

Journées Nationales de Thermoélectricité 2023

22-24 novembre 2023 - campus Paris-Saclay



Avec le soutien financier de :

université
PARIS-SACLAY

GRADUATE SCHOOL
Engineering and
Systems Sciences

université
PARIS-SACLAY

GRADUATE SCHOOL
Physique



GDR NANOMATERIALS FOR ENERGY APPLICATIONS

INSTITUT DE
L'ÉNERGIE
SOUTENABLE

université
PARIS-SACLAY

Comité d'organisation

David Bérardan (ICMMO)

Philippe Lecoeur (C2N)

Jérôme Saint-Martin (C2N)

Nathalie Vast (LRI)

*Merci au Centre de Nanosciences et de Nanotechnologies (C2N)
pour le prêt gracieux des locaux*

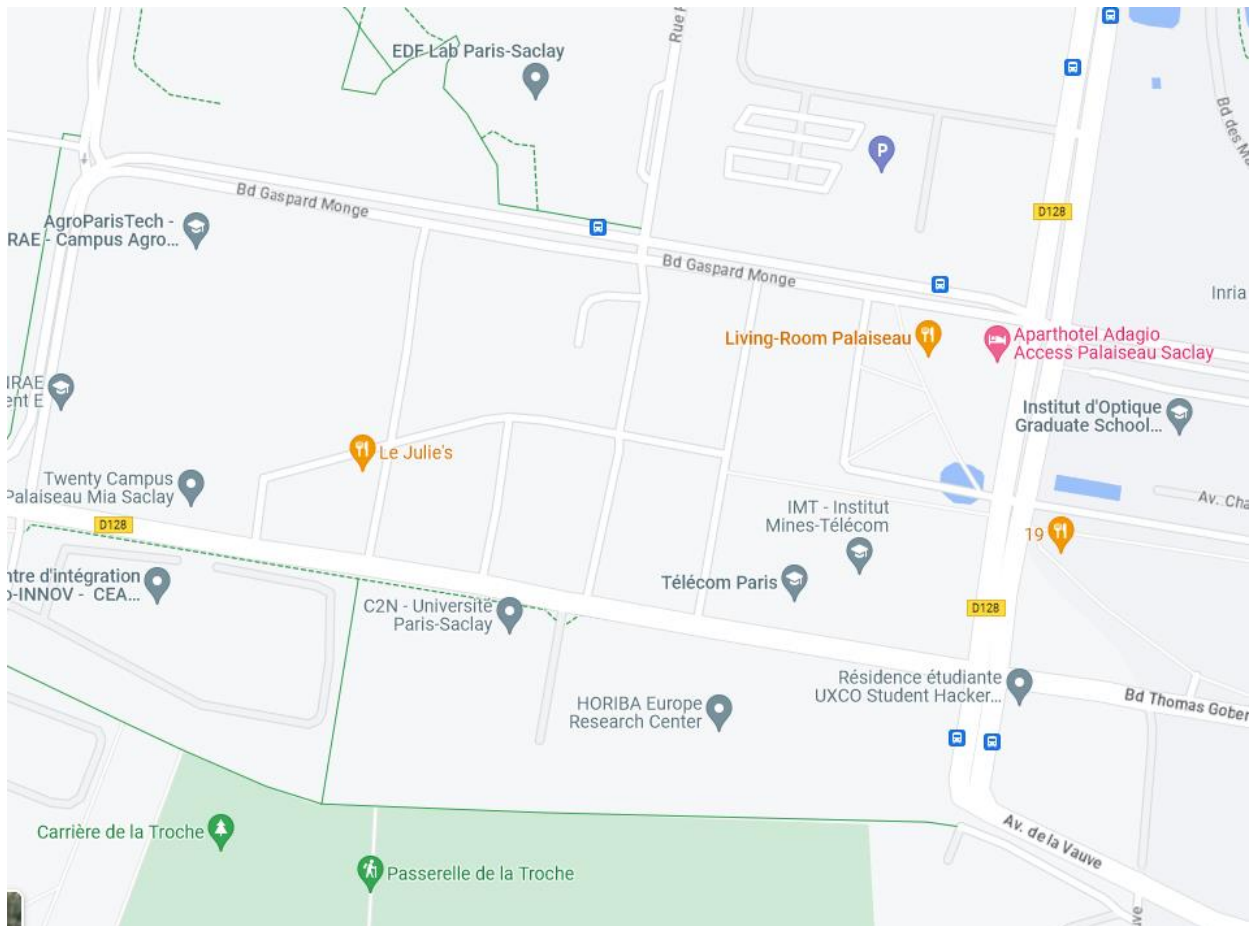


Informations pratiques

Lieu des JNTE : Centre de Nanosciences et de Nanotechnologies (C2N).

