Book of Abstracts

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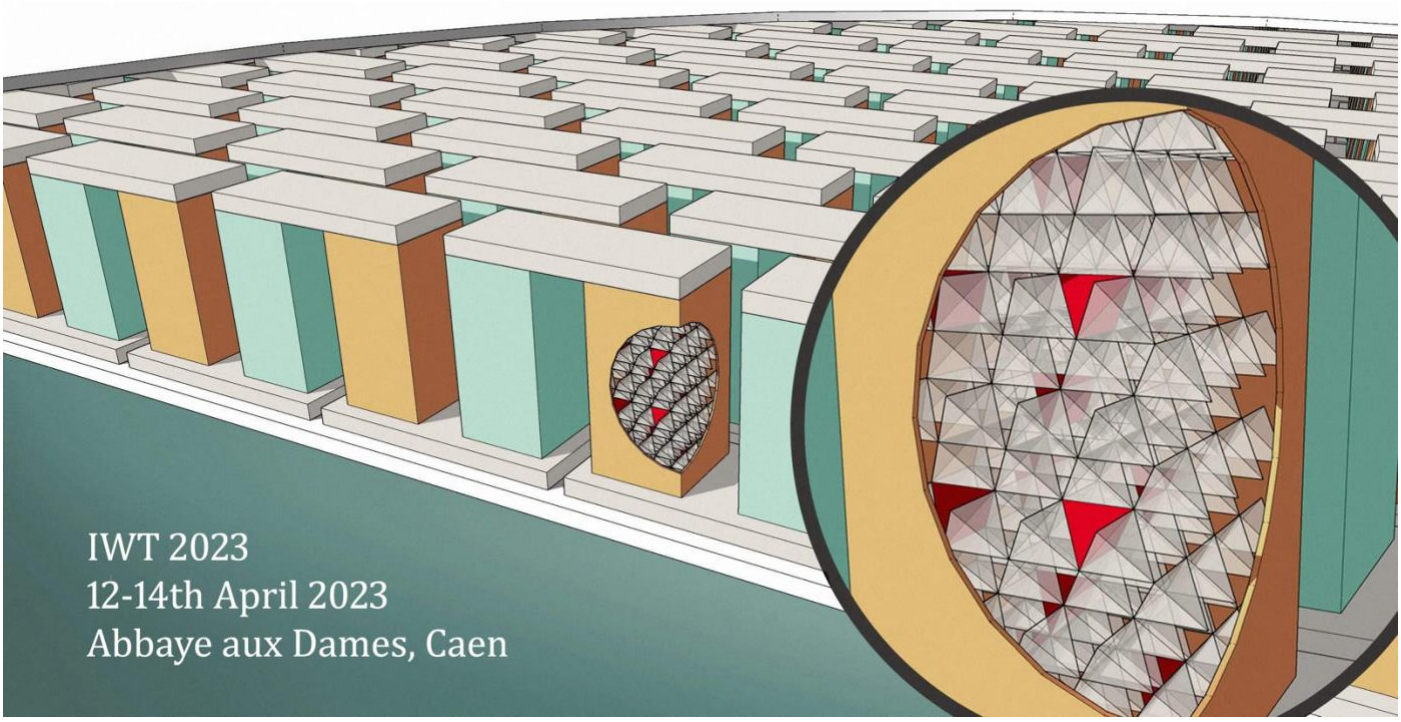

SUMMARY

Our journey toward operating wearable sensors and actuators based on body heat harvesting

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Abstract

In this talk, we are going to introduce our efforts on operating wearable sensors and actuators based on body heat harvesting. We demonstrate that conventional inorganic materials can be used in wearable systems despite their bulky and rigid nature. In particular, we proposed a bracelet-like modular design of a thermoelectric module with a heat sink integrated with Li-S battery for body heat harvesting. This continuously produces power up to 378 μW, operating a commercial glucose sensor (64 μW) and storing the remainder in the Li-S batteries. In addition, we show our recent demonstration that chargeless power operates continuous monitoring of glucose level through a sensor and insulin injection when necessary with a designed actuator for targeting type I diabetes patients. A battery can be charged through body heat harvesting. For personal thermoregulation, we propose a mat-like flexible thermoelectric system based on rigid inorganic bulk materials. Using portable batteries as power sources, the refrigerated skin temperature was lowered by several degrees which is adequate for humans to perceive coldness, according to theoretical analysis. These show potential for wearable refrigeration and body heat harvesting.

Keywords: Body heat harvesting, wearable thermoelectric device, flexible thermoelectric device

*Speaker

Overview of research activities on thermoelectrics at CEA-Liten

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Abstract

The French Alternative Energies and Atomic Energy Commission (CEA) is a key player in research, development and innovation in four main areas: defence and security, low carbon energies (nuclear and renewable energies), technological research for industry, fundamental research in the physical sciences and life sciences. CEA-Liten institute is dedicated to the energy transition. Its activities focus on several key areas, such as solar energy, smart grid management, batteries storage and hydrogen with the view to improving energy efficiency and circular economy approach. CEA-Liten is also involved in thermoelectrics for more than 20 years. During this time, CEA-Liten has worked on the development of materials and devices, from theory to industrialization, in both thin films and bulk technologies. The use of green materials has always been a guiding principle in our materials development, as well as their nanostructuration to improve their performances. Moreover, our thermoelectric devices developments have been determined by our targeted applications, mainly for thermal management and energy harvesting. This presentation will review our last research in both materials and devices for thin films and bulk technologies, but also for our new and recent technology based on additive manufacturing.

Keywords: materials, devices, nanostructuration

*Speaker

Development of thermoelectric modules consisting of Heusler alloys

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Abstract

Thermoelectric power generation (TEG) using waste heat is expected to serve as one of the energy recovery systems to improve energy utilization efficiency and reduce CO2 emissions. To facilitate the practical application of TEG, the enhancement of durability of thermoelectric module is indispensable because the place around exhaust heat is a harsh environment for electronic devices. In this study, thermoelectric modules consisting of the Heusler alloys were fabricated. For the low temperature waste heat below 600 K, the Heusler alloy of Fe2VAl having a high thermoelectric power factor around 300-400 K is employed. The Fe2VAl alloy exhibits high mechanical strength and excellent oxidation resistance until 850 K. To achieve the high durability for the thermoelectric module, Fe2VAl-Cu electrode joint is directly formed by diffusion bonding without joining material. Although the thickness of diffusion layer is 2-3 μm, the shear bonding strength is over 100 MPa and the electrical resistance is below 1×10-10 Ωm2. Using this bonding technique, a durable Fe2VAl thermoelectric module without electrical output loss at the electrode joint can be fabricated. The Fe2VAl module consisting of 18 p-n pairs can exhibit power density of 0.7 W/cm2 on the heat source of 673 K. It is confirmed that the bonding condition can be maintained after the heat cycling test between 323 K and 573 K for 10,000 cycles or the long-term annealing test of 773 K for 100 h. The durable Fe2VAl thermoelectric module is suitable to the construction of TEG for automotive waste heat recovery. For the middle temperature waste heat around 800 K, the half-Heusler alloys of TiNiSn (n-type) and FeNbSb (p-type) are examined. The direct TiNiSn-Cu and FeNbSb-Cu joint also formed by the diffusion bonding. In these cases, because the constituent elements of these half-Heusler alloys can form intermetallic compounds with Cu, the thickness of diffusion layer is larger than Fe2VAl-Cu bonding and increased to 50-100 μm. Details of the evaluation of electrode joint on the half-Heusler alloys will be presented.

Keywords: thermoelectric module, Heusler alloy, diffusion bonding, thermoelectric power generation

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Improving the reliability and efficiency of nanostructured PbTe-based thermoelectric materials and modules

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Abstract

PbTe-based materials are among the best performing thermoelectrics in the intermediate temperature range. Significantly improved thermoelectric properties have been achieved within the last 2 decades thanks to novel strategies such as band engineering and all-scale hierarchical architecturing. These advancements lead to increasing interest in the fabrication of modules based on these high-performance materials. Maximum conversion efficiencies ηmax _˜ 12% in cascaded modules made from nanostructured PbTe-based materials have been demonstrated for ΔT _˜590 K. (1) In our ongoing work, we address the material stability and fabrication of contact layers, which are instrumental for the fabrication and reliable long-term stability of PbTe-based thermoelectric legs and modules.

The material stability at elevated temperatures is a major concern, particularly for p-type PbTe. High Na-substitution, while beneficial for the high-temperature electrical properties of p-type PbTe, can also negatively impact the material stability due to the formation of Na-rich precipitates. (2) We achieved a significant improvement in the material stability of p-type Pb0.993-xNaxGe0.007Te by preventing the formation of Na-rich precipitates. This was achieved by reducing the Na-content to $x = 0.02$ from the previously used $x = 0.04$, while still maintaining high thermoelectric performance with zTpeak _˜ 2.2 at 813 K. The improved material stability is demonstrated through temperature-dependent 3-point bending measurements. (3) The fabrication of contact layers for PbTe-based materials is a long-standing challenge for module development. The fabrication of PbTe legs with contact layer materials like Fe or Co-Fe alloys by co-sintering causes the formation of cracks due to mismatch of the coefficients of thermal expansion and a significant increase in electrical resistance. To address this issue, we explore alternative contact and module fabrication processes. We successfully fabricated crack-free p-type Pb0.973Na0.02Ge0.007Te legs with Fe thin film contact layers using RF magnetron sputtering with contact resistances ρc _˜ 30 $\mu\Omega$ cm2. Measurements of the power generation characteristics of p-type Pb0.973Na0.02Ge0.007Te single leg elements with sputtered Fe contact layers showed increased electrical resistance at elevated temperatures due to poor Fe layer adhesion, indicating the need for further improvements.

