exhaust gases. This work determines the electricity saving that is led to reduction in energy consumption, and thus, reduction in cost saving. As well as, estimation of the simple payback period was accomplished. The results based on the operational information which was collected from Vassiliko Cement Works Public Company Ltd (Cyprus).

16:15 - 17:45

Design of an Air-Cooled Thermoelectric Generator through Modeling and Simulation, for use in Cement Industries

K. Charilaou[1], T. Kyratsi[1], L. Louca[1]

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Huge amounts of thermal energy are ejected to the environment from modern power plants. Similar levels of waisted energy are encountered in cement industries, where their production process generates significant amounts of energy that is lost through the exhaust gases. One way of exploiting this waisted energy is the use of ThermoElectric Generators (TEGs), which have the ability to convert thermal energy into electrical when a temperature difference is applied on their two sides. The idea is to install TEGs on the exhaust pipe (chimney) so that its one side is naturally heated. However, the challenge is the cooling of the other side, which has to be appropriately designed in order to produce the expected electric power.

The purpose of this work is to design an air-cooled TEG, through modeling and simulation, in order to maximize the produced power. Various design options are modeled using their 3-dimensional geometry and then used to analyze the thermo-fluid behavior of the TEG. The physical models account for fluid flow, heat transfer and their interactions, and a detailed 3-dimensional multiphysics model (COMSOL) is used for to study their response. The design considers various aspects like the shape and size of the device, flow characteristics, number of thermoelectric modules parallel and perpendicular to the flow and fins for increasing convention. This detailed model provides the necessary information (temperature differences across the thermoelectric module sides) that is used to calculate the produced power. Each design is evaluated, and the significant design variables are identified, given specific design parameters. At the end, the best design with the highest electric power production is proposed.

16:15 - 17:45

Design of a Thermoelectric Generator for Cement Industry Applications: Modeling, verification and Sensitivity Analysis

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The growing awareness for global warming and increasingly stringent environmental regulations gave incentives for developing new technologies for environmentally friendly energy production. One such technology is Thermoelectric Generators (TEG) that has applications in power plants, which are lately attracting attention from the research community. The goal of these efforts is to efficiently recover the massive amount of energy that is dumped into the atmosphere by the exhaust gases of transportation and industrial processes. The use of TEGs allows partial recovery of the exhaust gas energy and convert it into electricity by a noiseless, pollution-free and reliable process with no moving parts. The hot side of the TEG can be put in contact with the exhaust gases while the lower temperature, on the cold side, can be achieved by different cooling approaches.

The current paper focusses on the use of TEGs in the cement industry where production processes have significant energy losses through their exhaust gases. More specifically, modeling and simulation is used to analyze various TEG designs and optimize their performance for maximum electric power generation. Models that account for fluid flow, heat transfer and their interactions are used. First a simple 1-dimensional model is developed and verified against a detailed 3-dimensional multiphysics model (COMSOL). The simpler and computationally efficient model is then used to run an initial parameter investigation using a standard orthogonal array of the Taguchi design of experiments method. An L12 orthogonal array with four parameters at four levels is employed. The parameters include geometry of the device as well as configuration of the thermoelectric modules. This process identifies the significant parameters that are finally used to further explore the design space using the 3-dimensional multiphysics model. At the end of this procedure a design with the maximum power generation is identified.

16:15 - 17:45

Improved Performance of TEG Systems for Vehicle Purpose: Bending Prevention

Y. Pyo[1], G. Kim[1], Y. Jung[1], C. Cho[1], Y. Bang[1]

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The technologies for recovering the waste heat from vehicle exhaust gases include thermoelectric generator (TEG), turbo generator and Stirling engine. Among them, TEG could be an promising technology to improve the system efficiency of vehicles because the efficiency of thermoelectric modules have been recently improved and operating temperature ranges of the module are pertinent to exhaust gases. In addition, TEG has the advantage of relatively simple structure. The TEG systems convert thermal energy of the exhaust gases into the electrical energy. However, the thermal expansion and contraction of the modules, which caused by the continuous variation of exhaust gas temperatures depending on the operating conditions, leads to a poor efficiency of the TEG systems. In this study, two types of springs were used to mitigate the thermal stress when fastening the thermoelectric modules. Fin structures in the high temperature side of the thermoelectric module have been modified to minimize the thermal stress. And a horizontal supporter in the low temperature side of the thermoelectric module was installed to mitigate the thermal stress. In this experiment, the thermoelectric module made from skutterudite materials are used, and can apply up to 600°C. 24 modules in total are mounted on the simulated exhaust gas pipe; 12 modules are on the top of the pipe and other modules on the bottom. The thermoelectric modules were installed in parallel and in series to compare their performance. As a result, modules in series type have more advantage over those in parallel type when a flow rate of simulated exhaust gases is higher. The serial configuration of the thermoelectric modules could be more beneficial to the TEG systems extension for more electric power production.

Acknowledgements

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16:15 - 17:45

Evaluating series/parallel arrays of SiGe nanowires based micro thermoelectric generators

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In the internet of things framework, harvesting technologies will play an important role in extracting modest amounts of energy to power enormous wireless arrays of sensors. In order to face this challenge, Silicon based thermoelectric microgenerators have been designed [1].

Parallelly, a novel methodology to grow bottom-up in-situ boron doped SiGe NWs have been developed. With this technique, efficient thermoelectric (TE) 1D nanostructures can be easily integrated into microgenerators (μTEGs).

Nevertheless, due to the intrinsic properties of SiGe, the maximum thermal gradient achievable in the devices (about 23 K) is only able to produce some mV. This value is not high enough to power the great majority of low energy microelectronics existing nowadays. Therefore, the solution goes through implement such generator platforms in series and parallel arrays, in order to increase both output voltage and current according to the load needs.

This work asses the feasibility of integrating up to 7 of this μTEGs platforms in series in the same micromachined chip and up to 4 in a parallel configuration. The results show a great improvement in the voltage or current output (thus the power) whereas no significant parasitic loses among platforms are spotted.

Finally, some lessons are learnt and the develop of new devices designs, which will include more platform density per chip area, would foresee and place low resistance bridging paths in parallel to each platform in order to have a resistent system against eventually damaged ones.

[1] I. Donmez Noyan et al., “All-silicon thermoelectric micro/nanogenerator including a heat exchanger for harvesting applications,” J. Power Sources, vol. 413, no. September 2018, pp. 125–133, 2019.

16:15 - 17:45

Optimization of thermoelectric generator based on High Manganese Silicides and Mg(Si,Sn) solid solutions

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Silicide-based Thermoelectric generators (TEG) present a perspective as a device for applications connected with waste heat recycling applications in mid-range temperatures. Such materials as silicides are biologically safe and available for low prices, which are promising for designing sustainable generators. To design these TEGs we propose to use magnesium silicide and magnesium stannide solid solutions and higher manganese silicides (HMS) for p- and n-type branches of thermoelectric modules of such generators. These materials are providing maximum TEG efficiency and power.

Nevertheless, this pair of materials have a different coefficient of thermal expansion and mechanical characteristics. Coefficient of thermal expansion of Mg (Si, Sn) solid solutions is higher than in HMS and has it's meaning in the range from 15% to 44% depending on temperature. Besides Young's modulus in operating temperatures of Mg (Si, Sn) solid solutions are almost two times lower than Young's modulus for HMS (app. 80 GPa vs 160 GPa). These factors lead to the destruction of the generator's modules and as a result, a decrease of TEG operating characteristics.

The modeling process was carried out in COMSOL Multiphysics software in order to simulate silicide TEG operating in various temperature regime. This model includes thermal, electrical and mechanical physic interfaces. The dependences of TEG power and COP have been obtained. Mechanical pressure, stresses, and strains have been evaluated. Several solutions to dissipate local stresses have been proposed: the optimization of n- and p-type leg form and size, the variation of soldier layer thickness and compound. The proposed model may be used to improver silicide TEGs construction, this optimization leads to higher mechanical reliability and effectiveness.

Other Materials

16:15 - 17:45

Room: Panorama

Chairs: Marison Martin Gonzalez, Luis Fonseca, Alexander Burkov

16:15 - 17:45

Thermoelectric Effect in Metal Dental Restorations

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This submission represents the third in a series of poster presentations that began with “Frogs’ Legs, Thermoelectricity, and Hans Christian Oersted”, which was presented at ICT2017 in Pasadena, California, and continued with “Thermoelectric Eddy Current in Bio-Compatible Materials”, which was presented at ICT2018 in Caen, Normandy.

The common theme of this work is the influence that thermoelectric effects may have on the neurological system in humans and animals.

Dentists place metals, mixtures of metals, and dissimilar metals in contact with each other in people’s mouths, and the mouth is subjected to temperature differentials on a regular basis.

The poster intended for presentation at ECT2019 in Limassol focuses on the efforts made by the dental profession to ensure that the thermoelectric effects induced in metal dental restorations are not able to dissipate electrical potentials through the nerves in people’s heads.

(Search terms: thermoelectric, potential, eddy, current, amalgam, dental, fillings)

16:15 - 17:45

Optical characterization of polycrystalline p-type ZnSb

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[2]University of Applied Sciences Upper Austria, Austria
[3]TEGnology ApS, Hedensted, Denmark

In this work we investigate the optical properties of spark plasma sintered polycrystalline p-type ZnSb:Ag at room temperature both by spectroscopic ellipsometry in the wavelength range from Infrared (IR) to NIR-VIS-UV and by Raman spectroscopy. The elemental composition was determined by energy dispersive X-ray analysis (EDX). From that we found Sb inclusions (islands) with a spatial extent in the range of 100 – 200 µm. The samples were mechanically polished to achieve optical quality.

In the IR range, two distinct features were found in the (pseudo)dielectric functions. One corresponds to a Drude term related to free carriers, the other arises at a photon energy of about 100 meV at a carrier concentration of p □ 40 □ 1019 cm-3. This structure corresponds to direct intervalence band transitions from the light hole to the heavy hole band near the X-point in k-space which is in good agreement with recent bandstructure calculations. We also have estimated the contribution of interband transitions to the static dielectric constant as about 23, which is also in very good agreement to published data of undoped ZnSb. The NIR-VIS-UV spectral range is dominated by a broad band centered at about 2 eV, with a sharper structure at about 1 eV. The latter is assigned to the direct interband transition at the X-point in k-space which is in very good agreement with recent bandstructure calculations.

Raman measurements were performed using three excitation lasers (532 nm, 633 nm and 785 nm). The Raman modes found in this work are in very good agreement with the literature. In accordance with the EDX analysis additional Raman modes were found at 109 – 114 cm-1 and 147 - 153 cm-1 which can be attributed to the Sb inclusions.

16:15 - 17:45

Thermal decomposition and thermoelectric decline of mechanically alloyed ZnSb upon temperature cycling

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[1]University of Cologne, Germany
[2]German Aerospace Center (DLR), Institute of Materials Research, Germany
[3]Justus Liebig Universty Gießen, Germany

For almost two centuries the stoichiometric 1:1 compound in the system of zinc and antimony has been investigated in terms of its semiconducting and thermoelectric (TE) properties.[1] The advantage of the substitution of toxic or rare elements, like lead or tellurium, and the engagement of rather abundant zinc and antimony, that are lower toxic, fuelled the interest in Zn-Sb-compounds in recent years.[2] Although widespread research on the compound ZnSb was published[3], reports on the thermal instability that would hinder its application as a thermoelectric material are rare. Although independent groups discussed the problem of zinc diffusion and evaporation at higher temperatures, still Zn-Sb-compounds are often claimed to be a group of materials with “promising”[3] or “excellent”[4] TE properties, that are comparable to state-of-the-art TE materials[5, 6]

Herein we reassess ZnSb as a TE material in consideration of its crystal structural and physical transport properties behaviour upon heating. Syntheses via the sophisticated route of crystal growth from the binary melt in quartz ampoules and recently reported mechanical alloying (MA)[6] were carried out to obtain single phase ZnSb. Temperature treatments upon different atmospheric conditions were used to mimic the conditions that the material would be exposed to in an application scenario. Already after short heat exposure at 573 K, the material decomposition can be observed by XRD and DSC. The TE properties of consolidated pellets of both bulk- and MA-ZnSb were measured, showing that upon temperature cycling between room temperature and 573 K, TE values could not be reproduced. These changes of the values of the TE properties, i.e. Seebeck coefficient and electrical conductivity, may be assigned to the decomposition and accordant phase shifting of the material.