10 Bd Thomas Gobert, 91120 Palaiseau

GPS : 48.712621, 2.197098



Dîner de gala : restaurant « Living-Room Palaiseau », 10 Bd Gaspard Monge, 91120 Palaiseau (550 m). Le restaurant est à 50m de l'arrêt de bus « place Marguerite Perey » : bus 91.06 et 91.10 qui desservent notamment Massy-Palaiseau. Un bus/5min environ en heure de pointe, 1 bus/25 min après 21h, jusqu'à minuit environ.

Fiches horaires sur :

<https://me-deplacer.iledefrance-mobilites.fr/fiches-horaires/bus>

Déjeuner post-formation du jeudi midi : restaurant-brasserie « 19 », 19 Cours Gilbert Simondon, 91120 Palaiseau (500 m).

Programme des sessions de formation

Mercredi 22 novembre

14h-15h accueil des participants

15h-18h30 modules de formation consacrés aux films minces. Intervenants : Philippe Lecoer et Julien Chaste, du Centre de Nanosciences et de Nanotechnologies. Le Module 1 sera consacré plus spécifiquement à la croissance des films minces, le Module 2 à la métrologie appliquée aux films minces.

Jeudi 23 novembre

3 modules de formation seront consacrés à la physique/chimie numérique. Intervenants : Jelena Sjakste du Laboratoire des Solides Irradiés et Jérôme Saint-Martin du Centre de Nanosciences et de Nanotechnologies.

8h30-9h30 **Module 1** d'introduction. Ce module expliquera comment calculer le coefficient de Seebeck dans les matériaux et les dispositifs et couvrira les méthodes numériques pour les transports d'électrons et de phonons tels que la méthode des éléments finis (TCAD) pour les dispositifs, les équations de transport de Boltzmann (BTE) pour le formalisme semi-classique, le formalisme de Landauer et les fonctions de Green hors équilibre pour les simulations quantiques de transport cohérent. La plupart de ces méthodes reposent sur des données sur des matériaux provenant de modèles ajustés aux expériences, ou provenant de la théorie fonctionnelle de la densité (DFT).

9h30-10h10 **Module 2**. Ce module fournira une introduction à la DFT et à la théorie de perturbation de la fonctionnelles de la densité (DFPT), ciblant des extrapolations efficaces pour calculer la structure électronique (interpolation de Wannier), la dispersion des phonons (extrapolation avec la méthode de transformation de Fourier).

10h10-10h40 **pause café**

10h40-12h10 **Module 3**. Ce module traitera des méthodes et des codes pour calculer et interpoler le couplage électron-phonon et l'interaction phonon-phonon, et présentera les limites des codes existants.

12h30-13h30 **déjeuner au bar-brasserie « 19 » (500m environ)**

Programme des sessions scientifiques

Jeudi 23 novembre

13h30-14h accueil des participants

14h-14h15 mot de bienvenue

Comité d'organisation des JNTE 2023

Christophe Candolfi, directeur du GIS thermoélectricité

14h15-14h45 **conférence invitée : Laure Biniak (Institut Charles Sadron, Strasbourg)**
Porous conducting polymers for low grade waste heat energy harvesting?

14h45-15h45 Session 1 (chairman : Soufiane El Oualid)

Lucas le Gars, Laboratoire CRISMAT, Caen

Doping strategies in thermoelectric sulfides

Adrien Moll, Institut de Chimie Moléculaire et des Matériaux d'Orsay, Orsay

High-Entropy Oxides: a new strategy for the design of innovating thermoelectric materials

Ilayda Terzi, Institut Jean Lamour, Nancy

Investigating Both Electronic Structure and Thermoelectric Transport Properties of SnBi₂Te₄

15h45-16h30 **Posters et pause café**

16h30-17h **conférence invitée : Céline Barreteau (Inst. de Chimie des Matériaux Paris-Est, Thiais)**
Discovery and optimization of thermoelectrics materials using high-throughput calculations and machine learning

17h-18h Session 2 (chairwoman: Jelena Sjakste)

Raja Sen, Laboratoire des Solides Irradiés, Palaiseau

Role of dimensionality, size, and transport-direction in governing the drag Seebeck coefficient of doped silicon nanostructures: A first-principles study

Sami Merabia, Institut Lumière Matière, Villeurbanne

Thermoelectricity and thermal transport of single molecule junctions

Pascal Boulet, Laboratoire MADIREL, Marseille

Density Functional Theory Investigation of High Performance Thermoelectric Ge-Sb-Te Nanosheets

À partir de 20h : repas de Gala au restaurant Le Living Room, Palaiseau (550 m du lieu du colloque)

Vendredi 24 novembre

8h30-9h30 Session 3 (*chairman : Mickaël Beaudhuin*)

Ruchi Bhardwaj, Institut de Chimie des Matériaux Paris-Est, Thiais

Effect of Low Purity Elements on Thermoelectric Performance of In-filled Skutterudites