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Keywords: lead telluride, mechanical properties, power generation, module, contact layer, diffusion barrier

Incommensurate Nowotny Chimney-ladder Phases - Potential Thermoelectric Materials

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Abstract

Nowotny chimney-ladder phases (NCLs; MXg) consist of transition metals M and group 13-15 elements X and are regarded as Hume-Rothery's electron compounds. This compound family covers simple commensurate formulas such as RuAl2 and Ir3Ga5, and more complicated incommensurate ones as Cr11Ge19, Rh17Ge22 and MnSig (HMS, g_˜1.73). HMS is known as a potential p-type thermoelectric (TE) material and typically exhibits the TE power factor of P_˜1mW/K2m and zT_˜0.2-0.3 at 800 K. The TE performance can be further enhanced to P_˜2.5 mW/K2m and zT_˜0.8 at 800 K by an appropriate partial substitution of Mn/Si sites (1). We will demonstrate the detailed structure analyses and our recent efforts to improve TE properties of this system.
Besides the HMSs, there is a potential n-type counterpart in NCLs, namely FeGeg (g_˜1.52). This compound is also reported to be incommensurate (2). We have discovered that the germanide is nearly a line compound with quite a narrow single-phase range of the g-value. However, by applying a high pressure _˜500 MPa using spark plasma sintering (SPS), the g-value can be slightly increased, corresponding to a small amount of electron doping. Currently, zT value is around 0.6 at 700 K, but can be increased by the reduction of lattice thermal conductivity through a partial substitution of Si to the Ge sites.

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Keywords: Incommensurate Compounds, Crystal Structure, Nowotny Chimney, ladder phases

*Speaker

Large Room Temperature Anomalous Transverse Thermoelectric Effect in Kagome Antiferromagnet YMn6Sn6

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Abstract

Abstract: Kagome magnets possess several novel nontrivial topological features owing to the strong correlation between topology and magnetism that extends to their applications in the field of thermoelectricity. Conventional thermoelectric (TE) devices use the Seebeck effect to convert heat into electrical energy.1 In contrast, transverse thermoelectric devices based on the Nernst effect are attracting recent attention due to their unique transverse geometry, which uses a single material to eliminate the need for a multitude of electrical connections compared to conventional TE devices. Here, a large anomalous transverse thermoelectric effect of $\approx 2\ \mu$V K–1 at room temperature in a kagome antiferromagnet YMn6Sn6 single crystal is obtained.2 The obtained value is larger than that of state-of-the-art canted antiferromagnetic (AFM) materials and comparable with ferromagnetic systems. The large anomalous Nernst effect (ANE) can be attributed to the net Berry curvature near the Fermi level. Furthermore, the ANE of the AFM YMn6Sn6 exceeds the magnetization scaling relationship of conventional ferromagnets. The results clearly illustrate that AFM material YMn6Sn6 is an ideal topological material for room-temperature transverse thermoelectric applications.

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Keywords: antiferromagnetism, thermoelectrics, Nernst effect, Kagome magnet, topological materials

*Speaker

Engineering the electronic band structure of SnTe with resonant levels and band convergence

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Abstract

Over the last few decades, the dimensionless thermoelectric figure of merit, ZT, of various chalcogenide semiconductors has been enhanced thanks to band structure engineering tools that notably include resonant levels (RL) and band convergence. Alloying with elements that give rise to a RL at the edge of either the valence or conduction bands provides a convenient way for optimizing the power factor of semiconductors.(1-3) These impurity atoms distort locally the electronic band structure beyond the rigid-band model. A significant increase in the thermopower and, hence, in the power factor can be achieved when the chemical potential resides in this distortion. Furthermore, the convergence of several band extrema that lead to an increased number of degenerate valleys also yields enhanced power factor. In this presentation, we will discuss how the interplay between both mechanisms can result in a significant improvement in the thermoelectric performance of SnTe at high temperatures.
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Keywords: Chalcogenides, Resonant level, Band convergence

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Sintering solution processed nanoparticles: a way to tune microstructure through surface chemistry

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Abstract

Nanoparticles can be used as tunable precursors to produce macroscopic solids with specific structural features by controlling the density and microstructure of the solids through the consolidation process. The consolidation process, such as hot pressing or spark plasma sintering, is preferred in order to provide the material with densities as close as possible to the respective theoretical density. The characteristics of the particles, such as size, shape, composition, and surface chemistry, determine the sintering process and therefore dictate densification, grain growth, and the final microstructure of the material. A nanoparticle can be considered as a multi-structured system consisting of an inorganic nanocrystalline domain, named the inorganic core, surrounded by surface species. Both the inorganic and surface species are tunable parameters in the design of nanoparticle-based precursors. The surface chemistry of the nanoparticles can be adjusted during sintering to achieve a solid with specific targeted features. Two approaches to controlling the surface chemistry of the particles need to be separated. One refers to the particle termination atoms, the other to the connected adsorbates that can be covalently bonded molecules or electrostatically adsorbed ionic groups. The surface adsorbates, intentionally or unintentionally introduced, are critical to controlling densification, grain growth, and the final microstructure of the material. Herein, we will discuss the structural properties controlled through different surface species and discuss their effect on the electrical and thermal transport to evaluate their potential as thermoelectric materials.

Keywords: Nanocomposite, nanoparticles, solution processing

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Crystal structure and thermoelectric properties of new sphalerite derivative phases in the ternary system Cu-Sn-S: Cu5Sn2S7 and Cu22Sn10S32

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Abstract

Copper tin sulfides (CTS) are extensively studied for their promising thermoelectric properties.1-6 They are recognized as a very attractive class of materials owing to decent performances and compositions consisting of non-toxic, eco-friendly and earth-abundant elements. A recent reinvestigation of the Cu2+xSn1-xS3 system has revealed the existence of two new sphalerite derivative phases: Cu5Sn2S7 (x = 0.143),7 an ordered monoclinic phase, and Cu22Sn10S32 (x = 0.063),8 a semi-ordered cubic phase.
Cu5Sn2S7 exhibits a degenerate p-type semiconducting behavior with exceptionally high hole mobility originating from the interplay between atomic ordering and charge delocalization. Despite a relatively high thermal conductivity (≈ 4 W m-1 K-1 at 700 K), this compound is characterized by a promising figure of merit ZT reaching 0.16 at 700 K.7 Cu22Sn10S32 also exhibits a degenerate p-type semiconducting behavior with very low thermal conductivity (0.5 W m-1 K-1 at 700 K) related to its semi-ordered cationic distribution inducing very effective localized disorder, leading to a promising figure of merit ZT reaching 0.33 at 700 K.8

In this presentation, will be discussed the structure-thermoelectric properties relationships of

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these new sphalerite derivative CTS phases using a combination of powder and single crystal X-ray diffraction, precession-assisted electron diffraction tomography, transmission electron microscopy, X-ray absorption and Mössbauer spectroscopies, first principles calculations and transport properties measurements. These results allow to clarify the nature and the crystal structure of some phases occurring in the Cu-Sn-S ternary system.9 Finally, strategies used to optimize the thermoelectric properties of both phases will be briefly discussed.8,10

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Keywords: CTS materials, Crystal structure, XRD, Transport properties

Synthesizing Triple Half-Heusler to Explore Larger Compositional Space

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Abstract

Half-Heusler materials have been extensively researched for their potential in thermoelectric materials as well as for their prospective usage in spintronics and magnetic applications. The concept of double half-Heusler (DHH) was recently proposed as a potential strategy to reduce lattice thermal conductivity for better thermoelectric performance. In this talk, I will expand this idea further to triple half-Heusler (THH). THH phase Mg2VNi3Sb3 was successfully synthesized by following an unconventional valence balance strategy. The lattice thermal conductivity (L< 2.5W/m K) is much lower than half-Heusler standards (L> 10W/m K) or DHH (L=8-10W/m K). In addition, both p and n-type conductions were achieved by tuning the composition of THH. Not just only the synthesis of THH with very low lattice thermal conductivity can be a new direction for high-performance HH thermoelectrics, but the largely expanded compositional space for the exploration of quarternary half-Heusler materials were proposed.

Keywords: Half Heusler, Thermal Conductivity, Alloying, Optimization, New Material

*Speaker

Multifunctional nitride and oxide thin film for thermoelectrics and energy harvesting

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Abstract

Thermoelectric devices have the potential to contribute to energy harvesting in society by directly converting heat into electricity or vice versa. However, the conversion efficiency of thermoelectric devices of today is limited. In this invited lecture, I present an overview of our work on CrN-, ScN-, and Ca3Co4O9-based thin films. We have introduced a two-step sputtering/annealing method for the formation of highly textured virtually phase-pure Ca3Co4O9 thin films. These can further be deposited on flexible mica substrates, enabling flexible inorganic thermoelectric thin films that withstand repeated bending. They can also be made as free-standing films and as nanoporous materials for reduced thermal conductivity. ScN thin films exhibit an anomalously high power factor (S2s) for transition metal nitrides, but has high thermal conductivity, thus its ZT is low (_˜0.2). To reduce lattice thermal conductivity, potential strategies are nanostructuring, alloying, nanoinclusion formation and defect generation. Pure CrN exhibits n-type conduction with a high power-factor enabled by a high electron concentration thermally activated from N vacancies. Further investigations on the nitrogen/chromium stoichiometry have shown possibilities of switching the type of carriers yielding a p-type semiconductor behaviour of CrN in contrast to the well-known n-type CrN.

Keywords: Nitride, oxide, Thin film, Sputtering

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Improvement of thermoelectric conversion properties by controlling electronic structure in Heusler-type Fe2VAl compounds

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Abstract

The Heusler-type Fe2VAl compound exhibits a semiconductor-like temperature dependence of electrical resistivity over a wide temperature range of up to 1200 K and beyond (1). Electronic structure calculations have predicted the presence of a sharp pseudogap at the Fermi level (EF) due to the hybridization effects, which has been demonstrated by infrared and photoelectron spectroscopy. The existence of this sharp singularity in the density of states (DOS) makes this material strongly attractive for potential thermoelectric applications.
According to Mott's theory, the Seebeck coefficient is inversely proportional to the absolute value of the density of states at EF and is proportional to its energy gradient. In a pseudogap system, the density of states at EF is low, and the its energy slope is steep. Therefore, by optimizing the energy position of EF in the pseudo-gap, a significant increase in the Seebeck coefficient can be expected. Indeed, because of the sharp increase in the DOS on both sides of the pseudo-gap, the thermoelectric power of Fe2VAl compounds can be increased significantly by fourth-element doping (2) or off-stoichiometry (3). According to previous reports, the Seebeck coefficient increases up to 70 μV/K in the p-type and –130 μV/K in the n-type by hole and electron doping. Recently, there have been reports on the improvement in the thermoelectric properties of Fe2VAl compounds with the addition of several doping elements and the doping of elements with nonstoichiometric compositions (4). Therefore, Fe2VAl compounds with a pseudo-gap system have attracted attention as a new environmentally friendly thermoelectric material.