16:15 - 17:45

Effect of magnesium doping on thermoelectric and magnetic properties of copper chromite ceramic samples

V. Kytin[1], A. Duvakina[1], D. Zinoviev[1], E. Kupriyanov[1], I. Korsakov[1], V. Kulbachinskii[1]

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Copper chromite (CuCrO2) demonstrates large Seebeck coefficient and relatively small heat conductivity [1,2]. However, the thermoelectric figure of merit of CuCrO2 is strongly limited by low electrical conductivity at least at low temperatures. Low electrical conductivity limits also the application of this material in optoelectronics as p-type transparent conducting oxide. Doping of copper chromite with group II elements such as magnesium essentially increases its conductivity. Ceramic, micro- or nanostrctured material often have significantly smaller heat conductivity compared to single crystals and thus higher thermoelectric efficiency.

In this work we report the results of the investigation of thermoelectric and magnetic properties of CuMgxCr1-xO2 samples synthesized by solid phase method. Magnesium content varied from 0 to 3 at. %. At room temperature Seebeck coefficient decreases from nearly 700 mV/K in pristine material to about 250 mV/K for the copper chromite with 3 at. % magnesium content. Seebeck coefficient increases with temperature in all investigated temperature range for all obtained Mg content. Resistivity of investigated samples decreases by several orders of magnitude with an increase of Mg content from 0 to 3% at. %. Temperature dependence of resistivity can be explained in frame of hopping conductivity in the presence of Coulomb gap in the density of states. Heat conductivity of the samples with Mg was lower than heat conductivity of the pristine copper chromite ceramic. As a result, the thermoelectric figure of merit increases with increasing the Mg content.1. R. Daou, R. Frésard, V. Eyert, S. H. Maignan, A. Maignan, Science and technology of advanced materials, 18, 919 (2017). 2. T. Okuda, N. Jufuku, S. Hidaka, N. Terada, Physical Review B, 72, 144403 (2005).

16:15 - 17:45

Nanocomposites of Bismuth Telluride for Thermoelectric Applications

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The purpose of this study was to investigate the scalable production of bismuth telluride nanocomposites in which variable concentrations of reduced graphene oxide are introduced as a nano-additive in an effort to improve thermoelectric properties. Batches of appropriately-doped bismuth telluride were prepared on the 25-30 g scale using mechanochemical methods. Colloidal exfoliation and blending, together with ultrasonication was used to mix the ceramics with graphene oxide. Hot pressing was utilized both to consolidate the ceramic and to reduce the graphene oxide. Here, the thermoelectric properties of the composites will be presented and contrasted with those of composites obtained from physically mixing the thermoelectric phase with graphene nano-platelet additives. Investigations, using a combination of X-ray diffraction, scanning electron microscopy and spectroscopic measurements reveal that the synthetic method presented here produces high-purity materials, with an even distribution of the additive within the ceramics microstructure. Raman spectroscopy suggests that the additive exist mainly as defective graphitic inclusions.

16:15 - 17:45

Microstructure, mechanical, thermoelectric properties of high-temperature electrode material based on ZrB2

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High electrical and thermal conductivity, low Seebeck coefficient and the coefficient of thermal expansion adjusted to high-temperature thermoelectric materials, are the properties required for hot site electrode materials in high-temperature modulus. Zirconium diboride, a new candidate for this application, has metal-like electrical properties, very low Seebeck coefficient, and quite high thermal conductivity, moreover, its coefficient of thermal expansion matches with the most popular high-temperature thermoelectric materials.

In this work pristine ZrB2 and its composites containing 20 vol.% of B4C or SiC were sintered using PECS technique. Electron microscopy SEM observations revealed homogenous microstructure of samples. The relative density of pristine polycrystalline ZrB2 was 97% and it increased to 99% in composites. Young modulus of all samples exceeded 460 GPa. Hardness and toughness of materials increased with an additive of secondary phase and were comparable with literature data: HV around 18 GPa and KIC around 4.5 MPa m0.5.

ZrB2- SiC composite is the most suitable from examined materials, to be used as a hot site electrode in high-temperature TEGs. The coefficient of thermal expansion of this composite was 6.2•10-6 K-1. Thermal conductivity in room temperature was 90 W/m K, decreasing with the increase of temperature. All prepared materials exhibited metal-like behavior, with high electrical conductivity and Seebeck coefficient about 5 V•K-1, which well corresponds to electronic structure calculations.

Acknowledgments:

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16:15 - 17:45

First principle investigation of electronic and thermal properties of Stanene/h-BN hetrostructure

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In this manuscript, we reported Electronic and thermoelectric properties of Stanene/h-boron nitride (Sn/h-BN) hetrobilayer using first principle within the frame work of Density Functional Theory with inclusion of spin orbit coupling. Electronic band structure revels that Sn/h-BN hetrobilayer has a direct band gap at Dirac points and the meager effective mass leads to higher carrier mobility. From density of states and projected density of state we can also depict that the Stanene has unsaturated π-orbitals near valence and conduction band which suggest that charge carriers can transport only through Stanene layer thus h-BN proved to be a prime substrate for hetrostructure. Also seebeck coefficient, power factor and thermal conductivity are obtained in temperature range of 100-800K. Positive value of seebeck coefficient shows p-type nature of hetrobilayer. Seebeck coefficient increases linearly within the temperature zone of 100-350 K, suggesting the diffusive thermo-power generation. Intensification in figure of merit is also expected, because of low thermal conductivity and high electrical conductivity. Other thermal properties such as free energy, entropy, specific heat and line width also calculated for Sn/h-BN hetrobilayer. Our result suggests that Sn/h-BN hetrostructure can be a potential candidate for Nano-electronics and thermo-electronic application.

16:15 - 17:45

Temperature and magnetic field dependences of thermoelectric properties of $Bi_{1-x}Sb_x$ solid solutions in the range x = 0 – 0.25

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[1]National technical university "Kharkiv polytechnic institute", Ukraine

Bi1 xSbx solid solutions are known as the best n-type thermoelectric (TE) materials for use at temperatures below ~ (150-200) K. In recent years, interest in studying Bi1 xSbx crystals and thin films has grown due to their exhibiting properties characteristic of 3D-topological insulators. Conventionally, TE properties are controlled by creating solid solutions (to reduce thermal conductivity) and additional doping (to get necessary charge carriers concentration n(p)). To obtain optimal values of n(p), one should conduct measurements in weak magnetic fields where the Hall coefficient does not depend on magnetic field B, and magnetoresistance quadratically depends on B. Thus, it is necessary to determine the weak field boundary Bc, which is especially important for Bi1 xSbx alloys, for which Bc is very small.

The goal of this work was to measure the dependences of Bc on composition (x=0–0.25) and temperature (T=77–300 K) for polycrystalline Bi1 xSbx samples. We obtained the magnetic field and temperature dependences of the Hall coefficient, magnetoresistance, and electrical conductivity for 38 Bi1 xSbx alloys with different compositions, and determined Bc for different compositions and temperatures. It was established that composition dependences of Bc and TE properties exhibit distinctly non-monotonic character. We confirmed the presence of concentration anomalies of TE properties that we had observed earlier in the range x=0–0.1 for samples prepared using other types of heat treatment and interpreted as the manifestation of electronic phase transitions [1]. The non-monotonic behavior of the dependences at x > 0.1 were explained by qualitative changes in Bi1-xSbx band structure at certain compositions, changes in relative contribution to conductivity by charge carriers from different energy bands with changing Sb concentration, and a high sensitivity of the Bi1-xSbx energy spectrum to external influences.

[1] E.I. Rogacheva, A.A. Drozdova, O.N. Nashchekina, M.S. Dresselhaus, G. Dresselhaus, Appl. Phys. Lett. 94, 202111 (2009).

16:15 - 17:45

Electrochemical behaviour of expanded graphite electrodes for thermogalvanic cells and thermally-chargeable capacitors applications

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In recent years, the thermos-electrochemical cells (TECs) based on liquid electrolytes are receiving increased attention as an alternative thermoelectric technology; i.e., thermoelectric generators and thermally-chargeable capacitors. In the former, the thermoelectric voltage is produced via temperature dependent electrochemical reactions of redox couples at the hot and cold electrodes, where as in the latter it is created by the formation of electronic double layers at the liquid-electrode interfaces. TECs present many promising features such as high Seebeck coefficient values, raw material abundance and cost-effective fabrication processes. However, they suffer from low electrical conductivity and the limited temperature range of applications. To this end, ionic liquids are actively explored for their intrinsically high electrical conductivity as well as their large temperature and electrochemical windows. From the device aspect, the power-output of TECs can be enhanced greatly by using nano-structured carbon materials with large effective surface area while keeping down the production cost.

Here we present the electrochemical investigations of different expanded graphite electrodes in combination with several ionic liquid based electrolytes. Traditional methods such as open circuit potential measurements, cyclic voltammetry and electrochemical impedance spectroscopy are used, coupled with the thermoelectric characterizations. These results allow a better understanding of the thermos-electrochemical energy conversion in thermogalvanic cells and the charge storage efficiency in thermally-chargeable capacitors. Furthermore, the most promising electrodes are then implemented in a prototype TEC to compare its performance to conventional metallic electrodes.

This work is supported by European Union’s Horizon 2020 research and innovation programme under the grant agreement No 731976 (MAGENTA).

16:15 - 17:45

Isotropic Intra-layer Resistivity in Orthorhombic LaSb2 due to an Imperfect Structure

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LaSb2 forms a layered orthorhombic structure with an easy cleavage plane perpendicular to the c-axis. Orthorhombic materials generally exhibit anisotropic transport properties; however, the intra-layer resistivity is here found to be isotropic in single crystals grown from a self-flux. The intra-layer transport properties in LaSb2 is expected to be close to isotropic, as the a- and b-directions are structurally similar and with unit cell axes lengths that differ by only ~2 %. However, having no measurable anisotropy in magnetic fields from -9 to 9 T and at temperatures from 10 to 300 K is unlikely without an underlying structural mechanism. Examining single crystal X-ray diffraction patterns collected at APS reveals a structural mechanism for the observed isotropy, as diffraction intensity is observed where systematic absences are expected, which demonstrates a mixing of the a- and b-directions. This structural mixing could be the origin of the exotic properties exhibited by LaSb2, however at this point it is unknown whether it is twinning or stacking faults. Evidence of this mixing is presented here together with the thermal conductivity, electrical resistivity and Seebeck coefficient from 10 to 300 K is presented together with the magneto resistance from -9 to 9 T at 10 K. Additionally, some have previously reported LaSb2 to be air sensitive; however, no bulk degradation is observed for a powdered sample after 5 years of storage in air.

16:15 - 17:45

Thermoelectric properties of Zn_4Sb_3 obtained by cold sintering process

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[2]ICMATE - CNR, Padova, Italy
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[4]Università di Torino, Italy

Zn4Sb3 is a p-type thermoelectric material with one of the highest thermoelectric figure of merit in the intermediate temperature range [1]. It received considerable attention in the last two decades especially because of its low thermal conductivity, about 0.9 W/mK at room temperature. Nanostructuring this material is considered a strategic route to reduce its thermal conductivity and improve thermoelectric performance limiting the bipolar effect by selectively scatter minority carriers [2].

Cold sintering process was recently introduced [3] and demonstrated effective to obtain good levels of densification for various ceramic materials at temperatures below 200°C. It normally uses water and temperature to drive a dissolution-precipitation process that significantly reduce the sintering temperature. Cold sintering process was tested on several compounds, on ceramic-polymer composites, and it was considered for bonding applications.