Chuang Jia, School of Materials Science and Engineering & Jiangsu Key Laboratory for Advanced Metallic Materials, China, *maintenant* à Institut de Chimie Moléculaire et des Matériaux d'Orsay

High thermoelectric performance in ZrNiSn through electron injection and boosting carrier mobility

Sana Salami, Institut Lumière Matière, Villeurbanne

Electronic/thermal transport and thermoelectric phenomena in implanted diamond nanostructures

9h30-9h45 Présentation du GDR NAME

9h45-10h15 **Posters et pause café**

10h15-10h45 **conférence invitée : Guillaume Savelli (CEA Liten, Grenoble)**

Additive manufacturing technology for thermoelectric developments

10h45-11h45 Session 4 (*chairwoman: Judith Monnier*)

Amandine Duparchy, Institute of Materials Research, German Aerospace Center, Cologne

Insight on the stability of thermoelectric Mg₂(Si,Sn) and the role of Mg diffusion

Florentine Guiot, Institut des Sciences Chimiques de Rennes, Rennes

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

Maxime Baudry, CEA Liten, Grenoble

Nanostructuring of silicon germanium produced by additive manufacturing

11h45-12h15 **Prix Coqblin + mot de clôture**

A partir de 12h30, plateaux repas

Conférences Invitées

Porous conducting polymers for low grade waste heat energy harvesting?

Quentin Weinbach¹, Swapneel Vijay Thakkar¹, Naoures Hmili¹, Alain Carvalho¹, Marc Schmutz¹, Doru Constantin¹, Jérôme Combet¹, Nicolas Stein², Laurent Simon³, Laure Biniek^{1*}

1. Université de Strasbourg, CNRS, Institut Charles Sadron UPR22, F-67000 Strasbourg, France

2. Université de Lorraine, CNRS, ILL, F-57000 Metz, France

3. Université de Haute-Alsace, CNRS, Institut de Science des Matériaux de Mulhouse UMR 7361, 3Bis rue Alfred Werner, 68093 Mulhouse, France

email: laure.biniek@ics-cnrs.unistra.fr

Current research trends in organic thermoelectricity mainly focus on polymer materials that are developed as thin films. Controlling the polymer crystallinity and doping level have yielded record power factor ($2.9 \text{ mW m}^{-1}\text{K}^{-2}$)¹. However, one can expect a detrimental increase of electronic contribution to the thermal conductivity in such highly doped samples. In addition, maintaining a stable temperature gradient is rather difficult in such thin films and implementing them into a TEG is technologically challenging.

Complementary to this strategy, we focus our attention on developing lightweight and a few cm scale polymer materials that present superior control over thermal conductivity, by implementing porosity. We describe here the different strategies to produce such materials with varied porous structure. We use a combination of electron microscopy, spectroscopy and XR-scattering techniques to reveal their structure at different scale. We evaluate the TE properties and discuss the structure-properties relationships. In particular, the channel like macroporous structure yields record low thermal conductivity due to the control of the low solid and gaz heat conductions.² Finally, the measurement of the output TE performance through the one leg set-up demonstrates for the first time the potential of the porous materials to generate power (few μW) out from a small temperature difference ($36 \text{ }^\circ\text{C}$).³

¹ Durand, P.; Leclerc, N. et al. *Advanced Energy Materials*, 2022 ,12, 202103049

² Q. Weinbach et al., *J. Mater. Chem. C*, 2021, 9, 10173

³ Q. Weinbach et al, *Front. Electron. Mater.* 2022, 2:875856.

Discovery and optimization of thermoelectrics materials using high-throughput calculations and machine learning.

C. Barreteau, ICMPE, CNRS, UMR 7182, 2 rue Henri Dunant, 94320 Thiais, France

The development of thermoelectric devices requires new high-performance materials. Traditionally, this has been done in two ways: by optimising known thermoelectric materials or by discovering new materials with promising properties. However, although the experimental investigations are the most efficient way to improve and/or to discover thermoelectric properties, these methods are time-consuming, which limits the possible advances in thermoelectric materials. At the same time, the rise of high-speed calculations has made possible to explore and/or to optimize, in a systematic and accelerated manner, families of known thermoelectric materials as well as new families.

In this presentation, I will review the advances in high-throughput calculations related to the identification of new families of stable compounds for thermoelectric applications, as well as the screening of compounds in the same family to find the most promising one. We will also look at the recent contribution of machine learning methods to these investigations.

Additive manufacturing technology for thermoelectric developments

G. Savelli¹, G. Roux¹, M. Baudry¹

1. CEA Liten, Université Grenoble Alpes

email: guillaume.savelli@cea.fr

For 10 years, development of Additive Manufacturing (AM) technologies has considerably increased, mainly due to optimized tool and processes. AM technologies are mainly focused on metals and polymers materials development. More recently, first tests have been performed to test this manufacturing technique to few thermoelectric (TE) materials (Bi_2Te_3 , MnSi , SiGe). Indeed, this technique offers some advantages compared to standard sintering methods (complex shapes at both materials and devices level, new possible materials microstructures, simplified manufacturing processes for TE devices, etc.) despite tools processes are not fully adapted to these materials.