In this talk, we will also present the results of our electronic structure and crystal structure analysis of Heusler-type Fe2VAl compounds, including the latest research results on how we are improving the performance of Fe2VAl compounds.

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*Speaker

Enhancement of phonon scattering in thermoelectric half-Heusler compounds by non-equilibrium synthesis

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Abstract

Preventing phonon transport remains one of the most challenging tasks to improve the thermoelectric performance of certain materials such as half-Heusler compounds. On the other hand, established strategies such as alloying or grain boundary refinement have almost exhausted their potential to further reduce the lattice thermal conductivity (L). It is still unclear how to further improve the phononic scattering of materials. In this talk, I will show that thermal conductivity can be drastically reduced by non-equilibrium synthesis. Two unconventional strategies for thermoelectric studies will be presented, including cryogenic milling and high-pressure sintering. A maximum L reduction of 83% was achieved at room temperature with a relative density greater than 95%. Our work uncovers the phonon transport properties of half-Heusler compounds under unconventional microstructures, showing the potential of high-pressure compaction and cryogenic milling to advance the performance of thermoelectric materials.

Keywords: half, Heusler, non, equilibrium synthesis, high, pressure sintering, phonon scattering, cryogenic milling

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Optimization of the thermoelectric properties in self-substituted Fe2VAl

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[3]Institut Charles Gerhardt – Univ Monpellie – France

Abstract

Thermoelectric properties were determined in self-substituted Fe2VAl Heusler alloys (Fe2V1+xAl1-x, - 0.1 < x < 0.1), pursuing the goal of their optimization. A parabolic band model fitted to experimental plots of Seebeck coefficient versus charge carrier concentration at 220 K yielded values of the density of states (DOS) effective mass, m_vˆ*=3.7m_e and m_cˆ*=13.7m_e for the holes and electrons, respectively (m_e is the bare electron mass). The measured Sommerfeld coefficient of the electronic specific heat is consistently smaller in p-type Fe2V0.92Al1.08 (gamma_p = 7.8 mJ mol-1 K-2) than in n-type Fe2V1.07Al0.93 (gamma_n = 11.5 mJ mol-1 K-2). First principles calculations of the DOS lead to the theoretical values m_vˆ*=2.4m_e, m_cˆ*=13.0m_e and gamma_n/gamma_p =1.9, in good agreement with the experimental values. These direct comparison of calculations with experiments unambiguously show that the heavy electrons arise from flat Fe eg conduction bands. Calculations of the optimum thermoelectric power factor (PF) show that it is nearly reached experimentally in n-type Fe2V1.03Al0.97 (PF = 6.6 mW m–1 K–2 for n = 1.4 × 10ˆ21 cm 3) whereas p-type Fe2V0.985Al1.015 (PF = 2.7 mW m–1 K–2 at p = 6.7 × 10ˆ20 cm-3) is not yet optimum. The easier optimization of the thermoelectric properties in n-type self-substituted Fe2VAl can be traced back to the larger effective DOS mass of its electrons.

Keywords: power factor optimization, first principles calculations, specific heat, Heusler alloys, Fe2VAl

*Speaker

Phonons in complex crystals

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Abstract

Exploiting the structural complexity of crystals at the scale of their unit cell is a well-established strategy in the search for efficient materials for energy conversion, which aims at disentangling and separately engineering heat and charge transport. Structural complexity, which can easily result in unit cells in the nanometer range that contain a large number of atoms of various types, is known to be an efficient way for designing thermal properties and the underlying phonon spectra. In the search for low lattice thermal conductivity in the field of thermoelectricity, one of the main strategies is the use of complexity at multiple length scales, from structural complexity within the crystal unit cell, to disorder, short range order, and nanostructuring. This route has resulted in the discovery of clathrates with exceptionally low lattice thermal conductivity but essentially unaffected and tunable electronic properties. On the other hand, phonons measurements have revealed the existence of long-living acoustic phonons in the clathrates questioning the origin of their low lattice thermal conductivity (1). Another interesting case is that of High Entropy Alloys which exhibits a strong chemical disorder at the level of their unit cell leading also to a poor lattice thermal conduction. In this talk, I will first review spectroscopic measurements by means of neutrons and/or X-rays of the phonon spectrum and transport properties and the comparison with perturbative ab initio DFT calculation (2,3). We will see how the complexity acts on propagative phonons and is responsible for the anomalous behaviors in temperature of the lattice thermal conductivity without requiring the presence of strong anharmonicity or defects in clathrates. From this knowledge, a simplified thermal model is proposed for analyzing their thermal properties and extract microscopic properties from macroscopic measurements (4). In a second part, I will introduce our recent measurements of phonons in High Entropy Alloys and show that these systems present a unique phonon dynamics at the frontier between fully disordered and ordered materials, characterized by long-propagating acoustic phonons in the whole Brillouin zone. W will see that the whole attenuation behavior can be understood in terms of scattering from force-constant fluctuations (5). (1) P.F. Lory et al., Nat. Comm. 8, 491 (2017)
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Keywords: Phonons, structural complexity, thermal conductivity

*Speaker

Semconductor nanowire thermoelectrics: gate-controlled ZT, giant reduction of thermal conductivity, thermoelectric-gating

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Abstract

Nanoscience and technology offer a formidable playground for thermoelectrics, allowing to exploit phononic and electronic band engineering, to develop hybrid soft-condensed matter systems with unique tunability features, to engineer novel device architectures with superior thermoelectric performances. In this frame, the semiconductor nanowire technology provides nanoscale building blocks for exploring novel paradigms for thermoelectric energy conversion and harvesting.
Building on the epitaxial growth of III-V semiconductor nanowires, we engineer prototypical nanodevices enabling superior control of the thermoelectric figure of merit (1), also using unconventional gating approaches which exploit electrolytes (2-4). Resorting to twinnig superlattice nanowires, we demonstrate ten-fold reduction of thermal conductivity while preserving electric mobility and conductivity as well as Seebeck coefficient (5). The Soret effect in polyelectrolytes is exploited to realize heat-driven iontronic transistors based on individual InAs nanowires (6).
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Keywords: nanowires, electrical transport, ionic, gating, thermal conductivity

*Speaker

Lattice dynamics and thermoelectric properties of type IX clathrates Ba24Ge100

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Abstract

Type IX clathrates such as Ba24Ge100 and Ba24Si100 have three different cages in which Ba guest atoms are intercalated. Previous works have shown that Ga substitution on Ge sites of Ba24Ge100 can lead to very low thermal conductivity of less than 1 W.m-1.K-1 and ZT as high as 1.25 at 950 K. Thus the Ga-alloyed Ba24Ge100 clathrate is the clathrate compound with the lowest lattice thermal conductivity (about 0.3 W.m-1.K-1). Furthermore, at low temperatures, Ba24Ge100 is superconducting and experiences a structural transition involving significant changes in the charge density of the guest Ba atoms whose microscopic mechanism is not understood yet. All these physical properties are driven by or take influence on the lattice dynamics of Ba24Ge100. Thus, the phonon properties require a better understanding, especially the dynamics of the guest Ba atoms.
In the present work, we investigated the effect of the host cage structure on the low energy vibrational dynamics in the type IX germanium clathrate by combining inelastic neutron scattering and *ab initio* simulations.

We report on the guest dynamics in Ba24Ge100 and evidence the existence of guest vibrational modes at about 3 meV, at much lower energy than those in type I clathrate Ba8Ge46-xZnx and in a similar energy range as for Ba24Si100.
We show a strong anisotropy of the vibrations of Ba guests in the open and very asymmetric Ge20 cages like in the case of Ba24Si100, which points at a general behavior in the type IX clathrates. We observe a strong change in the spectral weight of these modes when the compound undergoes a temperature-induced structural transformation in the temperature range 190-230 K. Our DFT calculations successfully approximate the essential features in the dynamics of the high-temperature Ba24Ge100 structure.

Keywords: Clathrates, Inelastic Neutron Scattering, Anharmonicity

*Speaker

Carrier concentration tuning of highly conductive tungsten-based Magnéli phase oxide W18O49 with inherently low lattice thermal conductivity

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Abstract

The crystal structure of tungsten-based Magnéli phase oxide W18O49 has tunnel-like one-dimensional voids, which can be expected to work as an effective phonon scattering center. However, reported thermal conductivity values of the oxide are significantly high, presumably because of its metallic electrical conductivity, which also causes very small negative Seebeck coefficient of the oxide. In order to optimize the electron carrier concentration of the oxide, we have synthesized (W1-xTix)18O49 ($0 \leq x \leq 0.25$) by solid state reaction followed by densification via spark plasma sintering (SPS). The Ti substitution decreased the electrical conductivity, increased the Seebeck coefficient, the power factor, and decreased both the electronic and lattice thermal conductivities. Although the samples entered a multi-phase region at $x \geq 0.2$, an inherently low lattice thermal conductivity of 0.4 W/Km of the oxide led to a significantly high ZT value of 0.50 at 1073 K for the sample at $x = 0.2$.

Keywords: tungsten oxide, carrier concentration tuning, highly conductive oxide, thermal conductivity

*Speaker

Magnesiothermy: An efficient route to mesostructured thermoelectric intermetallics

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Abstract

Thermoelectric (TE) devices belong to the bunch of alternative "green" energy technologies enabling the direct conversion of (wasted) heat into electricity and vice-versa.
Semiconducting intermetallics are among the best performing materials, whatever the temperature range considered from room temperature (Bi2Te3 and derivatives) to high temperature (Zintl phases or Si-Ge alloys above 1000 K). At intermediate temperatures, from about 600 to 800 K corresponding to many industrial propcesses exhausts, two families are of particular interest: (i) CoSb3-based skutterudites where the numerous possibilities of chemical substitution and/or insertion of heavy rattlers in the large cages of the structure enables to reach ZT values much above 1 on bulk samples (1) and (ii) transition metal silicides (higher manganese silicides or HMS, and beta-FeSi2) which have been already tested in industrial demonstrators, despite their moderate ZT, due to the availability and low cost of the constituting elements (2). Both families are characterized by two common features: (i) the necessity to decrease the thermal conductivity to improve the TE properties and (ii) the not straightforward synthesis due to the non-congruent melting of the phases.