We investigated the cold sintering process to obtain dense Zn4Sb3 at temperatures well below 200 °C, reported as the minimum temperature for Zn lose under dynamic vacuum. We also present and discuss thermoelectric properties of the obtained material, together with mechanical and morphological properties, and we compare results with other low temperature sintering techniques [4].

References:

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16:15 - 17:45

Improved extruded thermoelectric materials of the company RMT

M. Nazarenko[1]

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By improving the extrusion technology of bismuth-antimony tellurides, the RMT has developed new extruded thermoelectric materials (TEM) with increased thermoelectric figure-of-merit (Z). The P-type materials have maximum Z values 3.28-3.32×10-3 K-1 in the range of electrical conductivity 900-1100 Ohm-1×cm-1. The corresponding Z values for the N-type in the same range are Z = 2.82-2.87×10-3 K-1. A wide variation of electrical conductivity allows applying miniature thermoelectric coolers (TECs) for cooling and temperature stabilization in temperature ranges from 225 to 350 K. Using improved TEM, miniature TECs with the pellets height of 0.3 mm were manufactured and tested. The test results showed that these TECs have the maximum temperature difference by 2-3 K higher and energy consumption by 10-15% lower than standard RMT miniature TECs.

Invited III

9:15 - 10:45

Room: Panorama

Chairs: Mercuri Kanatzidis

9:15 - 9:45

Electronic and ionic thermoelectric effects with conducting polymers

X. Crispin[1]

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Heat-to-electricity conversion through thermoelectric effects are fascinating phenomena with many potential technological applications from waste heat energy harvesting, IR camera, e-skin to interactive building. We give an overview of those phenomena in electronic or ionic conducting polymers.

In the first part, we summarize our finding on the electronic thermoelectric properties of the p-type polymer called poly(3,4-ethylenedioxythiophene) (PEDOT) [1]. PEDOT thermoelectric aerogels are presented with their applications in dual pressure and temperature sensors [2]. We then focus on the recent advances made in the lab regarding n-type conducting polymers [3].

In the second part, we explore the ionic thermoelectric effects in both mixed ionic electronic polymer conductors [4]. This phenomenon is used to create materials orthogonal sensitive to humidity, temperature and pressure [5].

In a third part, we investigate on ionic polymer conductors. Giant Seebeck effects are found with coefficients that reache 10 mV/K. This effect enables charging a supercapacitor for energy harvesting of intermittent heat sources; but also switching a transistor, thus creating a smart pixel for high temperature sensitivity [6]. The concept of non-aqueous ionic thermoelectric polymers is further explored to obtain both negative and positive ionic Seebeck coefficient and build the first ionic thermopiles [7].

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9:45 - 10:15

Advanced thermoelectric transport simulations in complex bandstructure and nanostructured materials

N. Neophytou[1], V. Vargiamidis[1], S. Foster[1], C. Kumarasinghe[1], P. Graziosi[2], M. Thesberg[3], D. Chakraborty[1], L. de Sousa Oliveira[1]

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Nanostructured materials materials are a promising direction for new generation thermoelectric materials as they offer thermal conductivities close or below the amorphous limit, as well as improved power factors in some cases through energy filtering. Specifically, incorporation of disorder at various (hierarchical) length scales using a combination of alloying, grains, surfaces, etc., seems to be a very successful strategy. In addition, current efforts involve a plethora of complex bandstructure materials, that offer multiple opportunities for tuning the parameters that control the ZT figure of merit. For proper performance optimization and identification of new design directions, however, advanced simulations are needed, which can capture the geometrical complexity of the nano-features, the local material properties and material variations, carrier scattering events, etc.

Advanced simulations can also be employed to extend the simpler, analytical models that are commonly employed, but break down when the structures become complex, or when the feature sizes become similar to the characteristic length scales of the heat/charge carriers. This work, describes the development of advanced simulators related to the extraction of thermoelectric transport properties of nanostructures and complex bandstructure materials. Quantum and semiclassical transport studies related to thermoelectric performance optimization in materials with embedded nanoinclusions, voids, and superlattice-type barriers are discussed. Band alignment studies on the thermoelectric properties of complex bandstructure materials based on DFT studies coupled with Boltzmann transport are also discussed. In both cases, the aim is to provide deeper understanding in thermoelectric transport, that could not have been reached from simplified considerations, and then be able to design guidelines that capture those details.

10:15 - 10:45

Development of advanced half-Heusler based elements for thermoelectric applications

Y. Gelbstein[1]

[1]Ben-Gurion University, Israel

In the recent years, many efforts are being made for development of efficient thermoelectric materials with advanced performances. Such materials require properties optimization, which in many cases involves nano features for enhancement of the figure merit via the reduction of the lattice thermal conductivity. Taking into account that thermoelectric generators, directly converting heat into electricity, exhibit a major stability advantage for long-term operation, compared to other competing conversion methods, the stability of nano-featured bulk thermoelectric materials is a major issue for consideration. Such converters usually operate under high temperatures and large temperature gradients conditions, which can affect the stability of the nano-features embedded in the bulk thermoelectric main phases. As an example, one popular production method of nano-featured bulk materials is based on rapid consolidation (e.g. Spark Plasma Sintering) of nano powders obtained by melt spinning or energetic ball milling. Yet, grain coarsening effects can result in gradual deterioration of the nano-structures and thermoelectric performance degradation upon long-term high temperatures operation.

In the current research, an alternative, thermodynamic nano-features generation approach in half-Heusler based thermoelectric materials, was considered, using controlled phase separation conditions according to the relevant phase diagrams. Specific systems showing a miscibility gap, including the TiNiSn-TiNi2Sn quasi-binary system, promoting spinodal decomposition and nucleation and growth reactions will be discussed. Furthermore, the potential of generating TiNiSn-based thermoelectric couples, containing poly-crystalline n-type and single-crystal p-type half-Heusler legs, with similar coefficients of thermal expansion values will be described in details. For the latter, new acceptor dopants, enabling an electronic optimization of the p-type leg, based on ab-initio calculations and experimental validation will be presented. A comparison between the performance of such half-Heusler thermoelectric materials and the currently applied state of the art materials will be also given, taking into account the various involved parameters for practical long-term operation of such devices.

Chalcogenides V

11:15 - 12:45

Room: Panorama

Chairs: Anne Dauscher

11:15 - 11:30

Improving the Thermoelectric Performance of Rare-Earth Tellurides Using Band Structure Engineering

D. Cheikh[1], B. Hogan[1, 2], S. Gomez[1], T. Vo[1], P. von Allmen[1], B. Dunn[2], J. Fleurial[1], S. Bux[1]

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Lanthanum telluride (La3-xTe4) has recently emerged as a high-efficiency, high-temperature n-type thermoelectric material. The performance of La3-xTe4 stems from a complex defect thorium phosphide (Th3P4) crystal structure, where La3+ vacancies enable a wide range of carrier concentrations. This results in an inherently low thermal conductivity (κ) and favorable values for thermopower (S) and electrical resistivity (ρ). With an optimized defect stoichiometry, the dimensionless figure of merit, ZT = S2T/ρκ, can achieve values as large as 1.1 at 1275K.

To further improve the thermoelectric performance of this system, we investigated methods to modify the electronic band structure to induce favorable thermoelectric properties. Here we will present computational results showing the introduction of 4f electrons of other rare-earth (RE) elements (Pr and Nd) resulted in a sharp peak in the density of states (DOS) near the Fermi level of these RE3-xTe4 compounds. The peak in the DOS was predicted to increase the Seebeck coefficients of Pr3-xTe4 and Nd3-xTe4 by 25% and 100%, respectively, over La3-xTe4 at equivalent carrier concentrations. Pr3-xTe4 and Nd3-xTe4 compounds were then synthesized using a mechanochemical approach and compacted using spark plasma sintering (SPS). Both materials were found to have improved Seebeck coefficients in agreement with our computational predictions. Additionally, ZT was found to increase by 40% for Pr3-xTe4 and 10% for Nd3-xTe4 compared to La3-xTe4.

11:30 - 11:45

Interplay between electronic structure, crystal defects and electron transport properties in tetrahedrites studied from ab initio calculations

J. Tobola[1], P. Levinsky[2, 3], J. Hejtmanek[4], C. Candolfi[5], A. Dauscher[5], B. Lenoir[5]

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We present results of electronic structure calculations in copper-based minerals, tetrahedrites/tenntanites (Cu,M) 12 (Sb-As)4S13 (M - transition metal element), which exhibit propensity to form energy band gap at the Fermi

level for particular number of electrons [1]. Moreover, it was found that specific phonon properties in these systems were responsible for very low thermal conductivity [2]. On the whole, complex crystal structure, containing five inequivalent atomic sites and offering wide opportunities to tune electron and phonon transport properties via substitution or vacancy defect formation, make these materials very attracting for thermoelectric conversion. Here, we focus mostly on electronic structure characteristics near the Fermi level, when substituting or doping on Sb-site (Cu 12 Sb 4-x Te x S 13 [3], Cu 12 Sb 4-x As x S 13 [4]) or Cu-sites. The Korringa-Kohn-Rostoker (KKR) method with the coherent potential approximation (CPA) was employed to account for chemical disorder and allowing to study both electronic density of states and dispersion curves with complex energy as well as to investigate energetic aspects such as the site preference of dopants and their crystal stability. Furthermore, following very recent experimental X-ray investigations demonstrating crystal lattice distortion (from I-43m to I-42m) in Cu12Sb4S13 compound (unlike Cu12As4S13) at low temperature [5], the effect of unit cell symmetry lowering on energy bands features is discussed from KKR computations.

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11:45 - 12:00

Thermal stability, oxidation resistance and protective coatings for tetrahedrites

R. Coelho[1], E. Branco Lopes[1], A. Pereira Gonçalves[1]

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Tetrahedrites are very attractive for thermoelectric applications due to their low cost, relatively high figure of merit (zT) and natural abundance. New ways to improve the zT values of tetrahedrites are constantly being explored using different approaches, like doping with s-, p- and d-elements or by changing the synthesis methodology.

To develop a good and reliable thermoelectric device, capable to work for long periods without maintenance, is fundamental to be based on stable, high-performance thermoelectric materials, with capacity to maintain their efficiency at the working temperatures without changes. However, previous studies reported that tetrahedrites have a limited phase stability and suffer from sulfur sublimation and oxidation at high temperatures, which pointed to a maximum working temperature of 350ºC and the need to search for protective coatings [1-3]. In the present work, preliminary results on the thermal stability, oxidation resistance and protective coatings for $Cu_{11}MnSb_4S_{13}$ and $Cu_{10.5}Ni_{1.5}Sb_4S_{13}$ tetrahedrites, with good thermoelectric performance, are presented.

The tetrahedrites were submitted to heat treatments at 450 °C for 1000h under different environments, like argon atmosphere, vacuum or coated with boron nitride and exposed to air. Oxidation and sulfur losses were investigated, indicating that the materials are stable at this temperature if properly protected. However, the samples coated with boron nitride were degraded, without any signs of tetrahedrite phases, which indicates that boron nitride cannot be used as a protective coating for tetrahedrite.

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12:00 - 12:15

Study of NiS2 as p-type thermoelectric material

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Current commercially available thermoelectric materials contain rare, expensive and toxic elements, being necessary to develop new, cheap, abundant and environment-friendly alternatives. Metal sulfides are interesting candidates, as they can fulfill these requirements. However, many sulfides with potential for thermoelectrics were not studied until now. A family of sulfides yet poorly explored is the vaesite-based one. Vaesite, NiS2, is a transition metal chalcogenide with pyrite structure. It has 12 atoms per unit cell, distributed in two crystallographic positions, Ni(4a) and S(8c). In equilibrium conditions, NiS2 was reported to be a stoichiometric compound stable up to 1020ºC [1], but previous works suggested that it is an intrinsic non-stoichiometric compound, with variable metal and stable anion concentrations. Deviations from stoichiometry, corroborated by changes in the unit cell parameters, were seen to have important consequences in the electrical and magnetic properties [2,3].