This presentation will review the state-of-the-art of this innovating technology for TE materials and devices development, focusing on current technological advances and TE performances obtained but also still current limitations.

Présentations orales

Doping strategies in thermoelectric sulfides

Lucas Le Gars¹, Pierric Lemoine², Bernard Malaman², Koichiro Suekuni³, Bernard Raveau¹, and Emmanuel Guilmeau¹

¹Laboratoire CRISMAT, CNRS, ENSICAEN, Université de Caen Normandie – Normandie Université ;
CRISMAT-ENSICAEN, IUT-Caen, Université de Caen Normandie, Caen, France – France

²Institut Jean Lamour – Institut de Chimie du CNRS, Université de Lorraine, Centre National de la Recherche Scientifique – France

³Interdisciplinary Graduate School of Engineering Sciences – Japan

Email : lucas.le-gars@ensicaen.fr

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 friendly thermoelectric materials. Copper-rich sulfides constitute an important class where univalent copper is the dominant element, offering the possibility of creating hole carriers in the conductive "Cu-S" network for the generation of p-type thermoelectrics. This is exemplified by minerals such as bornite (Cu_5FeS_4), germanite derivatives like $\text{Cu}_{22}\text{Fe}_8\text{Ge}_4\text{S}_{32}$, stannoidite ($\text{Cu}_8\text{Fe}_3\text{Sn}_2\text{S}_{12}$), colusites ($\text{Cu}_{26}\text{T}_2\text{M}_6\text{S}_{32}$, where $\text{T} = \text{V}, \text{Cr}, \text{Nb}, \text{Mo}, \text{Ta}, \text{W}$; $\text{M} = \text{Sn}, \text{Ge}$), synthetic compounds like Cu_2SnS_3 , kesterite ($\text{Cu}_2\text{ZnSnS}_4$), and tetrahedrites ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) (1).

A recent study of the $\text{Cu}_{2+x}\text{Sn}_{1-x}\text{S}_3$ system has unveiled the existence of a new phase $\text{Cu}_5\text{Sn}_2\text{S}_7$ ($x = 0.15$) (2). While Cl for S substitution has been already reported and shown to modify strongly the structure and thermoelectric properties (3), the effect of cationic aliovalent substitution on the transport properties has not been investigated to date. In my presentation, I will discuss the impact of Zn for Cu and Sb for Sn substitution on the crystal chemistry and thermoelectric properties of $\text{Cu}_5\text{Sn}_2\text{S}_7$.

(1) P. Lemoine et al., *Angewandte Chemie Int. Ed.* 61 (2022) e202108686

(2) V. Pavan Kumar et al., *J Mater. Chem. A.* 2021.9.10812-10826

(3) G. Guélou et al., *J. Mater. Chem. A.* 2021.33.9425-9438

High-Entropy Oxides: a new strategy for the design of innovating thermoelectric materials

A. Moll¹, A. Kumar¹, D. Berardan¹, N. Dragoe¹

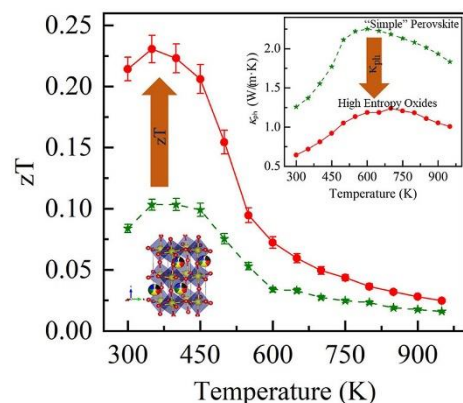
1. ICMMO (UMR CNRS 8182), University of Paris-Saclay, Orsay, 91405, France

email: adrien.moll@universite-paris-saclay.fr

High Entropy Oxides (HEOx) are a new class of materials proposed by Rost *et al.* in 2015 [1]. Similarly to high entropy alloys, HEOx are made of at least 5 cations randomly distributed on the cationic sublattice, maximizing the configurational entropy (ΔS) compared to enthalpy (ΔH) in the Gibbs free energy ($\Delta G = \Delta H - T\Delta S$). This concept opens opportunities to design new materials with tunable and unique properties. The first reported HEOx, $(\text{Mg}_{0.2}\text{Cu}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$ with rocksalt structure has shown promising properties (e.g. colossal dielectric constants [2]), and several other structures were discovered since with various possible applications.