To address both problems, we applied a magnesiothermic process, inspired from the industrial Kroll process (3), for the synthesis of (Ni-doped and In-inserted) CoSb3, (V-doped) MnSi1.74 and (Co-doped) beta-FeSi2 (4). Starting from cheap and air stable oxides, we showed that after short and low temperature annealing, high purity submicron powders are obtained, leading after spark plasma sintering to mesostructured materials with significantly reduced thermal conductivities. Additionally, the high crystallinity of the powders enabled the structural characterization of the composite chimney-ladder structure of HMS and of the stacking faults in beta-FeSi2.

After a description of the experimental procedures, the different synthesis reaction mechanisms identified by powder X-ray diffraction will be presented. A careful examination of the microstructure of the materials by electron backscattering diffraction and transmission

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electron microscopy will be used to discuss its influence on the thermal conductivity and overall TE behaviour of the materials. The discussion will be opened to the applicability of this synthesis route to other classes of TE intermetallics.

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Keywords: Magnesiothermy, silicides, mesostructure, thermal conductivity

Exploration of half-Heusler and metal phosphide thermoelectric materials

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Abstract

There is a continued need for performance improvement and discovery of new thermoelectric materials for energy generation, taking into account sustainability of materials and production. In this presentation, I will give an overview of recent work on the use of Cu interstitials in half-Heusler alloys and discovery research into new metal phosphide compositions.
Interstitial metals have emerged as a possible substitute for heavy alloying elements in half-Heusler thermoelectrics (1). We have undertaken a systematic exploration of the impact of excess Cu on the properties of n-type TiNiSn (2-3), recently achieving zT = 1 at 800 K, significantly without use of Hf. Empirical band and Callaway modelling were used to identify optimal compositions and suggest that Cu behaves substantially different from much better explored interstitial Ni.

Metal phosphides have recently been attracting attention as possible high performance thermoelectrics. Complex structures can support low lattice thermal conductivity, whilst covalent bonding should in principle support decent electrical properties. We have investigated three ternary compositions: two based on abundant Cu, namely MgCuP and CaCuP (4) and a silver analogue, CaAgP (5) that has attracted interest as a possible nodal line semimetal. These three materials have different crystal structures and show differences in thermoelectric parameters, but all achieve a similar zT = 0.4-0.5 at 800 K.

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Keywords: half, Heusler alloys, metal phosphides, materials discovery, thermoelectric characterisation

BiCuSeO-based oxychalcogenides: recent developments and defect chemistry

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Abstract

Since 2010, layered oxychalcogenide materials, with general formula RCuChO, (with R a trivalent cation and Ch a chalcogen element), have emerged as promising p-type thermoelectric materials. They are moderate (Bi) to large (rare-earth) band gap semiconductors and they can be easily hole doped by substituting A2+ in the trivalent cation site or by Cu vacancies to optimize the charge carrier concentration. Due to moderate carriers mobility, their promising ZT values mainly originate from their very low lattice thermal conductivity values, of the order of 0.3 W.m-1.K-1 at high temperature. By combining carriers concentration optimization and band structure engineering or microstructure optimization, a large figure of merit can be reproducibly obtained, with ZT values that reaches ZT $\approx$ 1.5 around 650∘C, which makes these materials very performant in in this temperature range. However, their actual potential for applications is limited to date by the absence of efficient n-type counterparts. In this talk, I will briefly summarize the thermoelectric transport properties of this family of materials and discuss how these properties are linked to the crystal structure, the microstructure and the electronic band structure. I will also give an overview of the recent results that have been obtained towards the optimization of these properties, and of the recent theoretical studies devoted to the defect chemistry and phase boundary mapping of BiCuSeO, and the new perspectives they open.

Keywords: oxychalcogenides

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First-principle investigations on n(PbTe)-m(Bi2Te3) system compounds

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Abstract

Owing to their low lattice thermal conductivity, compounds of the n(PbTe)-m(Bi2Te3) homologous series have been reported in the literature with good thermoelectric (TE) properties (1,2).
Among these layered chalcogenides, the Pb2Bi2Te5 compound has been evidenced with two different stacking sequences (3,4). In order to understand the differences in their properties, we have determined the electronic and the thermoelectric properties of this compound with the two different stacking sequences from first principle calculations and Boltzmann transport theory and analysed the electronic density of these compounds by using the quantum theory of atoms in molecules (QTAIM).

To explain the low lattice thermal conductivity observed in the compounds of the (PbTe–Bi2Te3) quasi-binary system, a full theoretical study of the electronic structures, transport behaviour, and lattice dynamic properties of various intermediate compounds (PbBi2Te4, PbBi4Te7 and Pb2Bi2Te5) has been performed. Furthermore so as to improve the TE properties of these compounds, the band engineering approach has been implemented by applying biaxial tensile and compressive strains.

Finally, we have investigated the strain effects on the electronic and thermoelectric properties as well as on the stability of PbBi2Te2S2 , PbBi2Te2Se2 and PbBi2Te4 monolayers.

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Keywords: Thermoelectrics, Layered chalcogenides, Strains, Monolayers, DFT, Transport properties, QTAIM.

*Speaker

Computational attempts to go beyond conventional theories for exploration of thermoelectric properties of practical materials

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Abstract

Conventional theories of materials' properties have been already established due to extensive efforts of genuine efforts by pioneers to date. For thermoelectricity, multiple properties determine the overall performance of energy conversion from heat to electricity and vice versa, and we can easily learn trade-off and correlated relationships among the materials properties required for thermoelectricity. On one hand, the theories and the relationships allow us to decide what to try next based on our current understandings, in addition to helping us to understand and interpret the experimental facts (1,2). On the other hand, however, the trade-off or correlated relationships among the multiple properties often confine our new efforts into the theories or the relationships.
Computational approaches to materials science are not confined to what are referred to simulations which literally try to simulate the realities. The computations on the atomic level including first principles calculations, lattice dynamics and molecular dynamics calculations enable to go beyond the understandings limited by the conventional theories, thereby extend our understandings (3-5). This primarily because those calculations do not rely on the conventional theories, based only on the underlying fundamental theories like quantum mechanics or classical mechanics.

In this presentation, we are going to discuss what sort of calculations are needed in this community and what else are needed for further explorations of thermoelectric materials, with selected examples of materials containing governing factors that determine thermoelectric properties.

Acknowledgment: This series of studies are supported by KAKENHI "Crystal Defect Cores" (Grant No: JP19H05786) in part.

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*Speaker

New intermetallic thermoelectric materials among using high-throughput calculations and machine learning

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Abstract

The development of thermoelectric devices requires new high-performance materials. One way to answer this need is to identify new materials that might have promising properties. To make the investigation of new candidates easier and more efficient, a dual approach, combining first-principles calculations and experiments is interesting. In our method, we combine massive screening calculations, applied to a large set of compositions, to highlight stable and non-metallic compounds to experimental investigation of the most promising screened materials.
We focus our investigations within the ternary intermetallic compounds *T*-*M*-*X*, where *T* is a transition metal, a rare earth or an alkaline earth metal, *M* is an element from the first line of the transition metal and *X* is a metalloid (1,2). For tens of prototypes, all the possible *T*-*M*-*X* combinations have been investigated by DFT calculations and additional studies as phonon structure or BoltzTrap calculations, can be provided to go further. After those theoretical steps, experimental investigations are done to confirm the calculations, in particular the stability, and measured thermoelectric properties on the most promising compounds such as SrCuP and SrCuSb (3).

In our quest to new semiconducting and stable materials, we keep improving our screening method in order to investigate even more compounds while reducing the number and time of calculations. In this aim, machine learning technics have been applied to some intermetallic prototypes, such as the Heusler phase to optimize our screening.

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Keywords: High, throughput calculations, intermetallics, machine learning

Chalcogenide-based high entropy alloys as thermoelectric materials for power generation

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Abstract

High entropy alloys (HEA) have recently attracted much attention in the fields of materials science and engineering (1-6). A bibliographic search from the Chemical abstract Service database indicates that more than 11000 papers have been published on HEA since 2002. Most of these references deals with materials containing mainly transition metal elements (Ti, Cr, Fe, Cu, Mo, Co, Ni, Nb, Ta, Pt, ...), occasionally combined with metals or non-metals of the principal elements ((Al, Si, P, ...).

Because of the lattice distortion effects, which reduce phonon velocity and enhance the scattering of phonons, high-entropy alloys generally have low lattice thermal conductivity (7-9). As high-entropy sulfides, Cu5Sn1.2MgGeZnS9 has been reported with a ZT value of 0.58 at 773 K (10). The high-entropy metal chalcogenide (Ag,Pb,Bi)(S,Se,Te) alloy has been investigated and it was found that it is a n-type semiconductor with low L and good power factor resulting in a figure of merit of 0.54 at 723 K (11). Recently, a n-type PbSe-based high-entropy material formed by entropy-driven structural stabilization has been studied for its thermoelectric properties. The ZT value was found to reach 1.8 at 900 K (12).

Modelling HEAs transport properties constitutes a challenge due to the large cell size that must be simulated. Nonetheless, we have recently undertaken the investigation of PbSnTeSe as a HEA by first principle, Boltzmann transport and Green-Kubo formalisms to evaluate its thermoelectric performance. In this talk we will both present the methodology that we have implemented to investigate PbSnTeSe and compare our results and approach with those from the literature.