In this work, we explore the potential of the pure vaesite for thermoelectric applications. The synthesis of bulk NiS2 was done by the solid-state method, followed by hot-pressing, which, after optimizing the conditions, resulted in dense pellets suitable for the electrical transport properties measurements. The electrical resistivity and Seebeck coefficients were measured between 20-300 K, indicating a semiconducting behavior for NiS2. Small power factors were observed at room temperature, but the large Seebeck coefficients observed point to the possibility of a good thermoelectric performance through charge carrier tunning.

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12:15 - 12:30

Structural characterization and thermoelectric properties of indium thiospinel

P. Wyzga[1, 2], I. Veremchuk[2], C. Himcinschi[1], U. Burkhardt[2], W. Carrillo-Cabrera[2], M. Bobnar[2], C. Hennig[3, 4], A. Leithe-Jasper[2], J. Kortus[1], R. Gumeniuk[1]

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Disorder in the high-symmetry crystal structures has been often reported as a source of promising thermoelectric properties, mainly due to reduced thermal conductivity. Several examples were found among sulfur-based minerals e.g. tetrahedrite (interaction between lone pair electrons of Sb and Cu atoms) [1], chalcosite (high mobility of Cu ions) [2] or bornite (random distribution of vacancies and Fe/Cu atoms at the same position) [3]. Here, we present a study of binary In-thiospinel In1-x□xIn2S4, in which order/disorder of vacancies has a great impact on electronic and thermal transport properties [4].

Four samples of In1-x□xIn2S4 sulfide (x = 0.16, 0.22, 0.28, 0.33) were synthesized by solid-state reaction of constituent elements. Single-phase tetragonal β-In1-x□xIn2S4 polymorphic modification was found for In0.67□0.33In2S4. Additional In atoms in the crystal structure lead to stabilization of disordered cubic α-polymorph (x = 0.16 and 0.22) with statistically distributed vacancies at tetrahedral positions. Using combined diffraction, spectroscopic and microscopic analysis, In0.72□0.28In2S4 was confirmed to contain both α and β-modifications.

Although all samples show n-type conductivity and similar Seebeck coefficient α > |200| μV·K- 1 above room temperature (RT), a significant decrease of electron mobility μ (by factor of 103 at RT) and thermal conductivity κtot (3 times at RT) from ordered β- to disordered α-polymorph was observed. An extremely low κtot < 0.6 W·m-1K-1 was measured for cubic In0.84□0.16In2S4. Changes of electrical and thermal properties are counterbalancing each other and both α- and β-modifications are characterized by similar ZTmax ≈ 0.2 at 760 K.

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12:30 - 12:45

Pseudo 3D-Printed Earth Abundant Non-Toxic Cu2-xS with High Figure of Merit

M. Burton[1], M. Carnie[1], S. Mehraban[1]

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The go to materials for thermoelectrics are Bi2Te3 and PbTe for room temperature and mid-temperature applications respectively. ZT was shown to be ~1 in these materials since the 1950s.[1,2] Te is, however, a rare and toxic element, which has prevented the wide scale use of thermoelectrics. In 2014 He et al. showed that Cu deficient copper (I) sulphide (Cu2S) exhibits a maximum ZT of 1.7 at 1000 K.[3] The unique combination of all Earth abundant non-toxic components and a high ZT has led to their being a large interest in this material in the thermoelectric community. Many fabrication techniques have been studied since 2014, including melt-solidification,[4] mechanochemical synthesis,[5] ultrasonication and pressing,[6] chemical synthesis and hot pressing,[7] hydrothermal synthesis and hot pressing,[8] and hydrothermal synthesis and mechanical alloying followed by spark plasma sintering.[9–11] These techniques however, require high pressure, high temperature and lengthy fabrication times.

In contrast, printing can be achieved at ambient temperature and pressure and yield fast fabrication times. Printing has primarily focused on the production of films (~300 μm), due to the limitations of printing techniques being studied for thermoelectrics, e.g. screen printing.[12] More recently, 3D printing has been investigated for Bi2Te3.[13] Whilst this shows the potential of printed thermoelectrics, both toxic and rare elements were required.

In this work, we studied the thermoelectric performance of bulk polycrystalline Cu2-xS fabricated by low-cost ball milling of the constituent elements. Thermoelectric elements were printed from a water-based ink using carboxymethyl cellulose as a binder, with the aim of producing a commercially viable thermoelectric device. The effect of variation of the Cu stoichiometry on properties were studied. Thermoelectric characterization of the printed polycrystalline Cu2-xS, reveals peak ZT ~0.8 at 1000 K, which is comparable to examples in the literature for Cu2-xS produced in more laborious and energy intensive techniques.

Applications II / Modules III

11:15 - 12:45

Room: Megaron B

Chairs: Francisco Brito

11:15 - 11:30

Overtaking silicon photovoltaic efficiency by thermoelectric hybridization of perovskite solar cells

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[2]Massachusetts Institute of Technology, United States

Silicon solar cells dominate the photovoltaic (PV) market worldwide. Their high efficiencies, along with their relatively low cost, make them the most valuable solution up to date. However, it is well known that silicon solar cells are extremely sensitive to temperature, and they can lose up to 15 – 20% of their room temperature efficiency under normal operating conditions. In this perspective, less sensitive solar cells such as Cadmium Telluride (CdTe), Gallium Indium Phosphide (GaInP), and Perovskites, have been proposed as valuable alternative solutions. However, the room temperature efficiencies of these candidates materials are still lower than silicon based devices, making them not competitive enough. Hybrid Thermoelectric-Photovoltaic (HTEPV) systems, which recover solar cell heat losses to produce an additional power output, can be a suitable option to enhance the competitiveness of these kind of solar cells.

In this communication we report a rigorous experimental procedure aiming at the development and the characterization of a system composed by a triple-cation perovskite solar cell, and a bismuth telluride thermoelectric generator with optimized design. The results showed an absolute efficiency gain between 1.5 and 3.5% depending on the solar incoming power, corresponding to ≈ 10 – 25% of the sole PV efficiency. These gains, which are in very well accordance with theoretical estimations, were found to happen at typical operating temperatures of PV. Under these conditions the efficiency of the hybrid device was found to be higher than typical silicon solar cell efficiency. This experimental evaluation demonstrated in an accurate fashion the real potential of thermoelectric hybridization of solar cells.

11:30 - 11:45

Construction and Experimental Verification of Simple Model for Predicting Peltier Module Performance during PWM Driving

N. Isoshima[1], W. Sato[2], N. Tsukada[2], H. Ogawa[2]

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[2]Hitachi, Ltd., Japan

The Peltier module is a small electrical device that adsorbs the heat of a sample without using a fluid refrigerant. Peltier modules are often used in pulse width modulation (PWM) driving: PWM driving, square current pulses with a variable duty ratio are repeatedly applied to the module to control heat absorption. However, the decreases in heat adsorption and driving voltage (Peltier module performance) relative to the amounts for constant direct current (DC) modulation driving remain unclear for applications in which a Peltier module is used in PWM driving with a specified duty ratio. This paper presents a simple model for predicting Peltier module performance during PWM driving that is based on Ogawa's modified Ioffe theory, which is used for DC driving and has been extended for PWM driving. The model is based on two assumptions: (1) the Peltier effect and Joule heating are steady and have time-averaged values during each PWM cycle, and (2) the temperature fluctuations of each module component during each cycle are sufficiently small for a pseudo-steady state to form. Thus, the unsteady term is omitted from the heat conduction equation for the module, the Peltier effect term and Joule heating term are multiplied with the duty ratio for PWM driving. Testing showed that the model accurately reproduces measured data over a wide range of temperature differences and duty ratios, including the decrease in driving voltage with the duty ratio. The proposed model is thus well-suited for designing Peltier modules used in PWM driving.

11:45 - 12:00

Highly integrated silicon thermoelectric microgenerator

M. Salleras[1], M. Dolcet[1], A. Stranz[1], J.M. Sojo[2], M. Pacios[2], À. Morata[2], A. Tarancón[2], L. Fonseca[1]

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The Internet of Things ecosystem is expected to grow exponentially in the next few years. The need for distributed power everywhere precludes the use of batteries for such sensors, as replacing batteries when exhausted becomes unfeasible. That is where harvesting technologies have an important role in extracting energy present in the environment.

To tackle this issue, and taking advantage of microfabrication technology in MEMS industry, our objective is to obtain a thermoelectric microgenerator based on silicon. The device itself is made with silicon with a top-down approach and obtaining a thermally isolated silicon platform which establishes a thermal gradient between two regions in the microstructure. Thousands of silicon nanowires are integrated by bottom-up approaches bridging these two regions and, thanks to their promising thermoelectric properties, a power density of up to 10-100μW/cm2 is obtained with external temperature gradients from 50ºC to 150ºC.

In different projects we have been optimizing the geometry of such thermoelectric microgenerators. Currently a novel geometry has been designed which allows the integration of up to 50 thermoelectric microgenerators in a single 0.5cm2 chip. In addition, the design has some features which facilitate the integration of a heat exchanger on top of the device, which will significantly improve the thermal gradient seen by the silicon nanowires. Some designs also have silicon microbeams with no nanostructure instead of silicon nanowires. This helps comparing the nanostructuring effect on the performance of the device in terms of power density output. We will show the latest results achieved with these highly integrated designs.

12:00 - 12:15

Detachable Contacts for Simultaneous Thermoelectric Characterization of Iron Disilicide

A. Micallef[1], C. Stiewe[1], G. Oppitz[1], S. Tiedke[2], E. Müller[1, 3]

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The efficiency of a thermoelectric material is quantified through the figure of merit zT, which is defined by its Seebeck coefficient (S), electrical conductivity (σ) and thermal conductivity (κ). We developed a Combined TE Measurement facility (CTEM) to simultaneously determine the above mentioned properties as well as the figure of merit by the Harman method up to 600 °C. A simultaneous measurement saves time, reduces the measurement error and makes properties comparison more reliable.

For high measurement accuracy, high quality soldered contacts between sample and holder blocks are necessary; besides low thermal and electrical contact resistances, the applied contact technique should allow for an easy dismounting of the unchanged sample after measurements for further use of the sample and holder blocks.

This study presents results on tested contact systems for n-type thermoelectric cobalt doped iron disilicide (Fe0.95Co0.05Si2). Different coating materials and techniques were tested on holder blocks and TE samples as diffusion barriers or adhesion layers. Low melting solders based on Bi, In and Sn were used as joints to allow suitable contacts and non-destructive detachment. For a selection of systems, the electrical contact resistance was studied in dependence on temperature using an in house-built controlled heating station. Further measurements have been performed by the CTEM. Microstructure analysis by SEM and EDX shows the contacting region before and after heat treatment, and reveals intermetallic reactions, interdiffusion zones and adhesion status. Cr-coating on the TE sample joined to Mo metal blocks by Bi32.5In51Sn16.5 solder was identified as a suitable solution. The results show a controlled influence of interdiffusion, good wetting behavior and suitable contact resistivity(≈25 μΩ·cm^2).

12:15 - 12:30

Global analysis of the assembly of Fe_2VAl and metal electrode through the study of the bonding process conditions.

V. Marchal-Marchant[1], G. Roy[1], C. van der Rest[1], O. Poncelet[1], P. Jacques[1]

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Fe2VAl-based thermoelectric modules are very promising for large scale applications since its constituent materials are abundant, non-toxic and low cost. However, the assembly of modules based on Fe2VAl compounds requires to properly bond this material to high electrical conductivity material such as copper. Furthermore, the assembly must remain efficient on the entire range of temperature at which Fe2VAl compounds show interesting thermoelectric properties, from 300K to 700K. At these temperatures, thermal ageing may induce significant modification of the microstructure at the interface between thermoelectric material and electrode. Moreover, copper is known to show poor oxidation resistance above 500K and its replacement by nickel or nickel-plated copper should be considered [1].