These materials recently attracted the attention for thermoelectricity. The large lattice distortion and mass fluctuations induced by multi-cations substitution enable the strong reduction of lattice thermal conductivity. Moreover, heavy doping is usually possible to control the charge carrier concentration. A large improvement of ZT can therefore be expected in HEOx compared to their single-cation equivalents.

In this presentation we will focus on the thermoelectric properties the high-entropy rare-earth cobaltates $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Pr}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_{1-x}\text{Sr}_x\text{CoO}_3$ ($0 \leq x \leq 0.1$) [3]. We will show that the multi-cations substitution and Sr^{2+} doping result in an increased power factor compared to the single-cation compound $\text{La}_{0.95}\text{Sr}_{0.05}\text{CoO}_3$. This effect can be attributed to the variations of Co-O-Co bonds angles with ionic radii. Moreover, phonon scattering enhancement induced by the chemical and structural disorder of these systems largely reduces the lattice thermal conductivity. As a result, a maximum ZT of 0.22 is measured at 350 K in $(\text{La}_{0.2}\text{Nd}_{0.2}\text{Pr}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_{0.95}\text{Sr}_{0.05}\text{CoO}_3$, which is one of the best p -type oxide materials reported at this temperature. This result shows the interest of this strategy for the design of new thermoelectric materials.



[1] C. Rost *et al.*, Nat. Commun., 6 (2015) 8485, DOI 10.1038/ncomms9485

[2] D. Berardan *et al.*, Phys. Status Solidi RRL 10 (2016) 328–333, DOI 10.1002/pssr.201600043

[3] A. Kumar *et al.*, J Materiomics, 9 (2023) 191-196, DOI 10.1016/j.jmat.2022.08.001

Investigating Both Electronic Structure and Thermoelectric Transport Properties of SnBi_2Te_4

I. Terzi¹, K. Pryga², B. Wiendlocha², Petr Levinský³, B. Malaman¹, B. Lenoir¹, C. Candolfi

1. Institut Jean Lamour, UMR 7198 CNRS – Université de Lorraine, 2 allée André Guinier-Campus ARTEM, BP 50840, 54011 Nancy Cedex, France

2. Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Aleja Mickiewicza 30, 30-059 Krakow, Poland

3. FZU – Institute of Physics of the Czech Academy of Sciences, Cukrovarnická 10/112, 162 00, Prague 6, Czech Republic

email: llayda.terzi@univ-lorraine.fr

Homologous series of $(\text{A}^{\text{IV}}\text{Te})_n(\text{Bi}_2\text{Te}_3)_m$ in which A^{IV} is Ge, Sn or Pb and n and m are integers, are theoretically investigated as potentially useful thermoelectric compounds due to their narrow bandgap and layered, complex crystal and electronic band structures stemming from their well-known parent compound Bi_2Te_3 . Up to now, most of the results on this series have been obtained from cold-pressed samples with low density yielding moderate peak zT values of 0.25 at room temperature [1,2]. In addition, these values are likely overestimated due to the combination of in-plane and out-of-plane transport parameters. In this work, comprehensive first-principles calculations of the electronic structure of SnBi_2Te_4 will be discussed with the results of experimental thermoelectric transport properties. Additionally, optimization of the carrier concentration through doping will be further presented.

REFERENCES

[1] L.A. Kuznetsova, V.L. Kuznetsov, D.M. Rowe, *Journal of Physics and Chemistry of Solids*, **61**, 1269–1274 (2000).

[2] B.A. Kuropatwa and H. Kleinke, *Journal of Inorganic and General Chemistry*, **638**, (15), 2640–2647 (2012).

Role of dimensionality, size, and transport-direction in governing the drag Seebeck coefficient of doped silicon nanostructures: A first-principles study

Raja Sen¹, Nathalie Vast and Jelena Sjakste

1. Laboratoire des Solides Irradiés, CEA-DRF-IRAMIS, École Polytechnique, CNRS UMR 7642, Institut Polytechnique de Paris, 91120 Palaiseau, France

email: raja.sen@polytechnique.edu

Under the presence of a temperature gradient, the electric and heat currents experience a mutual drag via the interaction between charge carriers and phonons [1]. The effect of phonon-drag on the charge carriers leads to significant enhancement of the Seebeck coefficient of some materials and therefore presents a potential interest for thermoelectric devices [1]. However, the magnitude of phonon-drag, which in turn depends on the strength of carrier-phonon coupling and on the value of out-of-equilibrium phonon populations, is expected to diminish with the nanostructuring. To quantify the relative contribution of the phonon-drag Seebeck coefficient on the nanoscale, a detailed understanding of the dependence of the drag Seebeck coefficient on the dimensionality and size of nanostructures is necessary, and this can only be achieved through theory because of the impossibility to separately measure the diffusion and drag contributions to the Seebeck coefficient. In this talk, I will present our recent study of the influence of dimensionality, size reduction, and heat-transport direction in governing the drag Seebeck coefficient of doped silicon nanostructures [2]. Our theoretical approach is based on the solution of the partially coupled Boltzmann transport equations for the charge carriers and phonons, as well as on the fully ab initio description of carrier-phonon [3,4] and phonon-phonon interactions [5]. We have considered various nanostructure dimensionalities (Fig.1, left panel): 3D (grains), 2D (nanofilms) and 1D (nanowires). To the best of our knowledge, this is the first study that accounts for the anisotropy of the boundary scattering in different kinds of nanostructures as well as for the spin-orbit coupling for holes. Our results have been found in excellent agreement with the recent experimental findings of Refs. [6 a, b], concerning the impact of phonon-boundary scattering on the Seebeck coefficient of doped silicon nanowires (Fig. 1, right panel).