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Keywords: High entropy alloys, chalcogenides, ab initio methods, Boltzmann transport approach, Green, Kubo formalism

Ab initio description of electron-phonon and phonon-phonon scattering processes in density functional theory for the calculation of charge and heat transports

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Abstract

The future sparsity of carbon-based fuels, the increasing energy cost, together with the growing concern of society over environmental problems, make the performance improvement of energy conversion devices – thermoelectricity, photovoltaics – a topic of high importance. Such devices are mainly designed by using macroscopic models -the drift-diffusion for electronic transport, or the Fourier formalism for heat/energy transport- which assume local equilibrium and simplified (averaged) material properties for the carrier relaxation times. Huge progress has however been achieved in the description of scattering processes with methods based on the density functional perturbation theory (DFPT). We will show that electron transport characteristics of bulk semiconductors are well described within the approach that couples DFPT electron-phonon scattering rates with the semi-classical Boltzmann transport equation (BTE), and the same is true for phonon-phonon scattering rates for the thermal conductivity, with bismuth as an example. We will also discuss the electron and phonon coupled equations for thermoelectricity as well as the effect of nano-structuring on the Seebeck coefficient.
Acknowledgements:

Calculations have been performed using the Quantum ESPRESSO1 and EPW2 softwares. We acknowledge access to high performance computing (HPC) resources by the Partnership for Advanced Computing in Europe (PRACE Project No. 2019204962), by the French HPC centers of TGCC, CINES and IDRIS (GENCI Project 2210) as well as to the 3L-hpc local computer cluster partly supported by the DIM SIRTEQ (région Île de France) and École Polytechnique. Financial supports are also acknowledged: CEA ANCRE program (project Thermoint), Labex Nanosaclay ANR-10-LABX-0035 (Flagship project MaCaCQu), and ANR-21-CE50-0008 (project Placho).

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Keywords: Quantum caclulations: density functional theory and density functional perturbation theory, Semi, classical calculations: Boltzmann transport equation, High Performance Computing at Grand Équipement National de Calcul Intensif (GENCI)

Materials development, module fabrication, and module evaluation in thermoelectric power generation

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Abstract

There have been several important breakthroughs in boosting the figure of merit (zT) of thermoelectric materials over the past few decades. However, social implementation of the thermoelectrics proceeds very slowly. The emerging thermoelectric materials have not yet been fully explored for module development. It is also important to develop technologies for reliably and accurately evaluating the power generation characteristics of the modules for the social implementation. This talk addresses on recent progress in bridging the technological chasm between materials development, module fabrication, and evaluation methods for thermoelectric power generation.
In this study, high zT in the materials and corresponding high conversion efficiency in the modules have been demonstrated in PbTe and colusites (Cu and S-based systems)-based thermoelectrics (1,2,3,4). For PbTe, the zT was dramatically enhanced by nanostructuring and controlled doping. For colusites, zT was dramatically enhanced by carrier concentration tuning. In both systems, the improved electrical and thermal contact resistances between thermoelectric materials and electrodes and the optimized configuration of thermoelectric elements and modules led to high conversion efficiency in power generation in the modules. In interlaboratory testing, a module made of Ni-based alloy has been used as reference for power generation characteristics (5). Cross-checking of evaluation method was carried out using the reference module in characterization facilities developed the National Institute of Advanced Industrial Science and Technology (AIST) and the German Aerospace Center (DLR) to understand the differences in the evaluation methods from each other (6).

The PbTe-based materials and module were developed together with Prof. M. G. Kanatzidis of Northwestern University and Argonne National Laboratory. The colusites-based materials and module were developed together with Dr. K. Suekuni of Kyushu University, Dr. Y. Bouyrie of AIST, Dr. R. Chetty of AIST, and Dr. E. Guilmeau of CRISMAT. Interlaboratory testing performed together with P. Ziolkowski of DLR, Prof. E. Muller of DLR, Dr. R. Chetty of AIST. This work was supported as part of Research and Development Program for Promoting Innovative Clean Energy Technologies Through International Collaboration (JPNP20005) funded by the New Energy and Industrial Technology Development (NEDO).
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Thermal energy harvesting for the powering of industrial IoT sensors: from basic applications to complex measurements.

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Abstract

In the context of decarbonization and the reduction of energy consumption, thermoelectricity appears as a very interesting way to recycle waste heat. If a global use of thermoelectricity as an energy source remains conditioned to an improvement of the conversion efficiency of materials, it is already possible to use the current technology within functional devices. One of these applications consists in the use of thermoelectricity as a micro energy source to power connected sensors. The autonomy brought by using energy harvesting allows to avoid the costs due either to the wiring of sensors nor to the replacement of batteries, which is also critical for the environment.
In this talk we will discuss the different opportunities offered by thermoelectric modules for the powering of autonomous sensors focusing on industrial applications. Indeed, given the omnipresence of heat in industrial environment, thermoelectricity is of great interest for these applications. The first studies were focused on the power supply of simple sensors and the sending of measured data with a low energy communication protocol. Today it is possible to use thermal energy harvesting to power sensors including other functions. Indeed, the amount of wasted heat being particularly important in the industrial environment, it is possible to use this resource to offer connected sensors with higher performances than battery-operated sensors. The improvement of the performance of the connected measurement module can be achieved either by sending more data, by using more energy consuming communication protocols or by using embedded intelligence directly inside the module. We will give examples of recent developments made by the start-up MOÏZ in the industrial field and some perspectives for future development.

Keywords: thermoelectric device, energy harvesting, Industrial IoT

*Speaker

Elaboration and the study of transparent p-type thermoelectric properties of CuCrO2:Mg and CuI thin films

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Abstract

The interest of thin films for thermoelectric application growths in particular in the case of transparent application as smart windows. The material needs to have simultaneously coupled properties of electrical conduction with high Seebeck coefficients and high transparencies in the visible. To optimize these properties, the transport mode, the band gap, the carrier density but also microstructure must be tuned but it remains difficult in the case of p-type materials. This presentation focuses two p-type transparent materials in the aim to have this coupled properties. The studied compounds are respectively Mg doped CuCrO2 delafossite and g-CuI compounds deposited onto transparent substrates. Their optical and electrical properties were measured and will be discussed.
Transparence in the visible range of p-type Mg doped CuCrO2 delafossite annealed (550∘C) thin films deposited on fused silica reached 60% due to its large indirect band gap of 2.72 eV while a p-type polaronic electrical conductivity was clearly identified. This transport mode leading to have an electrical conductivity of 3.5 S/cm at 220∘C (0.6 S/cm at room temperature) with a large ($> 300\mu$V/K) and constant Seebeck coefficient with the temperature ((1)). More recently, new fast annealing process has already multiplied by a factor of ten the electrical conductivity at room temperature of films deposited on glass ((2)) which has open some interest for new investigations.

The temperature stabilized p-type g CuI thin films are concerned by a hole band transport conduction with a degenerated semiconductor behavior. The films have showed interesting performances as a Total Transmittance of 65% in the visible range, a carrier density $>$ 1019cm-3 with a mobility of 1.2 cm^{2}V-1s-1. A discussion about the CuI thin films stability with the temperature will be lead. The stabilized thin films reached a power factor of 66 μWm/K2 at 140∘C in air (limit of stability) which give a potential interest for transparent thermoelectric applications ((3)).

As a conclusion, in the aim to compare the p type transparent thermoelectric performances

*Speaker

of thin films, a new combined figure of merit called COPTTE is exposed which allowed us to compare the performances of our films with the literature (3).

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Keywords: p type Transparent Thermoelectric, Thin films, Delafossite, CuCrO2, CuI, COPTTE

Pulse electrodeposition of SnSe films for thermoelectric conversion

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Abstract

There is a recent and important growing interest in SnSe as an alternative to conventional thermoelectric materials containing toxic and rare elements such as bismuth telluride. Thus, its low thermal conductivity and high thermopower make it a promising material for thermoelectric devices (1). Most of the thermoelectric materials are used in a bulk shape. However, decreasing the dimensionality is beneficial for the thermal conductivity, according to theoretical (2) and experimental researches (3).
In this work, we report a study of electrodeposited SnSe films. A growth mechanism was proposed and a synthesis potential window was defined, in which the electrodeposition of SnSe films was investigated (4). The deposits exhibit typical polycrystalline needle-like grains, corresponding to the orthorhombic single-phase. Afterwards we focused our efforts to improve the quality of the SnSe films in terms of defects and crystallinity with the use of the pulse potentiostatic deposition. Thus, more compact and crystallized deposits were obtained with a Sn/Se ratio close to 1/1(5).

The thermal properties of the SnSe films were then simulated and characterized. The assessment of thermal conductivity was predicted through the resolution of Boltzmann transport equation (BTE) for phonons with a Monte Carlo (MC) method. A significant reduction in thermal conductivity was observed for thin thicknesses due to boundary scattering and ballistic phonon transport (6). This influence was verified experimentally for thicknesses below 300nm by Scanning Thermal Microscopy in 3ω configuration (7).

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Keywords: SnSe, Thin films, electrodeposition, thermal properties

Development of Fe-Al-Si Thermoelectric (FAST) Materials and Modules

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Abstract

To develop a new thermoelectric material that is low-cost and non-toxic with a sufficient power output for autonomous power supplies to drive sensor devices, in particular, at a low-temperature range below 400 K, we performed materials screening using first-principles band structure calculations (1,2). As a result, the ternary
*tau*1-Fe3Al2Si3 phase has shown potential as a thermoelectric material. Furthermore, we demonstrated that fine-tuning of the Al/Si ratio could control its conduction type and enhance the power factor without chemical substitutions (2). Relatively large power factors were obtained for p- and n-type materials below 400 K with high oxidation resistance and excellent mechanical properties (3). Recently, we enhanced the power factor at mid-temperatures using machine-learning-assisted synthesis (4,5). However, the remaining important issue is enhancing thermoelectric performance by optimizing microstructure and carrier concentration to drive sensors with higher power consumption. This presentation will briefly review the recent progress of earth-abundant thermoelectric material Fe3Al2Si3 and the development of power generation modules with some verification tests (5,6).

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Keywords: thermoelectric module, autonomous power supply, low temperature waste heat

*Speaker

High efficiency and output power in GeTe/Mg3Sb2-based thermoelectric generator

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Abstract

Recently, there have emerged many reports on thermoelectric generators (TEGs), claiming record-breaking efficiency values. However, we find two problems. One is the trade-off between the efficiency and the output power in the presence of electrical contact resistance. Thus, high efficiency does not necessarily lead to high cost-performance (W/$). The other is that there is no established consensus about protocols for efficiency measurement. The absence of guidelines makes it difficult to compare different results. Here, to break the trade-off, we develop GeTe/Mg3Sb2-based TEGs with minimal electrical contact resistance and total thermal resistances. Our TEG allows for simultaneous boost in the efficiency and the output power (10.1% and 1.94 W/cm2), owing to excellent material performance and high input heat flow.