To understand the influence of the bonding process on the properties of the assembly, we propose a global analysis based on characterization of the interface microstructure, measurements of surface contact resistance and Seebeck coefficient of the junction as well as the assessment of the effect of thermal ageing [2].

We tested several joining technologies and discriminated some processes based on the global analysis. The most promising technique is the use of a high temperature (1000K) silver-based brazing compound under high vacuum condition (10-4 mbar). This process leads to low surface contact resistance (<10μΩ·cm2), the appearance of a thin reactive layer at the interface, a weak change on the Seebeck coefficient and no major degradation of the assembly properties after heat treatment. Furthermore, those results were obtained for all three of copper, nickel-plated copper and nickel electrodes. Finally, this bonding process has been upscaled to manufacture a complete thermoelectric module with 36 thermoelectric legs and 37 electrodes in an induction vacuum furnace.

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12:30 - 12:45

Large area manufacturing of flexible thermoelectric modules through Hybrid Flexible Electronics

S. Mortazavinatanzi[1], A. Rezania[1], L. Rosendahl[1]

[1]Aalborg University, Denmark

It has been an interest to fabricate flexible thermoelectric generators in recent years to obtain a better conformability required in most of the waste heat recovery cases involving curved surfaces. Majority of the attempts with this regard carried out using the organic and or thin-film materials which are not efficient enough for the real-world applications. On the other hand, modules fabricated based on the best commercial bulk thermoelectric material like Bismuth-telluride (Bi-Te) based alloys are rigid, expensive and in small sizes which limits the applicability of them for the large area waste heat recovery and thermal management. Here a promising manufacturing concept called ”Flexible Hybrid Electronics - FHE” is utilized with the aim of cost-effective and high throughput manufacturing of the large-area flexible thermoelectric modules. Flexible Hybrid Electronics combines traditional silicon electronics and printed electronics manufacturing which results in much more flexibility and conformability comparing with silicon electronics as well as a higher degree of efficiency and functionality in comparison with printed electronics. The through additive nature of this method also yields in a faster, cheaper and more reliable manufacturing and also opens the door to integrate many manufacturing steps and to decrease the final product lead time. To proof this manufacturing concept, a flexible thermoelectric generator was fabricated with a desktop dispenser printer and pick & placing the Bismuth-telluride pellets. After final assembly and bonding the thermoelectric legs, the device functionality was tested by conducting thermoelectric functional tests and also cyclic bending test. The results show the ability of the flexible thermoelectric generator to produce power after different bending cycle and bending radius with a little change concerning the initial stage. It is also possible to fabricate the power electronic parts with the same method to have a fully flexible package at the same substrate in the future.

Heusler

11:15 - 12:45

Room: Megaron C

Chairs: Eric Alleno

11:15 - 11:30

Fast synthesis and thermoelectric properties of n-type half-Heusler, TiNiSn

K. Chen[1], C. Nuttall[2], R. Potter[2], K. Placha[3], R. Tuley[4], K. Simpson[4], J. Bos[5], M. Reece[1]

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[5]Heriot-Watt University, United Kingdom

The n-type half-Heusler TiNiSn exhibits good thermoelectric properties, mechanical properties and thermal stability, which makes it very promising for thermoelectric applications in the medium temperature range (~500 °C). However, the synthesis of TiNiSn often involves long annealing times (several weeks) to obtain single phase, which is a barrier to scaling-up. In this work, TiNiSn was synthesized by a combination of arc-melting (AM), mechanical alloying (MA) and spark plasma sintering (SPS). Ti, Ni and Sn wires were used as the starting materials and then arc-melted in a glove box to minimize oxidation. The samples after AM were a mixture of half-Heusler and full-Heusler, Ti6Sn5 and Sn, but single phase TiNiSn was achieved after MA for 5 h. After SPS, the samples had high density (~99.5% of relative density) and fine grains (200 ~ 800 nm). The total synthesis time was significantly shortened. Addition of Cu, which has been reported as an effective n-type dopant1, was used to optimize the thermoelectric properties of TiNiSn. Samples with Cu content lower than 10 mol. % are phase pure and a full-Heusler appeared with higher Cu content. The power factor of TiNiSn was improved with the addition Cu, which also reduced the thermal conductivity. The effects of addition Cu on the phase structure and transport properties of TiNiSn are consistent with previous reports.1 A maximum zT value of 0.63 was achieved at 773K for TiNiCu0.05Sn. The fast synthesis of TiNiSn with good thermoelectric performance presented in this work opens up the possibility of industrial scaling-up.

11:30 - 11:45

Amorphous and crystalline TaCoSn: study of a new thermoelectric material

F. Aversano[1], A. Ferrario[2], S. Boldrini[2], C. Fanciulli[3], M. Baricco[1], A. Castellero[1]

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[3]CNR - ICMATE, Italy

Half Heusler alloys are ternary intermetallic compounds with general formula ABX, where A is usually the most electropositive transition metal, B is a less electropositive transition metal and X is a main group element. The characteristic of these compounds is to contain 18 electron valence. Therefore is possible to use the elements combination of different groups of the periodic table to keep the electron valence count equal to 18. TaCoSn is a new composition which has been predicted to be stable trough ab-initio calculations [1,2], but has been experimentally verified only once by solid-liquid reaction [2].

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

The effect of mechanical alloying of elemental powders as a function of milling time is shown in Fig. 1. As milling proceeds, crystallographic reflections disappear leaving place to a broad halo, suggesting the progressive amorphization of the powders. The presence of an exothermic peak around 540 °C in the differential thermal analysis, Fig. 2, indicates the crystallization of the amorphous phase into a crystalline phase with half Heusler structure as shown in Fig. 3. After crystallization, an endothermic peak around 875 °C appears probably because of decomposition of the half Heusler phase, Fig. 2.

Bulk samples for thermoelectric measurements were sintered using two different methods. The effect of sintering processes and the starting powders on microstructural, structural, mechanical and thermoelectric properties is evaluated.

11:45 - 12:00

Enhanced thermoelectric performance in Fe-Ti-Sb Heusler system with Yttrium doping

A. Taranova[1], A. Kalugina[1], D. Karpenkov[1], V. Kurichenko[1], A. Novitskii[1], A. Voronin[1], A. Grytsiv[1, 2], V. Khovaylo[1]

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[2]Institute of Materials Chemistry and Research, University of Vienna, Austria

For the last decade, Heusler alloys have been investigated not only as materials with specific magnetic properties but also as a thermoelectric material operating in the middle temperature range. Among the various thermoelectrics, Heusler compounds have attractive transport properties, high thermal and mechanical stability. However, moderate thermal conductivity hinders the large-scale application of these materials.

In the present work, the effects of yttrium for titanium substitution on thermoelectric and structural properties of a Fe-Ti-Sb Heusler system were investigated. Polycrystalline bulk $Fe_{1.5}Ti_{1-x}Y_xSb$ (x = 0; 0.05; 0.1) was fabricated by a traditional arc melting technique. The obtained ingots were annealed in an evacuated quartz tube at 1073 K for 72 hours, followed by quenching in water. Finally, the resultant one-phased samples were ball milled and densified using the spark plasma sintering technique.

According to the X-ray phase analysis, no secondary phases were observed. The positive Seebeck coefficient indicates a p-type electrical transport behavior for all the samples. Surprisingly, the substitution leads to a moderate increase in the Seebeck coefficient and electrical resistivity. Furthermore, the thermal conductivity were decreased dramatically mainly due to enhanced the phonon scattering caused by heavier yttrium atoms. The details of the transport properties changes will be presented.

12:00 - 12:15

Role of secondary phases and interstitial Ni on thermoelectric properties of TiNiSn half Heusler alloys

F. Aversano[1], A. Ferrario[2], S. Boldrini[2], C. Fanciulli[3], E. Bassani[3], D. Marré[4], M. Baricco[1], A. Castellero[1]

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Half-Heusler intermetallic compounds have general formula ABX. In most cases, A and B are transition metals, while X is a main group element. The structure consists of three filled interpenetrating f.c.c. sublattices and one vacant f.c.c. sublattice (Wyckoff position 4d).

TiNiSn half-Heusler compound is a promising thermoelectric material, because of the high Seebeck coefficient and electrical conductivity, that lead to high power factor. However, thermoelectric properties of nominally equivalent samples show highly scattered values, likely due to the presence of secondary phases and different amounts of interstitial Ni occupying the Wyckoff position 4d, that affect the charge carrier concentration and energy band gap of samples produced in different batches. As shown by the ternary phase diagram, obtaining a pure single phase TiNiSn compound is difficult because small deviations from the stoichiometry promptly bring the system in a multiphase region of the phase diagram.

Aim of this work is to analyse the effect of secondary phases (Ni3Sn4, Ti6Sn5, TiNi2Sn) and interstitial Ni (TiNi1+xSn, with x = 0, 1.03, 1.06, 1.12) on the thermoelectric properties of TiNiSn alloy.

The master alloys were obtained by arc-melting, first preparing a pre-alloy TiNi and subsequently adding elemental Sn. Homogenization of the master alloys was achieved by an annealing at 850 °C for 3 weeks and at 650 °C for 2 weeks. Structural and microstructural characterizations were performed by X-ray diffraction and scanning electron microscopy. Thermoelectric properties were measured in a wide range of temperature (10 K – 723 K) using different characterization techniques. Charge carrier concentration was estimated through the Hall effect, electrical conductivity was measured both by Van der Pauw method and the four probe method, Seebeck coefficient was measured using differential methods.

The thermoelectric properties of the different samples are critically discussed in terms of presence of secondary phases or interstitial Ni.

12:15 - 12:30

Effects of tin for antimony substitution on the thermoelectric properties of the $Fe_{1.5}TiSb_{1-x}Sn_x$ Heusler alloy

A. Kalugina[1], A. Taranova[1], D. Karpenkov[1], V. Kurichenko[1], A. Novitskii[1], A. Voronin[1], A. Grytsiv[1, 2], V. Khovaylo[1]

[1]National University of Science and Technology MISIS, Russia
[2]Institute of Materials Chemistry and Research, University of Vienna, Austria

Heusler alloys have attracted significant attention as promising thermoelectric materials for last decade. Half Heusler (HH) compound consists of XYZ as the main chemical composition, where X is a transitional metal, a noble metal, or a rare-earth element; Y can be a transitional metal or a noble metal; and Z is a main group element. Recently it was reported that excess of Fe atoms in HH Fe1.5TiSb system led to excellent thermoelectric performance.

In This work will research substitution according to Fe1.5TiSb1-xSnx (x = 0, 0.5, 0.1). Polycrystalline balk samples Fe1.5TiSb1-xSnx were fabricated by conventional induction melting followed by ball milling and spark plasma sintering consolidation. The resultant high-dense disk-shaped specimen were sealed in evacuated quartz tube and annealed at 1073 K for 10 hours. XRD revealed that all the samples were single-phase without any traces of secondary phases.

Transport properties measurements indicated the decrease of the Seebeck coefficient and the electrical resistivity upon Sb to Sn substitution. Further were the thermal conductivity was slightly dropped from 3.55 Wt/m·K for Fe1.5TiSb to 3.37 Wt/m·K for Fe1.5TiSb0.95Sn0.05 respectively. More details of transport properties evolution will be presentation.

Organics

14:15 - 15:30

Room: Panorama

Chairs: Xavier Crispin

14:15 - 14:30

Low and high thermal conductivity states in polymer thermoelectric

T. Degousée[1], F. Liscio[2], D. Gentili[3], M. Cavallini[3], V. Untilova[4], L. Biniek[4], X. Xu[5], M. Palma[5], S. Milita[6], M. Brinkmann[4], O. Fenwick[1]

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[4]Institut Charles Sadron, CNRS – Université de Strasbourg, Strasbourg, France
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Recent progress in organic thermoelectric materials has been achieved by improvement of the power factor (PF) via doping and structural engineering of the polymer chains. Yet, the effects of morphology and doping on the thermal transport are often neglected. Using the 3ω technique, we have measured the in-plane thermal conductivity of two types of doped polymer: 1) thin films of highly-aligned poly(3-hexylthiophene-2,5-diyl) (P3HT) doped with 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) and 2) drop-cast P3HT doped with iron(III) p-toluenesulfonate hexahydrate (Fe-Tos), a ferric salt. We used grazing-incidence wide-angle X-ray scattering (GIWAXS), optical spectroscopy, electron diffraction or atomic force microscopy (AFM) to characterise the morphological changes induced by chain alignment and/or doping. Our results show that highly-aligned films and isotropic films can both exhibit an electrical conductivity above 100 S/cm. On the other hand, both alignment and doping of the polymer chain can increase the thermal transport. The molecular packing adopted in the crystalline regions by the doped semi-crystalline polymers appears as a key parameter of the improved thermal transport, as does the rigidity of chains in the amorphous regions of the films. The implications of these findings for polymer thermoelectrics will be discussed.