References : [1] J. Zhou et al., Proc. Natl. Acad. Sci. U.S. A. 112, 14777 (2015). [2] R. Sen, N. Vast, and J. Sjakste, Phys. Rev B (Letters) 108, L060301 (2023). [3] J. Sjakste et al., J. Phys. Condens. Matter 30, 353001 (2018). [4] R. Sen, N. Vast, and J. Sjakste, Appl. Phys. Lett. 120, 082101 (2022). [5] L. Paulatto et al., Phys. Rev. B 87, 214303 (2013). [6] (a) K. Fauziah et al., AIP Adv. 10, 075015 (2020), (b) N. Bennett et al., Appl. Phys. Lett. 107, 013903 (2015).

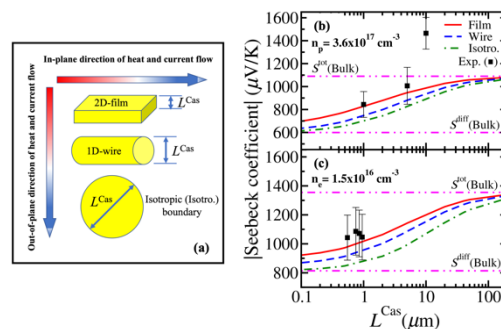


Figure 1: (Left panel): Schematic diagram shows the in-plane and out-of-plane direction of heat and current flow in the examined nanostructures. Right panel: Variation of the total Seebeck coefficient as a function of the silicon nanostructure size (L_{Cas}) at 300 K. Experimental data are from Refs. [6a, b].

Thermoelectricity and thermal transport of single molecule junctions

F. Tabatabaei¹, T. Niehaus¹ and S. Merabia¹

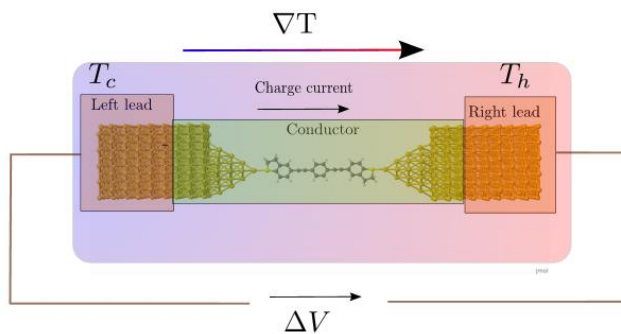
1. Institute Light and Matter, CNRS and Université Lyon 1, Villeurbanne, France

email: samy.merabia@univ-lyon1.fr

Determining the thermoelectricity of molecular junctions has encountered the difficulty of experimentally measuring thermal currents through a molecule. Very recently, the thermal conductance of single molecule junctions has been recently determined experimentally by scanning probe techniques [1,2] opening the door to quantify the thermoelectric efficiency displayed by these junctions. In this contribution, we present the thermoelectric properties of single molecule junctions as modelled by a combination of ab-initio DFT calculations and molecular dynamics simulations. We focus on junctions made of OPE3 derivatives, a single molecule commonly considered in nanoelectronics and which electronic transport properties have been extensively investigated.

We first demonstrate that first-principles calculations yield values of figure of merit in good agreement with experiments [3]. We also show that these molecule junctions may realize Peltier cooling by applying a bias voltage in a three gate terminal device [4]. We discuss how to reach optimal conditions amounting to nanoWatt cooling powers. We eventually show that cross-linking OPE3 is a promising strategy to enhance the figure of merit ZT of the molecule junction. The increase of ZT is shown to be related to the broadening and shift of the LUMO level of the molecule induced by cross-linking [5]. These results unveil an innovative strategy

to improve the thermoelectric properties of molecule junctions.



[1] Nico Mosso et al., "Thermal transport through single-molecule junctions", *Nano Letters*, 19 (2019) 7614-7622.