Keywords: thermoelectric generation, efficiency measurement, contact resistance

*Speaker

Thermographic detection of failure in thermoelectric module

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Abstract

Infrared lock-in thermography has been successfully applied to obtain a 2D image of failure in a thermoelectric (TE) module. One of the issues for the widespread application of TE generation is the stabilization of electrode contact with low resistance during the operation. We have visualized the failures with high resistance based on their Joule heating. Although the concept is simple, several considerations arising from peculiar characteristic of thermoelectric materials were necessary: Peltier heat, low heat generation from the failure and Joule heating of TE material itself. To eliminate the Peltier heat influence, AC source of several 100 Hz was applied as commonly adopted. As with the low heat generation, a high current density, typically 2 A/mm2, was enough to detect. Finally, the Joule heating from the failure was distinguished from that of TE material using the lock-in detection, that is, the heat mass of the failure is smaller than that of bulk TE material resulting in low time constant so that lock-in detection that can extract a signal relevant to an aimed frequency is efficient. The observed images clearly indicate the position of failures, and thus it is useful for the failure analysis of TE modules as well as for in-situ observation due to the non-contact detection.

Keywords: module, failure analysis, electric contact, lock in detection

*Speaker

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Influence of thermoelectric properties on the output power density of a new design of planar μ-TEG

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Abstract

Heat recovery systems based on thermoelectric microgenerators (μ-TEGs) can play an important role in the development of wireless, energy-autonomous electronics. However, to date, the power density that can be recovered with μ-TEGs at small temperature differences is limited to a few microwatts or less, which is not yet sufficient to power a wide range of wireless devices. To develop more efficient μ-TEGs, the material, device, and system requirements must be considered simultaneously. In this study, an innovative design of an in-plane μ-TEG TEG integrating bismuth telluride and forming sinusoidal trenches is reported. Using 3D numerical modeling, the influence of boundary conditions, parasitic effects (electrical and thermal contact resistances), and transport properties of thermoelectric materials on the output power of these μ-TEGs are investigated in detail for a small temperature difference of 5 K between the hot and cold sources. Compared to wave-shaped trenches, this new shape enables an increase in output power. The results show that either the thermal conductivity or the Seebeck coefficient of the active n- and p-type semiconductors are the key parameter that should be minimized or maximized depending on the magnitude of the parasitic effects.

Keywords: thermoelectric microgenerators power density numerical modeling transport properties

*Speaker

Ab initio calculations of the thermoelectric phonon drag effect in semiconductor nanostructures

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Abstract

With the advance of materials fabrication techniques and increase of computational power during the past two decades, the research aiming to enhance the efficiency of thermoelectric devices, with the search of new materials and manipulation of materials properties at the nanoscale, has attracted significant interest. In general, the efficiency of thermoelectric materials, measured by the figure of merit ZT, directly depends on the Seebeck coefficient of the material. In the present work, we have studied, by combining the density functional theory calculations of the electron-phonon (1,2) and phonon-phonon (3) interactions, the enhancement of the Seebeck coefficient due to electron-phonon coupling, known as the "phonon-drag" effect (4). To account for this effect, we have solved the linearized Boltzmann equation for electronic transport in presence of non-equilibrium phonon
populations introduced by a temperature gradient (5). In order to understand the phonon drag effect at the nanoscale, we have studied the effect of direction-dependent nano-structuring effect on the Seebeck coefficient of silicon. We will present our recent results related to phonon and/or impurity limited carrier mobility, as well as the variation of the Seebeck coefficient of bulk and nanostructured silicon with temperature and carrier concentrations. Our results for n-doped silicon not only show a good agreement with the experimental data in both bulk samples (6) and nanostructures (7) but also pave the way to further understand the contribution of phonon-drag in other semiconductor nanostructures (8), which still remain largely unexplored.

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Bi2Te3 : Towards a Se free n-Type

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Abstract

For 50 years, the bismuth telluride Bi2Te3 has been the subject of a multitude of studies(1)-(6) due to its optimal thermoelectric properties at room temperature and below. Our investigations aim at finding a performant n-type material by controlling the amount of tellurium vacancies, either by playing with the Bi/Sb ratio and/or by introducing an extra element (7) that might react with Te, hence depleting the Te amount from the Bi2Te3 based material.
Our first studies are focused on the solid solution Bi2-xSbxTe3, which is a mostly known for being p-type material (x > 1). However, recently, it has been demonstrated that for a smaller amount of Sb (x < 1), the solid solution Bi2-xSbxTe3 behaves like an n-type material.(8) Moreover, this material seems to have better properties than Bi2Te3-xSex at room temperature (the actual n-type used in the industry). The aims here will be to find the optimal composition utilizing mechanical alloying as an easily reproducible and scalable synthesis technique.

Another part of our work is to try to control the number of Te-vacancy to reach a p-type material. Consequently, we have embarked in the study of the effect of an extra element M on the selenium free n-type compounds MyBi2-xSbxTe3, both for proposing a n-type counterpart to the performant well known p-type (Bi,Sb)2Te3 and for having optimal properties around room temperature.

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Keywords: Thermoelectricity, bismuth telluride, mechanical alloying

Chemical synthesis of single crystalline Ag2Te and Cu2Te nanorods

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Abstract

Metal tellurides such as Cu2Te andAg2Te are of high interest as thermoelectric material, converting heat into electricity and vice versa (1). In this work, pure monoclinic single crystalline Ag2Te and Cu2Te nanorods were synthesized by a two-step method. The rst step concerns the electrodeposition of self-standing Te nanorods in an ionic liquid medium, taking advantage of its templating properties (2-3).
These obtained nanorods are single crystalline with growth direction along the (001) axis in the hexagonal lattice. The average diameter of the as-deposited Te nanorods is 60 13 nm with less than 300 nm long. Afterwards, the resulting nanostructured Te lm is immerged in a dedicated silver-based bath in order to be transformed into Ag2Te binary compounds by a combined mechanism of chemical cementation and topotactic transformation. The chemical analysis reveals that the nal nanostructures exhibit a slight excess of silver and TEM-SAED analysis shows that they are still single crystalline with an increase of the initial diameter, less than 30%. HR-TEM highlights the presence of an intermediate stutzite phase and the hessite phase -Ag2Te is obtained at the end of the synthesis process (4).
This approach has been successfully extended to the synthesis of Cu2Te nanorods. Thus, by immerging Te nanorods in sulfate copper electrolyte in the presence of ascorbic acid as a reducing agent, the dismutation process takes place and a phase transition is observed from hexagonal Te to orhomboedral Cu2Te.
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Keywords: Tellurium, Ag2Te, Cu2Te, Nanorods, Chemical synthesis

*Speaker

Efficient optimization of the synthesis parameters of thermoelectric legs using a machine learning approach

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Abstract

The deposition of high-quality electrical contacts on thermoelectric (TE) materials is of uttermost importance for the fabrication of reliable and efficient TE generators (1,2). However, this challenging processing step is often neglected in academic researches. High-quality electrical contacts must present, at the same time, good adhesion on the materials as well as low electrical and thermal interfacial resistances. The simultaneous optimization of the contact material's composition and the numerous deposition parameters are generally realized using a highly time-consuming try-and-error approach.

This poster presents a new approach using machine learning (ML) which aims at optimizing more efficiently a large number of experimental parameters from a relatively small (_˜20) initial set of samples (3). This approach was applied to the direct synthesis of Yb4Sb3 TE legs by Spark Plasma Sintering by optimizing simultaneously the synthesis parameters (temperature, time, uniaxial pressure...) and the contact's composition (13 metals were considered) in order to minimize the electrical contact resistance. The prediction performances of different types of ML algorithms and data descriptors (both from experiments and online database) as well as the mechanical and electrical properties of a number of predicted samples are reported. Finally, the advantages and weaknesses of this ML approach applied to the optimization synthesis conditions are also discussed.

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Keywords: Electrical contact, Synthesis, Machine learning, SPS

*Speaker

Glassy thermal conductivity in Cs3Bi2I6Cl3 single crystal

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Abstract

As the periodic atomic arrangement of a crystal is made to a disorder or glassy-amorphous system by destroying the long-range order, lattice thermal conductivity, L, decreases, and its fundamental characteristics changes. The realization of ultralow and unusual glass-like L in a crystalline material is challenging but crucial to many applications like thermoelectrics and thermal barrier coatings. Herein, we demonstrate an ultralow (_˜0.20W/m·K at room temperature) and glass-like temperature dependence (2–400K) of L in a single crystal of layered halide perovskite, Cs3Bi2I6Cl3. Acoustic phonons with low cut-off frequency (20cm–1) are responsible for the low sound velocity in Cs3Bi2I6Cl3 and make the structure elastically soft. While a strong anharmonicity originates from the low energy and localized rattling-like vibration of Cs atoms, synchrotron X-ray pair-distribution function evidence a local structural distortion in the Bi-halide octahedra and Cl vacancy. The hierarchical chemical bonding and soft vibrations from selective sublattice leading to low L is intriguing from lattice dynamical perspective as well as have potential applications.

Keywords: metal halide perovskite, thermal conductivity, single crystal, solid state chemistry

*Speaker

Graphical User Interface for using active learning assisted by Bayesian Optimization applied to thermoelectric materials

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Abstract

With this poster, we will discover the diverse functionalities available in a user-friendly Graphical User Interface (GUI) developed at the National Institute for Materials Science (NIMS, MaDIS) for performing statistical data analysis, machine learning (ML) modelisation, and composition/process optimisation through Bayesian optimisation of thermoelectric materials without any coding knowledge required. Users only have to prepare a tabular datasheet as a *.csv or a *.xlsx file providing experimental features (e.g., compositional ratios, process parameters (e.g., ball milling, annealing, sintering)) and targeted properties (e.g., the figure of merit zT, conductivity/thermal conductivity, Seebeck coefficient). The GUI's first part is dedicated to selecting desired features and targets and performing a basic statistical analysis by visualising the fed data and interpreting their potential relationships through bar and scatter plots. The GUI's second part is dedicated to modelling statistical relationships using Pearson's linear correlation score to display the one-to-one linear correlations potentially existing between input features and targets. The user can also use various ML models with proven performances on tabular data, such as ElasticNet, RandomForest, and XBGoost regressors and use leave-one-out or k-fold cross-validation techniques in a few clicks to train their models and attempt to predict targeted properties. In addition to model training and prediction capabilities, the importance of features in driving change in targeted properties is also autonomously displayed to ease the interpretation of ML model predictions and eventually shorten the number of salient features. Finally, on the last page of the GUI, users can add mathematical and experimental constraints to their compositional and process parameters. Those are then submitted with prepared experimental data to a Bayesian optimisation algorithm with the objective of improving chosen targeted properties. Users can optimise single or multiple targets simultaneously, such as minimising one feature while maximising another, with the ability to set equal or different ratios of importance between them. In addition, users can use their ML models instead of actual experimental data within the Bayesian optimisation to unbias their dataset. Overall, the GUI is a user-friendly and efficient tool for quick statistical data analysis, ML modelisations, and improving properties of thermoelectric materials through multiple steps informed by ML. The GUI is suitable for experimentalists and theoreticians desirous of using ML tools to improve their thermoelectric material performances.