14:30 - 14:45

Stoichiometric Control of Hybrid $Ag_{2-x}Te$ Nanoparticle/PEDOT:PSS Composites for Tunable Thermoelectric Performance

K. Mazzio[1], D. Kojda[1], B. Ryll[1], J. Niederhausen[1], K. Habicht[1], S. Raoux[1,23]

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Hybrid materials consisting of inorganic nanostructures embedded in conducting polymer matrices have emerged as promising systems for near room temperature thermoelectric applications. They are attractive due to the intrinsic low thermal conductivity of the polymer, utilizing nanostructuring as a means of further improvements via phonon scattering, the ability to engineer the hybrid interface to take advantage of energy filtering effects, and the possibility of utilizing high-throughput and solution processing for manufacture. Most hybrid materials reported in the literature have been p-type, owing to difficulties in n-type doping of conducting polymers in conjunction with the nature of the applied nanocrystals. Because both p-type and n-type materials are desirable for module development, there is a strong drive to compliment the advances in hybrid p-type materials with new n-type materials. Here we demonstrate the use of Te nanowires encapsulated in PEDOT:PSS as templates for the synthesis of Ag2-xTe/PEDOT:PSS hybrid materials via topotactic chemical transformation processes. This synthetic method allows us to engineer the composition of our hybrid materials, whereby we are able to directly influence the thermoelectric properties, including the production of both p-type and n-type hybrid materials from the same parent material. We gain an understanding of the electronic and morphological development of our materials via XPS, UPS, XRD, and TEM as the stoichiometry is changed in the Ag2-xTe nanoparticle component of the hybrids. These properties can then be related to the corresponding thermoelectric performance. Ultimately, we aim to show how these changes in the structure and composition relate to the thermoelectric properties in an effort to guide performance improvements in these and related hybrid material systems.

14:45 - 15:00

Fabrication and characterization of organic thermoelectric materials based on doped poly (3-hexylthiophene) and carbon nanotube forest

S. Mardi[1], K. Yusupov[2], P.M. Martinez[3], A. Vomiero[2], A. Reale[1]

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[2]Luleå University of Technology, Sweden
[3]University of Texas at Dallas, United States

Over the last decade, organic semiconductors have been extensively investigated due to their promising potential for thermoelectric applications. Poly (3-hexylthiophene) (P3HT) is one of the polymers which recently has been used thoroughly for thermoelectric applications. P3HT has large Seebeck coefficient. However, it exhibits low electrical conductivity for thermoelectric applications. So, it is important to increase the conductivity in P3HT layers. There were a lot of efforts made to increase the conductivity of P3HT, like using different molecular configurations, introducing fillers or tuning the electrical conductivity via additives.

Here, we have investigated the effect of Lithium salt and tert-butylpyridine (TBP) as dopants and highly-ordered carbon nanotube “forest” (CNTF) as a filler to enhance the electrical conductivity of P3HT. The pristine P3HT was dissolved in 1:1 chlorobenzene/dichlorobenzene solvent mixture. The P3HT was doped with TBP and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) solution (520 mg in 1 mL of acetonitrile). Solutions with different levels of doping were prepared.

For making thermoelectric devices, the CNTF was applied on the substrates, with further spin-coating of the polymer on top of the “forest”. Then the obtained films were annealed at 150 °C for 15 min under N2 environmental conditions. Seebeck coefficients, electrical conductivity, and the output power of the thermoelectric devices were measured by homemade systems under vacuum conditions. For comparison, similar samples without CNTF were also fabricated. The highest power factor value was achieved for the samples in the group with the lowest amount of dopant on CNTF. The Seebeck coefficient, electrical conductivity, and power factor in this sample were 91.9 μV/K, 130.22 S/cm, and 109.99 μW/mK2, respectively at 71 C. The same parameters for the optimal sample without CNTF were 172.0 μV/K, 0.44 S/cm, and 1.29 μW/mK2. This demonstrates that CNTF can be a very efficient tool to control and optimize thermoelectric properties of P3HT semiconductor.

Measuring Techniques

14:15 - 15:30

Room: Megaron B

Chairs: Alexander Burkov

14:15 - 14:30

A straightforward 2 omega technique for the measurement of the Thomson effect

I. Haïk Dunn[1], R. Daou[1], C. Atkinson[2, 3]

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We present a simplified, rapid, and accurate method for the measurement of the thermoelectric Thomson coefficient by the dynamical heating of a suspended wire by an alternating current. By applying a temperature gradient across the wire, we find that the response at the second harmonic of the excitation frequency is directly proportional to the Thomson coefficient. The absolute thermoelectric coefficient of a single material can therefore be extracted with high precision by using a phase sensitive detector. We test our method on platinum and nickel wires and develop both analytical and numerical models to determine the leading sources of error.

14:30 - 14:45

Influence of size effects on the absolute Seebeck coefficient of platinum

M. Kockert[1], R. Mitdank[1], A. Zykov[1], S. Kowarik[1, 2], S.F. Fischer[1]

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Platinum is used as thermoelectric reference material and in combination with other materials as thermocouples [1]. However, in recent years micro- and nanopatterning have become more interesting [2] and new challenges for metrology and its interpretation occur. For example, in order to determine the thermoelectric transport properties of nanowires, measurements are usually performed relative to thin films [3,4]. However, thin metal films have a reduced absolute Seebeck coefficient S_film compared to S_bulk [5,6]. Especially for metal-metal junctions, it is important to know the absolute Seebeck coefficient of the reference material. Deviations in the single-digit microvolt per Kelvin range can easily lead to misinterpretations of the measurement results.

Here, we present a measurement platform to investigate the influence of size effects on the thermoelectric transport properties of thin platinum films. Structual properties like the film thickness and the grain size are varied. We demonstrate that boundary and surface scattering reduce the thermodiffusion and the phonon drag contribution to S_Pt,film compared to S_Pt,bulk. A detailed discussion and a model to describe the temperature dependence of the absolute Seebeck coefficient and the influence of electron-phonon and phonon-phonon interaction on S_Pt is given.

Our work shows that by tailoring the microstructure a Seebeck coefficient of nearly zero can be achieved at room temperature, which is of interest for interconnects in low-noise applications.

14:45 - 15:00

Suspended silicon nanostructures for thermoelectric generation

E. Dimaggio[1], D. Narducci[2], G. Pennelli[3]

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[3]University of Pisa, Italy

Nanostructured silicon used as basic component for thermoelectric generators (TEGs) opens the perspective for the applications of these devices into the Internet of Things scenario, where they could be integrated on the same chip with the electric loads they should power, e.g. nodes of wireless sensor networks. For an evaluation of the thermoelectric properties of these nanostructures and a comparison with the conventional materials used for TEGs, reliable techniques for the measurement of the in-plane thermal conductivity κ have been developed. The most critical step in the process relies on the possibilities of suspending these nanostructures from the substrate, avoiding any thermal loss through it. To this end, test devices on SOI wafers have been defined through high resolution e-beam lithography, on both mono-crystalline and poly-crystalline silicon top layers. The so defined structures are suspended by a calibrated underetching of the buried oxide. In case of mono-crystalline silicon, prototypes made by combs of thin nanomembranes have been fabricated and the three-omega technique to determine κ has been applied. The nanomembranes are particularly interesting because they can guarantee both high conduction of current and good mechanical stability of the suspended structures. The effect of the surface roughness on the reduction of κ has been investigated. For the strained thin poly-crystalline film the suspension process is highly critical, and problems of mechanical stability arise. Therefore, we developed an alternate technique where micrometric windows are opened to laterally etch the oxide so as to suspend the film for a few microns. Two metal tracks placed on top of the film allow for a measurement of the film thermal conductivity that is independent of the temperature coefficient of its electrical conductivity. The technological processes developed in both cases and the measurement results will be shown and discuss.

15:00 - 15:15

Measurement and optimizing of COP in Peltier-cooling technique

D. Platzek[1], I. Cabezas[1], B. Still[1], G. Noriega[2]

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Research in thermoelectrics nowadays seems to be more focused on energy conversion from heat into electricity, rather than on heat pump applications. Even though, there are more applications using Peltier modules on the market than using Seebeck devices as thermoelectric power generator TEG. Whereas optimization of Seebeck coefficient, electrical and thermal conductivity works for both, Peltier and Seebeck applications, Peltier devices mostly are used with high power densities (e.g., in laser cooling, cooling box etc.), regardless of their energy consumption and thus their Coefficient of Performance COP. However, optimizing the application towards a high COP makes the Peltier technology competitive compared to other types of heat pump technology. Peltier technology even has some advantages as there are small size, good controllability and low maintenance.

This work describes a device to measure the COP of Peltier modules and a study of different modules and optimization of the COP based on theoretical calculations 1).

Panco´s measurement facility TEGeta, which originally was constructed to measure the properties of power generators TEG has been modified to measure the COP of Peltier devices when employed as thermoelectric heat pumps. Therefore an electrical heater is used to give heat to the specimen which pumps it to a reservoir. Temperatures and electrical power are measured and the heat of the heater and the used energy of the Peltier module are compared to estimate the COP.

Modules of different size and pumping capacity have been developed and fabricated to optimize the COP and measured in the TEGeta.

1) R.R. Heikes and R.W. Ure Jr.; Thermoelectricity: Science and engineering; Interscience publishers New York, London, 1961.

Acknowledgement: This work was partly funded by Bundesministerium für Wirtschaft und Energie aufgrund eines Beschlusses des deutschen Bundestages.

15:15 - 15:30

On improvement of speed of the complex absolute method of measuring of thermoelectric parameters of materials

V. Lysko[1], L. Anatychuk[1]

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To experimentally solve multiparameter problems on determining the optimal composition of multicomponent materials, the most effective dopants, and to work out the technological modes for obtaining materials, it is necessary to measure thermoelectric parameters of a large number of samples. Such measurements require considerable time, which is a real obstacle to solving these problems. Therefore, the problem of significant increase in the measurement performance becomes quite urgent.

The paper presents an analysis of the speed of measurements of the absolute method, as the most promising for developing high-precision equipment for complex measurements of electrical conductivity, thermoEMF, thermal conductivity and figure-of-merit of thermoelectric materials.

Based on a detailed analysis of the physical models of measuring equipment with the use of computer methods of searching for optimal measurement algorithms and design of measuring systems, new methods have been developed to improve speed. They consist in passing an alternating current through the sample under study, by using the forced heating of the hot side of the sample with a reference heater, as well as measuring under conditions of continuous monotonic heating of the sample under study. Computer models have been developed to find the optimal functions of controlling the currents of power supply to the thermostat heater, the reference and screen heaters, as well as the alternating current passed through the sample.

Some reduction in the time required for the measurement of the temperature dependence of the thermoelectric properties of a single material sample three or fivefold by the complex absolute method is achieved. At the same time, the accuracy in determining the thermoelectric figure of merit in the temperature range of 30 to 500 ° C remains at the level reached in previous works and is up to 5%, which is several times higher than the accuracy of the known analogues.