[2] Cui et al., "Thermal conductance of single-molecule junctions", *Nature* 572 (2019) 62

[3] A. Gemma, F. Tabatabaei et al., "Full thermoelectric characterization of a single molecule", *Nature Communications* 14 (2023) 3868

[4] F. Tabatabaei, S. Merabia, B. Gotsmann, M. Prunilla and T. Niehaus, "Molecular electronic refrigeration against parallel phonon heat leakage channels" *Nanoscale* 14, 11003 (2022);

[5] F. Tabatabaei et al., "Enhanced thermoelectric efficiency of cross-linked single molecule junctions", to be submitted

Acknowledgements: This work has been financially supported by the EU project EFINED (Project No. 76685).

Density Functional Theory Investigation of High Performance Thermoelectric Ge-Sb-Te Nanosheets

P. Boulet¹, J. TIAN^{1,2}, W. MA^{1,2,3}, M.-C. Record²

1. MADIREL, Aix-Marseille Université, Avenue de l'Escadrille Normandie-Niemen, 13013 Marseille, France

2. IM2NP, Aix-Marseille Université, Avenue de l'Escadrille Normandie-Niemen, 13013 Marseille, France

3. IJL, Université de Lorraine, Campus Artem, 2 allée André Guinier, BP 50840, 54011 Nancy Cedex, France

email: pascal.boulet@univ-amu.fr

The Ge-Sb-Te system compounds are well-known for decades for their properties as phase change materials used in information storage and retrieval applications. However, in recent years, 2D GeSb₂Te₄, which possesses a narrow band gap of 0.80 eV, have been investigated by theoretical approaches for potential thermoelectric applications [1]. The authors observed n-type power factors as high as 70.4 mW/(Km²) resulting in a zT value of 1.6 at 300 K and 3.8 at 700 K. This suggests that low-dimensional structures indeed offer superior thermoelectric performance for this materials family.

In this presentation, we will present the thermoelectric properties obtained from density-functional theory calculations coupled with the Boltzmann transport approach on the Sb₂Te₃, GeSb₂Te₄ and Ge₂Sb₂Te₅ in the form of bulk compounds as well as of nanosheets. We will show that the quantum confinement effect in the nanosheets effectively increases the Seebeck coefficient, reduces the thermal conductivity, and enhances the efficiency of the thermoelectric materials.

Reference

[1] Fang, W.-Y.; Rao, X.-X.; Cheng, J.; Xue, P.; Sheng, X.-f.; Liu, C.-J.; Zhang, P.-C. Vacuum 2023, 216, 112490.

Effect of Low Purity Elements on Thermoelectric Performance of In-filled Skutterudites

R. Bhardwaj¹, E. Alleno¹

¹Univ Paris Est Creteil, CNRS, ICMPE, UMR 7182, 2 rue Henri Dunant, 94320 Thiais, France

* The corresponding author e-mail: ruchi.bhardwaj@cnrs.fr

Keywords: Skutterudites, Cost-effective, Low-Purity, Power Generation,

Thermoelectric Generators (TEGs) are one of the alternatives for clean power generation, and their performance is strongly influenced by the properties of the material used in the device fabrication. For the commercialization purpose of TEGs, the main objective is to enhance the figure of merit and reduce the processing cost of the materials used in the device.

However, the cost and availability of high-purity elements have been identified as one of the hurdles to the widespread applications of thermoelectric (TE) materials. This has led to increased interest in the use of low-purity elements to synthesize efficient TE materials. Skutterudites (SKDs) based materials emerged as potential candidates for mid-temperature TE applications owing to their high thermal and chemical stability, mechanical strength, possibility of synthesizing similar n- and p-type materials and cost-effectiveness^{1,2}.

In the present work, we studied the effect of low-purity elements on the structural and TE properties of the n-type In-filled Co₄Sb₁₂ alloy. A series of samples with different levels of impurity elements were synthesized by the conventional melting-annealing process and consolidated by SPS. ICP analysis was performed to determine the impurity elements present in the precursors, which revealed that Pb is the major impurity. The presence of Pb in the synthesized samples was further confirmed by EDS and EPMA, which shows the formation of an In-Pb-Sb secondary phase that resulted in lesser In-content in the synthesized n-type alloy. This loss was partially compensated by taking an excess amount of In, which resulted in TE performance with a $ZT = 0.95$ at 750 K. This value is slightly lower than that achieved for the composition In_{0.22}Co₄Sb₁₂ synthesized using high-purity precursors. A detailed comparison between ZT values and the cost of the optimized alloys, shows that an excellent compromise between these two crucial parameters can be reached by using low-purity elements for the synthesis³.

Acknowledgments

This work was supported by the *Agence nationale de la recherche* project I-Hephaistos (ANR-21-CE08-0049).

References

- (1) Rull, M.; Moure, A.; Fernandez, J. F. F.; Martin-Gonzalez, M. S. Skutterudites as thermoelectric material: revisited. *RSC Advances* **2015**, *5*, 41653, 10.1039/C5RA03942H.
- (2) Rogl, G.; Rogl, P. Skutterudites, a most promising group of thermoelectric materials. *Current Opinion in Green and Sustainable Chemistry* **2017**, *4*, 50-57. DOI: <https://doi.org/10.1016/j.cogsc.2017.02.006>.
- (3) Chemdirect. <https://www.chemdirect.com/product-list/c/all?q=antimony%20powder> (Accessed on Apr 2023).