*Speaker

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Implantation effect on the thermoelectric properties of scandium and chromium nitrides thin films.

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Abstract

Thin films transport properties have been extensively studied over the past decades for thermoelectric applications. On the one hand, the low dimensionality of these materials often allows them to exhibit unique electronic transport properties. On the other hand, phonon scattering through point defect engineering still remain a challenge to obtain high performance thermoelectric thin films. In this context, the ion-implantation technique, widely used for semiconductor doping, may present itself as a useful technique to generate various types of defects into the film and decrease the mean free path of phonons without disrupting the electronic transport properties. In addition, this technique offers access to a wide range of usable ions, which allows the generation of defects and the doping of the material to be considered simultaneously, thereby controlling the concentration of charge carriers while decreasing the thermal conductivity of the lattice. This promising approach have been studied in the last few years for thermoelectric films and yielded encouraging results(1)(2). We propose in this work to study the influence of ion-implantation on the transport properties of transition metal nitrides thin films, in particular ScN and CrN, for possible thermoelectric applications (Fig. 1).

Keywords: thermoelectricity, implantation, defects, nitrides, thin films

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In situ diffraction study of the phase transformations occurring in the thermoelectric colusite Cu26V2Sn6S32

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Abstract

Interest in thermoelectric (TE) technology has been continuously growing in the last decade driven to the
necessity to limiting waste heat during energy transformation. Among the most promising TE materials at medium temperature, complex copper-based sulphides are of double interests as they are usually made of eco-friendly and low cost elements(1) and exhibit intrinsically low thermal conductivity.(2,3) Derivatives of the natural mineral colusite, with general formula Cu26A2E6S32, (A = V, Nb, Ta, Cr, Mo, W; E = Ge, Sn, As, Sb), are an emerging class of excellent thermoelectric materials.(4) As example, the ZT value of the colusite Cu26V2Sn6S32 rises to near unity at 675K, making this material one of the best p-type TE in this temperature region.(5) Its performances are mainly related to the coexistence of an ordered (P-43n) and a disordered (F-43m) forms obtained after sintering at 1023 K (i.e. sample H), leading to a very low thermal conductivity.(5),(6) In addition, colusite Cu26V2Sn6S32 is known to exhibit an intrinsic exsolution phenomenon supposed to be related to the coexistence of Sn-rich and Sn-poor colusites.(7,8)
In this study, we investigated by *in-situ* synchrotron powder diffraction the solid-state phase equilibrium as function of the temperature between the ordered and disordered forms of colusite Cu26V2Sn6S32. The use of high-resolution setup revealed a complex behavior with several phase transformations, probably related to a mutual interaction and kinetic effects.

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Keywords: Thermoelectric, Colusite, In situ diffraction, synchrotron

Scalability of the magnesiothermic process for mass production of skutterudites: preliminary results.

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Abstract

Thermoelectric materials TE (n- and p-type doped semiconductors) are materials that can convert thermal energy into electricity and vice versa based on Seebeck and Peltier effects. Thanks to this, thermal energy that is rarely useable or lost can be used as effectively as possible in productive applications. Therefore it could play an important role in a global sustainable energy solution.
Among the materials with the greatest potential for widespread thermoelectric development are skutterudites deriving from CoSb3. They are a well-known class of TE materials that have attracted a lot of research due to their interesting thermoelectric properties (1). They exhibit interesting electronic properties including high holes mobility and a large Seebeck coefficient, and their thermal conductivities can be reduced by inserting "rattlers" into their large structural voids, and they can achieve high performances, reaching figure-of-merit values close to 2 (2).

The synthesis of these materials by conventional melting/solidification methods is relatively challenging because of their slow double-peritectic formation at "low" temperature, which therefore requires long annealing duration. As a result, other methods are being investigated. Recently a new magnesiothermic method has been developed in order to simplify and shorten the synthesis duration (3,4).

Magnesioreduction offers various advantages over conventional melting and solidification processes, including (i) the use of oxide precursors, which are stable in air and far less expensive than the corresponding metals, (ii) lower temperatures and (iii) shorter reaction times thanks to the high reducing power of Mg.

In this poster, I will present my preliminary results about the scalability of this method applied to n-type skutterudites (In0.22Co4Sb12), as well as the first results on the magnesiothermic synthesis of the p-type skutterudite (Ce0.8Fe3.5Co0.5Sb12).

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Keywords: Skutterudites, Magnesioreduction, Scalability, XRD

Screening quaternary Heusler by machine learning for application in thermoelectricity

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Abstract

Heusler alloys, full and half-, thanks to their high versatility of compositions as well as their very interesting properties, are good candidates for thermoelectric applications. In the Heusler family, quaternary alloys also exist and allow to further increase the chemical diversity and so one to achieve more complex properties. However, due to the high number of combinations, traditional screening methods are not effective to target relevant compounds. To accelerate this research, it is advantageous to use machine learning methods. In our project, we are looking for new promising quaternary Heusler compounds screened within a dataset of 24 selected elements. First, a database of calculated thermodynamic, electronic and magnetic properties, obtain from DFT calculations (Density Functional Theory) on binary and ternary compounds was constructed. Then, a supervised learning with the neural network model was built to predict the enthalpy of formation and the density of state at the Fermi level (metallic or semiconductor character) of quaternary Heusler compounds. Our model presents comparable or superior performance than the state of art and allow to identify promising compounds among the 24ˆ4 possible configurations of our dataset.

Keywords: Machine Learning, DFT, Heusler

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Precursor phase with full phonon softening above the charge-density-wave phase transition in 2H-TaSe2

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Abstract

Research on charge-density-wave (CDW) ordered transition-metal dichalcogenides continues to unravel new states of quantum matter correlated to the intertwined lattice and electronic degrees of freedom. Here, we report an inelastic x-ray scattering investigation of the lattice dynamics of the canonical CDW compound 2H-TaSe2 complemented by angle-resolved photoemission spectroscopy. Our results rule out the central-peak scenario for the CDW transition in 2H-TaSe2 and provide evidence for a novel precursor phase above the CDW transition temperature TCDW. The phase at temperatures between T* (= 128.7 K) and TCDW (= 121.3 K) is characterized by a fully softened phonon mode and medium-range ordered (ξcorr = 100 Å - 200 Å) static CDW domains. Only TCDW is detectable in our photoemission experiments. Thus, 2H-TaSe2 exhibits structural before electronic static order and emphasizes the important lattice contribution to CDW transitions.

Keywords: Lattice dynamics, phonon softening, inelastic x, ray scattering, charge, density, wave, TaSe2

*Speaker

Structural analyses and thermoelectric properties of Cr2Sn3S7

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Abstract

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The design and optimization of thermoelectric (TE) materials rely on the intricate balance between thermopower (S), electrical resistivity (ρ) and thermal conductivity (k). Perfecting such a balance is key to reach high values of the figure of merit, ZT = S2T/ρk, necessary to improve energy recovery systems and thermoelectric cooling devices.1 Among the most promising TE materials at medium temperature, complex copper-based sulphides are of double interests as they are usually made of eco-friendly and low cost elements2 and exhibit intrinsically low thermal conductivity.3,4 Nevertheless, the TE performances of p-type copper-based sulphides are much better than those of n-type,5 limiting the potential of sulphides to be used in TE devices. Hence, it appears necessary to develop more performant n-type sulphide materials.

In this context, we have synthesized and studied the new sulphide Cr2Sn3S7. This compound, isotype of Cr2Sn3Se7,6 is characterised by a n-type semiconductor behaviour and a complex crystal structure leading to a very low thermal conductivity, which are promising features to develop good thermoelectric materials.

In this presentation, I will discuss on the relationships between chemical composition, crystal structure and properties (TE and magnetic) of Cr2Sn3S7 and some derivatives, using X-ray powder diffraction, scanning and transmission electron microscopies, magnetic measurements, spectroscopy techniques and transport measurements.

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Keywords: Sulfide, incomensurate stru ctures

Synthesis of β–FeSi2 by reactive sintering

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Abstract

Iron disilicide can be an outstanding candidate for thermoelectric application as it is composed of abundant, non-toxic, and cheap chemical elements.
Using FeSi2 doped with Co or Al can lead to high electronic properties exhibiting a power factor around 1-2 mW/m.K2 (1,2). However its thermoelectric performances still remain limited due to its quietly high thermal conductivity which is about 10.3 (440 K) (3), 4.3 (425 K)(2) and 6.2 (425 K) (2) W/m.K for pure FeSi2, Fe0.95Co0.05Si2 and FeSi1.92Al0.08, respectively.

Moreover, the time-consuming peritectoid reaction to transform FeSi + Fe2Si5 into β-FeSi2 can takes tens up to hundreds of hours at a temperature of about 1123 K.

Several routes can be investigated such as nanostructuring, an increase of the amount of point-defect, or a mass fluctuation, to enhance the phonons scattering and then, to decrease the lattice part of the thermal conductivity.

Here, we report the fast synthesis of β-FeSi2 by combining arc melting, mechanical milling, and spark plasma sintering (SPS) which permits to obtain dense pellets ($> 90\%$) and transforming FeSi + Fe2Si5 into β-FeSi2 mainly during the only 5 min of the SPS sintering step on a wide range of temperature and pressure from 773K to 1073K and 25MPa to 500MPa, respectively (4).