Other Materials II

14:15 - 15:30

Room: Megaron C

Chairs: Eckhard Mueller

14:15 - 14:30

Paramagnons: A New Paradigm for Designing Thermoelectric Materials

D. Vashaee[1], M.H.M. Polash[1], M. Rasoulianboroujeni[2], J. Heremans[3], V. Perelygin[1], A. Smirnov[1]

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[2]Marquette University, Afghanistan
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Thermoelectric materials progress based on the engineering of the electronic and phononic characteristics is reaching a plateau mainly because electrons are fermions and the Fermi-Dirac statistics impose an inverse relation between the thermopower and the carrier concentration. We discuss a new class of thermoelectric materials that can overcome this fundamental limit by utilizing magnons and paramagnons - bosonic quasi-particles that can play as a new independent variable not limited to the counter-balancing nature of the parameters that enter zT. Just as in the discovery of the spin-Seebeck effect, which led to the new area of spincaloritronics, where the spin angular momentum is transferred to the electrons, both the spin waves (i.e., magnons) and the local thermal fluctuations of magnetization in the paramagnetic state (i.e., paramagnons) transfer their linear momentum to electrons and increase the thermopower. Magnons in ferromagnetic metals have already led to thermopower increase by order of magnitude over the diffusion thermopower – the only example where a spin-based effect is much larger than a charge-based effect. Recent experimental results show that paramagnons can generate a substantial enhancement in thermopower as does the magnon drag. Hence, the mutual interactions between the conduction electrons and paramagnons in paramagnets can make a new class of thermoelectric materials. We will discuss the competing theories such as the spin-fluctuations and spin entropy to explain the underlying physics of the enhanced thermopower in the paramagnets. In particular, data from magnetic measurements and the electron paramagnetic resonance spectroscopy will be analyzed in parallel to the thermal and transport data to identify the critical parameters for design and optimization of paramagnetic semiconductors for thermoelectric applications.

14:30 - 14:45

From n-type to p-type behaviour of CrN thin films: the importance of stoichiometry

A. Le Febvrier[1], D. Gambino[1], G. Abadias[2], F. Giovanelli[3], B. Alling[1], P. Eklund[1]

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Transition metal nitrides in their thin film forms were and are still intensively studied for their mechanical properties. they also exhibit interesting electric properties which makes them suitable for other applications. More recently, CrN and ScN well known as a degenerated n-type semiconductor have shown promising thermoelectric properties with high Seebeck, low electrical properties and moderate thermal conductivity.

In this work, CrNx films were deposited by magnetron sputtering at 650 C on different substrates with different amount of reactive gas in the plasma. Under the present deposition conditions, over- and under- stoichiometry in nitrogen (CrN1 +/- x) is obtained in the epitaxial rock-salt structure. Structural (XRD), morphology (SEM) composition (RBS, ERDA, XPS) and electrical characterization were performed on the different CrN films. The thermoelectric properties of the films depend on the nitrogen content and on the substrate nature. The over-stoichiometry in nitrogen and/or Cr deficiency lead to a p-type semiconductor behaviour of CrN, with promising thermoelectric properties. The under-stoichiometry in nitrogen leads to a n-type semiconductor of CrN up to the metallic behaviour of the film when Cr2N is formed. Parallel DFT calculation on the effect of the different vacancies or interstitials confirmed the stability and the effect observed experimentally. Both, Cr vacancies and nitrogen interstitials are favourable and lead to a shift of the fermi level into the valence band, thus confirming the p-type character of the semiconductor material. The control of the semiconductor behaviour of CrN films can be tailored by controlling of the stoichiometry. These results are a starting point for designing p-type and n-type thermoelectric materials based on chromium nitride thin film, a material cheap and routinely grown at industrial scale.

14:45 - 15:00

Pronounced transport anisotropy in the type-I clathrate $Ba_8Au_{(6-x)}Ge_{(40+x)}$

G. Eguchi[1], A. Hariki[1], M. Ikeda[1], P. Tomes[1], N. Barisic[1], J. Kunes[1], M. Baitinger[2], D. Nguyen[2], M. Mihalkovic[3], A. Smontara[4], C. Allio[5], C. Krellner[5], P. Lory[6], M. de Boissieu[6], S. Pailhes[7], V. Giordano[7], H. Euchner[1], Y. Grin[2], S. Paschen[1]

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A central topic in the development of modern nano- and microtechnology is the engineering of heat and charge transport of semiconducting materials. Type-I clathrates are cubic materials in which guest atoms are weakly bound in a cage-forming network of six tetrakaidecahedra and two dodecahedra per unit cell. The rattling motion of the guest atoms in the cages is held responsible for their extremely low lattice thermal conductivity. Here we study Ba8Au(6-x)Ge(40+x), a representative that is particularly interesting because the rattling modes of Ba extend to extremely low energy [P.-F. Lory et al., Nat. Commun. 8, 491 (2017)], a situation where the rattling mode-acoustic phonon mode interaction has most drastic effects [M. Ikeda et al., Nat. Commun. 10, 887 (2019)]. Here we report an unexpected pronounced anisotropy in electrical and thermal transport, and discuss its origin.

15:00 - 15:15

Impact on organic solvents in combination with redox-couples on magnitude and sign of Seebeck coefficient and electrical current in thermoelectric generators

E. Laux[1], L. Jeandupeux[1], A. Homsy[1], M. Hofmann[1], P. Potty[1], H. Keppner[1]

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In previous work it was shown that Ionic Liquids as active substances in thermoelectric generators (TEGs) have the potential to reduce the thermal conductivity as compared to Solid state materials in conventional TEGs. Furthermore, it was observed that the Seebeck coefficient could be significantly increased. After a large variety of experiments it appears that the remaining bottleneck coming to high performance TEGs is due to finding ILs with increased negative Seebeck coefficient and sufficient current extraction. It appears furthermore, that higher current extraction for a given redox couple and concentration is linked to low viscosity. On the way to explore the effect of viscosity-induced current limitation, in a first step the Ionic liquids are substituted by a low-viscosity organic solvent such as Propylene carbonate (PC). The results showed that, indeed, the thermo-current increases significantly. It was further found that the Seebeck coefficient using this solvent exhibited high values such as 1.7 mV/K. Such high values were in previous work rather attributed to the use of ionic liquids. Surprisingly, by adding up to 10% of water to PC, the current and power is more than doubled, compared to pure PC. The paper studies the effect of combinations of solvent and redox-couples and tries to correlate the effect of water in solvent water mixtures looking at physical properties such as viscosity impact, but also on effects assumed to be due to charged carrier attachment at the electrodes.

15:15 - 15:30

Intermetallic semiconductor $FeGa_3$: Chemical nature and thermoelectric properties

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The intermetallic phases T(8)Tr3 (T(8) = Fe, Ru, Os; Tr = Ga, In) with FeGa3 type of structure are unusual examples of compounds with transition metals, where semiconducting behavior is observed. Quantum chemical analysis shows that Fe–Fe dumbbells of the ideal FeGa3 structure are significantly influenced by Fe–Ga contacts resulting in multicentre interactions. Furthermore, the structural reinvestigation on differently synthesized single crystals revealed an additional occupation of the empty prismatic sites by Fe, depending on the preparation conditions and leading to the composition Fe1+xGa3 ($0 \leq x \leq 0.018$). The additional Fe species yield in-gap states with a non-vanishing density of states at the Fermi level [1]. The thermoelectric properties of samples with different Fe content show clear enhancement of the electrical conductivity, with respect to stoichiometric FeGa3, supporting the influence of “self-doping”.

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Chalcogenides VI

16:00 - 17:00

Room: Panorama

Chairs: Cestmir Drasar

16:00 - 16:15

The Meta-Status and Ag-Additive Effects of Telluride Thermoelectric Compounds with Ag

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In recent years, research on various fault controls has been increasing greatly in the field of thermoelectric materials development. This reflects the deepening understanding of complex material microstructures that are realistically present, as opposed to attempting various interpretations with the assumption of uniform microstructure and uniform crystalline in the past. In this presentation, we report the various meta-states that appear in the Bi-Te, Pb-Te and Ge-Te systems (1, 2, 3, 4, 5, 6), the most representative materials in the Telluride thermoelectric material system, and reports on micro structure changes and changes of thermoelectric property with Ag additions. It also reports on the role of Ag in these microstructure changes.

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16:15 - 16:30

Stability of thermoelectric copper iodide, copper chalcogenides and solid solutions between them

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Copper iodide (CuI) is a multifunctional p-type semiconductor that has recently attracted much attention, also as a transparent thermoelectric material with figures of merit up to

ZT = 0.21.[1] Tellurium- and selenium-doped CuI exhibits considerably higher electrical conductivity (>20 S/cm) than pristine material. Mixtures of CuI and Cu2Te in 8:1 ratio show a transition between p- and n-type conduction. Copper chalcogenides, on the other hand, have gained interest because of ‘liquid-like’ copper atom behavior, which leads to seemingly promising thermoelectric properties.[2] However, both classes of compounds lack stability at elevated temperatures and under electrical currents. Mixtures of CuI and Cu2Ch may alter electrical and thermal conductivity by introducing vacancies. Iodine evaporates from CuI at elevated temperatures, which is traceable by in-situ PXRD. (Cu1.8Se)0.975(CuI)0.025 shows unusual behavior: the lattice parameter increases up to 190°C but then decreases until 270°C before normal thermal expansion occurs, suggesting an evaporation of iodine in this temperature range, leading to a decreased phase transition temperature and the formation of iodine vacancies. The ‘liquid-like’ behavior causes Cu migration in Cu2-xSe when exposed to electrical current, resulting in a Cu concentration gradient through the sample and a segregation of metallic copper at the negative pole. As the copper content of Cu2-xSe affects its thermal conductivity, thermoelectric performance is critically influenced. For large temperature gradients, the effect is more pronounced. The composition may range up to Cu1.7Se, depending on current and the time as, in-situ 3D X-ray diffraction tomography elucidated.

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16:30 - 16:45

Influence of Milling Media on Thermoelectric Properties of $Bi_{0.3}Sb_{1.7}Te_{3.0}$

I. Morioka[1], K. Hasezaki[1], K. Hanasaku[1], M. Bumrungpon[1], T. Hirai[1], R. Yasufuku[1]

[1]Tokushima University, Japan

Bi2Te3-based materials have a rhombohedral crystal structure with R3m space group and anisotropic physical and thermoelectric properties. Bi2Te3-based materials are the best thermoelectric semiconductor around room temperature and expected to use the waste heat recovery. Bi2Te3-based materials are needed to improve the thermoelectric property, because of low energy conversion efficiency. There is much research focused on developing preparation methods that improve the dimensionless figure of merit (ZT) values of Bi2Te3-based materials prepared are dopant addition, nanomaterial dispersion, and finely grained milling. In milling methods for producing Bi2Te3-based materials, the properties of the materials powder depend on the internal mechanics of the specific mill, the power supplied to drive the milling process, and the composition, size of the balls. The milling energy depends on the rotational speed and milling media. In the previous study, Kitamura et al. reported that un-doped Bi0.3Sb1.7Te3.0 prepared by mechanical alloying followed by hot pressing (MA-HP) which is different from the best composition of Bi0.5Sb1.5Te3.0 by melt growth has high thermoelectric properties [1]. In a present study, the influence on milling media on thermoelectric properties of Bi0.3Sb1.7Te3.0 using Si3N4 balls in a stainless-steel vessel were investigated by comparing the thermoelectric properties prepared by MA-HP with two different types of milling media and balls. The first was using conventional Si3N4 balls in a stainless-steel vessel, and the second was using yttria-stabilized zirconia (YSZ) milling vessel and balls as milling media respectively. The ZT prepared with YSZ milling and balls was a peak of 1.16 at room temperature, approximately 15% higher than that with Si3N4 balls in a stainless-steel vessel, and the thermoelectric properties influenced by the selection of appropriate milling vessels and balls.