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Keywords: Silicide, SPS, Reactive sintering, Thermoelectricity

Thermoelectric Materials for utilizing Automobile Waste Heat

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Abstract

Heat is one of the most waste forms of energy dumped in the environment and contributes to global warming as well as climate change. Thermoelectrics offer the conversion of waste heat into useful electricity. Therefore, mounting thermoelectric modules over the automobile harvest useful electricity from the waste heat emitting from the engines due to internal combustion, improving the fuel efficiency. In this study, we are focusing on developing efficient, environmentally friendly, and mechanical strength thermoelectric materials. The present work collectively discusses the progress made so far in the thermoelectric material's development along with the prediction of temperature range of waste heat emitting from the automobile engine. This work partially is supported by a grant project (JPNP21014) conducted by The Research association of Automotive Internal Combustion Engines (AICE) with support from the New Energy and Industrial Technology Development Organization (NEDO).

Keywords: Thermoelectric, waste heat

*Speaker

Thermoelectric properties of the Mn (Sb, Bi)2 (S, Se)4 series

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Abstract

Over the last decade, thermoelectric materials have drawn global interest in research and development especially due to the need to find new sustainable energy sources. Indeed, numerous sectors could take advantage of the thermoelectric material's capacity to directly convert the wasted heat into electrical energy, and then contribute to closing the energy crisis as well as global climate change.
For low and medium-temperature range applications (*i.e.,* below 700 K) best thermoelectric performances have been obtained by compounds that commonly exhibit scarce and toxic elements, which required complex and costly synthesis procedures. Those drawbacks prevent the use of these complex thermoelectric materials for large-scale applications. Many efforts have, therefore, been made to find new environmentally friendly thermoelectric compounds which not only exhibit high performance but also possess the potential to be produced on large scale.

Based on this trend, the high thermoelectric performance together with the potential for economical, large-scale production and dissemination make sulfide-based thermoelectric materials very promising candidates for building competitive thermoelectric generators (1). In 2012, the discovery of the tetrahedrite (2) compound highlighted an ultra-low thermal conductivity thanks in part to the antimony electron lone pair. Following that trend, new sulfur-based compounds, which exhibit a cation with an electron lone pair, have been investigated.

In this context, the synthesis process as well as the crystallographic and transport properties of the promising (Mn, Fe)(Sb, Bi)2(S, Se, Te)4 compounds will be assessed. Indeed, substituting Sb for Bi will induce a change in the conduction type from p- to n-type (815 μV/K for MnSb2S4 and -127 μV/K for MnSb2S4 at 400K) and the substitution of Mn by Fe will modify the magnetic behavior from antiferromagnetic to ferromagnetic.(3, 4)

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Keywords: Sulfur and selenide compounds, Transport properties

Unconventional synthesis and characterization of substituted rare-earth antimonides for very high temperature thermoelectric applications

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Abstract

Rare-earth antimonides raised a worthy interest from the past decades in the thermoelectric field. Indeed, their transport properties are suitable for thermoelectric applications, especially in the very high temperature range as illustrated by the well-known Yb14MnSb11 which shows a promising figure of merit of 1.2 at 1275 K. We have focused recently on the synthesis of ytterbium antimonide Yb4Sb3, which is on the close edge between Zintl phases and intermetallics. This compound displays a cubic anti-Th3P4 structure with a decent chemical flexibility, leaving space for the tuning of its transport properties. Previous studies showed that Yb4Sb3 exhibits a positive Seebeck coefficient of about 70 μV.K-1 indicating a p-type behavior, and a typical resistivity of a poor metal with values around 1.2 mOhm.cm at 1300 K. In this work, substitutions of Yb by La on the one hand, and Sb by Bi on the other hand were carried out and lead to the establishment of LaxYb4-xSb2.8Bi0.2 (x = 0.1, 0.2, 0.3) solid solutions existence. The uncommon synthesis routes achieved involving niobium tubes will also be detailed. The influence of the substitution of both Yb and Sb atoms on the transport properties will be presented and discussed. In addition, a discussion on the electronic and lattice thermal conductivity determination through both Dulong-Petit and Wiedemann-Franz laws will be carried out. As a main result, the figure of merit of Yb4Sb3 yielded encouraging values of about 0.6 at 1300 K.

Keywords: Synthesis, Rare, earth, Antimonides

*Speaker

A Tunable Structural Family with Ultralow Thermal Conductivity: Copper-Deficient Cu1−xxPb1−xBi1+xS3

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Abstract

Understanding the mechanism that connects heat transport with crystal structures and order/disorder phenomena is crucial to develop materials with ultralow thermal conductivity (), for thermoelectric and thermal barrier applications, and requires the study of highly pure materials. We synthesized the n-type sulfide CuPbBi5S9 with an ultralow value of 0.6–0.4 W m–1 K–1 in the temperature range 300–700 K.1 In contrast to prior studies, we show that this synthetic sulfide does not exhibit the ordered gladite mineral structure but instead forms a copper-deficient disordered aikinite structure with partial Pb replacement by Bi, according to the chemical formula Cu1/32/3Pb1/3Bi5/3S3.1 By combining experiments and lattice dynamics calculations, we elucidated that the ultralow value of this compound is due to very low energy optical modes associated with Pb and Bi ions and, to a smaller extent, Cu. This vibrational complexity at low energy hints at substantial anharmonic effects that contribute to enhance phonon scattering. Importantly, we show that this aikinite-type sulfide, despite being a poor semiconductor, is a potential matrix for designing novel, efficient n-type thermoelectric compounds with ultralow values.1 A drastic improvement in the carrier concentration and thermoelectric figure of merit have been obtained upon Cl for

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S and Bi for Pb substitution. The Cu1–xxPb1–xBi1+xS3 series provides a new, interesting structural prototype for engineering n-type thermoelectric sulfides by controlling disorder and optimizing doping.

Keywords: Gladite, Sulfide, Thermoelectric, Mechanical, alloying, SPS

Doping strategies in new sphalerite derivatives thermoelectric sulfides

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Abstract

Among the various possibilities offered by the periodic table, copper-rich sulfides represent a formidable source for the discovery of low cost and environmentally benign thermoelectric materials. Copper-rich sulfides form an important class where univalent copper is the dominant element, giving the possibility of creating hole carriers in the conductive "Cu–S" network for the generation of p-type thermoelectrics, as exemplified by bornite Cu5FeS4, germanite derivative Cu22Fe8Ge4S32, stannoidite Cu8Fe3Sn2S12, colusites Cu26T2M6S32 (T = V, Cr, Nb, Mo, Ta, W; M = Sn, Ge), synthetic Cu2SnS3, kesterite Cu2ZnSnS4, and tetrahedrites Cu12Sb4S13. (1)
In my poster, I will present the crystal structure, microstructure, and thermoelectric properties of sphalerite derivative compounds. I will especially discuss the effect of cationic and anionic substitution on the crystal structure and electrical and thermal properties of Cu5Sn2S7 and Cu22Sn10S32 and compounds.

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Keywords: spahlerite derivatives

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3D scanning precession electron diffraction analysis of nanodomains in thermoelectrics

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Abstract

Copper rich sulfides in the form of sphalerite derivatives exhibit well known thermoelectric performances, yet very little has been reported about these materials in wurzite-derivated structures.
In the article that we recently published (2), we explain how we synthesized a series of self-doped compounds Cu2+xMn1-xGeS4 through Cu for Mn substitution, and how a combination of techniques, i.e. x-ray diffraction and transmission electron microscopy (TEM), was used to characterize these materials from the crystal structure point of view.

Within the framework of TEM characterization, 3D electron diffraction (3D ED) techniques (1), and notably precession electron diffraction tomography (PEDT), has shown its usefulness in *ab initio* crystal structure determination of several kinds of nanostructured materials with a high precision, being now possible to produce a probe size as small as a few nm.

PEDT analysis revealed in our case the interconnected nature of the Enargite and Stannite-like nanodomains inside of the self-doped samples, that provide them with interesting thermoelectric properties.

In such cases, where multiple types of small domains are present in the sample under investigation, PEDT shows some limitations due to its nature. Instead, by scanning the electron beam across an area of the sample at each tomography step, as in SPET (precession electron

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diffraction tomography) (3), it would be possible to reconstruct the reciprocal space for different regions in the sample. This way, a large amount of information can be extracted from a single dataset acquisition, being able to perform crystal structure solution and dynamical accurate structure refinements on different domains as small as the electron beam size.

SPET relies on the comparison by cross-correlation between the acquired diffraction patterns and the reference known structures, being able this way to identify phase and orientation of a specific domain.

The future goal would then be to develop SPET analysis in such a way that, by comparing the diffraction patterns between each other instead, also unknown samples can be identified.

This technique therefore bears the potential for becoming a standard characterization technique for all kind of nanodomain-structured materials.

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Investigation of the magnetism impact on the thermoelectric properties in the spinel family

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Abstract

Sulfides exhibit interesting electronic properties, including high electronic mobility and the potential to exhibit very low thermal conductivity when possessing complex crystal structures. This makes them an attractive option for thermoelectric applications (1). Among sulfides, spinels have attracted significant research interest due to their interesting magnetic and electronic properties, which can exhibit metallic, insulating, or superconducting behavior. Some thiospinels have also been considered for their promising thermoelectric properties, with ZT reaching around 0.2 at 700K, as for example in CuTi2S4 (2-3).
The thermoelectric properties can be tuned by doping, but magnetism can also play a role. The impact of magnetism has already been observed in transition metal oxides such as misfits (4) or NaxCoO2 (5), in pyrites (6) or in CuGaTe2 chalcopyrites (7). Magnetism can induce entropic terms, beneficial for the thermopower S as for example in oxides with paramagnetic Co3+ and Co4+ (5), or can induce a modification of the band structure as in pyrites (6) and thereby modify S. More recently, a clear impact of magnetism has been observed in the thiospinel CuCr1-xTi1+ xS4 where, depending on x, a negative or positive magnetothermopower effect has been observed (8). The results obtained in these CuCr1-xTi1+xS4 thiospinels will be presented, together with recent results obtained in related thiospinels.

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