Reference

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16:45 - 17:00

Vacancies in SnSe single crystals in a near-equilibrium state

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We investigated type and concentration of intrinsic vacancies in single crystalline SnSe as a function of annealing temperature. The investigation is based on positron annihilation spectroscopy combined with transport measurements. Two types of single-vacancies were found in SnSe single crystals. Tin vacancies VSn dominate at the temperatures ≤ 500 K, while selenium vacancies VSe and vacancy clusters VSn + nVSe dominate at higher temperatures ≥ 600 K. This implies that actual stoichiometry of SnSe is temperature dependent and SnSe prefers a Se-rich composition at low temperatures and a Se-poor composition at higher temperatures. Se liberated from the structure with increasing temperature further reacts with SnSe and produces SnSe2. The vacancy clusters survive the α→β transition at ≈800 K and grow in size with temperature. The concentration of VSe and VSn + nVSe increases with temperature as well as the thermoelectric performance indicating the connection between excellent thermoelectric properties of SnSe and these point defects. The defects might help in increasing the power factor of the material due to a local increase in the DOS or an extra energy-dependent scattering. Further, they induce an enhanced scattering of phonons and hence a drop in thermal conductivity. We hypothesize that the concentration of defects remains much higher in single crystals than in polycrystals. The reason might be that such defects (being created due to the variation in the equilibrium stoichiometry with temperature) can accumulate at grain boundaries in PC while staying within the bulk in SC. The defects formed within the SC bulk keep their nanoscopic nature; hence, they can dissolve and precipitate upon cycling repeatedly.

Other Materials III

16:00 - 17:00

Room: Megaron B

Chairs: Yaniv Gelbstein

16:00 - 16:15

Low-grade thermal energy harvesting using ionic ferrofluids

S. Nakamae[1], K. Bhattacharya[1], M. Beaughon[1], M. Roger[1], J. Riedl[2], V. Peyre[2], E. Dubois[2], E. Laux[3], L. Jeandupeux[4], H. Keppner[3], B. Huang[5], Y. Shao-Horn[5]

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In recent years, thermocells containing liquid electrolytes and complex liquids such as ionic-liquids and nanofluids are attracting attention as an alternative thermoelectric (TE) material. Unlike in solids, several inter-dependent TE effects take place in liquids; most notably, the thermodiffusion, the electronic double-layer formation and the electrochemical (thermogalvanic) reactions, resulting in the Seebeck coefficient values that are generally an order of magnitude larger that the semiconductor counterparts. The power-output of thermocells remains rather low due to the low ionic conductivity of liquids. To this end, ionic-liquids with high ionic conductivity are actively studied. Additionally, the inclusion of charged colloidal particles has been shown to further enhance the Seebeck coefficient and the power output of thermocells.

In this work, ionic liquid based ferrofluids are studied as novel electrolytes in thermogalvanic cells. The impact of magnetic nanoparticle inclusion to the open-circuit output voltage (Seebeck coefficient), power output as well as their dependence on applied magnetic field were found to differ greatly from those in ferrofluids based on weak electrolytes (aqueous and organic solvents). Different hypothesis to interpret these experimental observations as well as technical insight into achieving higher thermoelectric conversion efficiency using IL-based thermogalvanic cells are proposed.

This work is supported by European Union’s Horizon 2020 research and innovation programme under the grant agreement No 731976 (MAGENTA).

16:15 - 16:30

Redox reactions in ionic liquids-based thermo-electric systems.

M. Bobrowski[1], S. Freza[1], I. Anusiewicz[1], P. Skurski[1]

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Neat Ionic Liquids (ILs) as well as their solutions with appropriate salts can play a role similar to that the bismut telluride semiconductor plays in the ,,traditional" thermoelectric devices. Ionic liquids (ILs) are salts that are liquid near ambient temperature. Unique physicochemical properties of ILs can be tuned by altering the ions and their combinations. The neat IL can manifest high Seebeck. On the other hand the system consisting of IL and redox salt can either manifest high Seebeck but it's higher if only the concentration of redox salt is lower. The redox couples were thought to play the same role when soluted in ionic liquids as the typical redox couples do in a typical solvents, i.e. they're responsible

for the current flow in liquids. Summarizing it seems the ions present in the system (ionic liquid + redox couple(s)) they take part in reversible reduction/oxidation reactions occuring at electrodes and maybe between individual ions.

In the current work we show the idea of the novel type of the thermo-electric device based on ionic-liquid material, and the results of quantum calculations of the redox reactions occuring in galvanic cell. We utilized the Born-Haber cycle and determined the redox potentials of all assumed half-reaction reactions and in turn detected which ions were involved in the electron exchange processes. The tendency of any ion to lose or gain electrons can be determined by calculating the redox potentials. Moreover, its value calculated for all selected reactions can be widely compared and can indicate on the the mechanism of electron conductivity present in ionic-liquid based thermo-galvanic cells.

Acknowledgements: The investigations were supported by grant no 731976 from European Union

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16:30 - 16:45

On the oxidation behavior of the thermoelectric material ZnSb

H. Riis[1], R. Madathil[1], R. Haugsrud[1], Ø. Prytz[1]

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The oxidation of intermetallic thermoelectric materials is important for their application. It can be beneficial if an oxide passivates the material and prevents changes to the material from the environment, and the oxidation rate is minimal at the operating temperature in the operating environment. Oxidation can also lead to degradation if it is too fast and/or leads to corrosion. In this study, we examine the oxidation behavior of ZnSb.

ZnSb samples were prepared by the hot-pressing method. Polished and cleaned samples were heated in air from 200-400°C for durations up to 200 h. Samples were studied by X-ray photoelectron spectroscopy (XPS) before and after heat treatment to determine the composition of the surface. Heat-treated samples were investigated further by scanning transmission electron microscopy (STEM) to determine the structure of the oxide layer. Energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy were used to map the elemental composition. The oxidation kinetics was studied by thermogravimetric analysis (TGA) in the same temperature region as previously specified.

XPS shows a thin oxide layer on polished samples before heat treatment. The oxide consists of ZnO and a Sb-oxide. Heat treatment changes the composition of the oxide to ZnO as determined by EDS. The oxide forms two distinct layers, a nanocrystalline layer followed by a columnar-like layer. A systematic mass gain is observed with TGA with parabolic time dependence.

16:45 - 17:00

Study of GaN, AlGaN and 2D electron gas thermoelectric properties and of electrical contacts for thermal sensors application.

C. Bryan[1], P. Faucherand[1], M. Plissonnier[2], G. Savelli[1]

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High power output can be obtained with new generation HEMTs (High Electron Mobility Transistor) which use AlGaN (Aluminium Gallium Nitride) / GaN (Gallium Nitride) heterostructures. A difference in energy gap and in polarisation between the two layers creates an accumulation of electrons at the interface which is called a 2D Electron Gas (2DEG). The low resistivity in the 2DEG allows for high electron mobility. High power dissipated by HEMTs can lead to them overheating (150°C - 300°C) and cause their degradation.

In-IC (Integrated Circuits) thermoelectric (TE) sensors using AlGaN and GaN, integrated close to the transistors, can be used to manage thermal flux and avoid HEMTs reaching critical temperatures.

The aim of this work is to study MOCVD (Metal-Organic Chemical Vapour Deposition) grown GaN, AlGaN and 2DEG TE properties which will be integrated into our sensors. A study of the electric contacts was carried out to use the least resistive ones in the sensor; electric contacts are often the most resistive parts of the devices. Temperature dependent TE properties of these materials will be presented; it is the first time that such measurements have been performed on 2DEG. The TLM (Transmission Line Measurement) method was used to measure the contact resistance for Ti/Al, Ti/Au, Ti/Au/Al and Ti/Al/Ni/Au contacts, in each case both non-annealed, and annealed at a number of temperatures, and the results compared. An improved understanding of contact annealing was obtained by TEM (Transmission Electron Microscopy) and XRD (X-Ray Diffraction) analyses of the contacts.

Nanomaterials II

16:00 - 17:00

Room: Megaron C

Chairs: Elli Symeou

16:00 - 16:15

Thermoelectric properties of SPS sintered Si/Al nano powders

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Nanostructured silicon is an attractive thermoelectric material meeting the requirements for sustainability and non-toxicity along with a competitive thermoelectric figure of merit ZT [1]. While silicon is abundant and tons of silicon waste are available from semiconductor industry [2] and cast-off of 1st generation solar cells, aluminum belongs to the most abundant elements and is also well-known as p-type dopant in silicon. In our work, we have investigated the effect of aluminum nanoparticles (AlNPs) on the thermoelectric transport properties. Commercial silicon and aluminum nano powders (0% ... 20 wt.%) were mixed and densified in an atmospherically controlled spark plasma sintering (SPS) furnace in the absence of oxygen and water. Additionally, we used porous silicon (pSi) sputtered with 100 nm aluminum as nanostructured base material to maintain high purity and introduce an intrinsic porosity. We show the influence of the aluminum concentration, the mixing procedure as well as the SPS synthesis conditions on the thermoelectric transport. In particular, we present temperature-dependent electrical conductivity, thermal conductivity, Seebeck coefficient, charge carrier density and Hall mobility. The samples' structure and chemical properties are measured by SEM, EDX and XRF. We show, that the charge carrier density and mobility and therefore the electrical conductivity can be increased by the addition of AlNPs. We further correlate the transport properties with the porosity of the samples, which reached up to 40% for the compacted commercial powders and up to 50% for the compacted pSi samples. We demonstrate, that thermal transport in Si/Al samples is dominated by the porosity, while the addition of up to 20 wt.% AlNPs does not significantly affect the thermal conductivity. Hence, electrical and thermal transport are decoupled and can be separately optimized.

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16:15 - 16:30

Optimising the nanostructure of Pb1-xGexTe to minimise thermal conductivity

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PbTe and GeTe-based compounds are promising thermoelectric materials for applications in the mid-temperature range of 500 K to 800 K. The PbTe-GeTe system undergoes spinodal decomposition (Fig.1) when cooled from above 850 K and complex nanostructures consisting of Ge-rich and Pb-rich domains are spontaneously formed. The dense arrangement of interfaces and the mass fluctuation involved in Pb-Ge mixing enhances phonon scattering and strongly reduces the thermal conductivity. Here we focus on the nominal composition Pb0.41Ge0.59Te and show that by tuning the synthesis procedure, we are able to control both the number of distinct phases in the samples as well as the pattern of domains and the density of interfaces between them. We also study the effect on the nanostructure and thermoelectric properties of thermal cycling our samples over the operating temperature range.

16:30 - 16:45

Preparation and characterization of nanostructured (GeTe)75(AgSbTe2)x(AgSbSe2)y thermoelectric materials

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Thermoelectric materials can be used for direct energy conversion from heat into electricity. The maximization of energy conversion can be obtained by tuning the ZT parameter that is derived from the material physical properties like the Seebeck coefficient, electrical and thermal conductivities. (GeTe)100-x(AgSbTe2)x TAGS are known materials for middle-temperature range applications, because of their very good electrical and thermal properties. The GeTe based material of TAGS exhibits high thermal and electrical conductivity but the Seebeck coefficient is too low and can be optimized by optimal doping. One of the methods to decrease thermal conductivity is nano-structurization by introducing nano AgSbTe2 inclusions into the matrix, however, that will also interfere with other thermoelectric properties. We analyzed the influence of AgSbSe2 addition on thermoelectric properties. For the purpose of this work there were synthesised AgSbSe2, AgSbTe2, GeTe and compositions (GeTe)75(AgSbTe2)y(AgSbSe2)x where x+y=25 and y=(0, 0.26; 0.51, 1.25, 6.25). In this paper, we described the preparation and thermoelectric properties materials consolidated by rapid Spark Plasma Sintering (SPS). For optimal doped TAGS-75 with addition of AgSbSe2 (y=1.25) we obtain stabilization of the cubic structure, increase of Seebeck coefficient by about 50% (from 50 to 100 μVK-1 in 325K), thermal conductivity decrease by 20% (from 1.2 to 0.95 Wm-1K-1 in 325K), electrical conductivity decrease by about 50% (1.8x105 to 9x105 Sm-1). Finally, the thermoelectric figure of merit ZT increased by about 40% (323-625K) and maximum value reached ZT=1.2 for optimally doped material, while 0.7 in 625K for undoped TAGS-75.

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