High thermoelectric performance in ZrNiSn through electron injection and boosting carrier mobility

Chuang Jia^{1,2}‡, BeiBei Zhu^{1,2}‡, Changmeng Pang^{1,2}, ChenChen Yuan^{1,2}, PengFei Xu³, Biao Xu³, Jing Bai^{1,2}, Li Tao^{1,2}, Feng Xue^{1,2}, Guodong Tang⁴**

¹School of Materials Science and Engineering, ²Jiangsu Key Laboratory for Advanced Metallic Materials, Southeast University, Nanjing 211189, China

³School of Chemical Engineering, Nanjing University of Science and Technology, Xuanwu, Nanjing 210094, China

⁴MIIT Key Laboratory of Advanced Metallic and Intermetallic Materials Technology, School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China.

* Authors to whom correspondence should be addressed: xuefeng@seu.edu.cn and tangguodong@njust.edu.cn

Abstract

Inert insulating oxides have been used as phonon scattering centers to reduce the lattice thermal conductivity of half-Heusler thermoelectric materials, but they often cause a decline in the electrical transport performance. In this work, the in-situ conductive semi-metal ZrTe₂ makes 15% decreased thermal conductivity and 42% increased electrical conductivity in ZrNiSn simultaneously. When the phase boundary scatters the mid-long wavelength phonons, it is not the obstacle for the electrons. Thanks to the decreased interfacial energy barrier and high mobility electron injection from ZrTe₂, even when the charge carrier concentration increases by 56% due to the in-situ ZrTe₂ induced bandgap decreasing, 190% improved mobility is also obtained. High zT ~0.9 is achieved at 873K in 4 at.% Te composited ZrNiSn through electron injection and boosting carrier mobility. These results have suggested a promising way to decouple the electron and phonon transport behaviors via forming the in-situ conductive secondary phase.

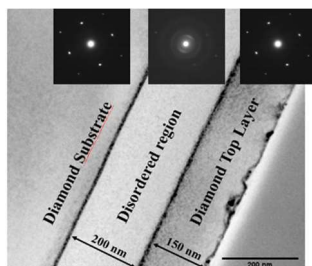
Electronic/thermal transport and thermoelectric phenomena in implanted diamond nanostructures

S. Salami¹, S. Pailhès¹, C. Adessi¹, V. Giordano¹, N. Mahonisi^{2,3}, Z. Mthwesi², S. Vignoli¹, R. Debord¹, R. Fulcrand⁴, N. Blanchard¹, A. Every², S. R. Naidoo^{2,3,5}

1. Institute of Light and Matter, CNRS, and University Lyon 1, Lyon, France
2. Department of Physics, University of Witwatersrand, Johannesburg, South Africa
3. DSI-NRF Centre of Excellence in Strong Materials, Wits University, Johannesburg, South Africa
4. Center for Structural Biology, CNRS, and Institute of Electronics and Systems, Montpellier, France
5. Materials Physics Research Institute (MPRI), Wits University, Johannesburg, South Africa

email: sana.salami@univ-lyon1.fr

The interaction between phonons and electrons is known to be at the origin of large values of the Seebeck coefficient at low temperatures, a phenomenon known as “phonon drag” in the Seebeck perspective in which a fraction of the phonon momentum, induced by an applied thermal gradient, is transferred to the electron gas. While phonon-drag produces high Seebeck values, the thermoelectric community has long ignored it, since it is associated with phonons of long mean free paths and therefore high lattice thermal conductivity. This was the case until 2008 when Boukai et al. [A. I. Boukai, et al., *Nature*, 451, 168–171 (2008)] confirmed in a study with Silicon nanowires, that it is possible to have a large phonon drag at high temperatures even if the system has low thermal conductivity. In 2015, the group of ZX Chen, at MIT published a paper where they rationalized it with ab-initio simulations by considering the coupling between the two Boltzmann equations (electron and phonon transport) through the electron-phonon interaction [J. Zhou et al., *Proc. Natl. Acad. Sci.*, 112, 14777–14782 (2015)]. In this project, we investigate the thermal and electronic transport properties of conductive channels embedded in crystalline diamonds. We aim to separate the phonon gas and the electron gas into two different media and try to have them interact to produce the phonon drag effect. In this oral presentation, I will discuss the realization of buried graphitic channels, our first transport measurements, and discussions.



A transmission electron microscopy image of one of our implanted diamonds illustrates the buried channel (disordered carbon) embedded in a crystalline diamond.

Insight on the stability of thermoelectric $\text{Mg}_2(\text{Si},\text{Sn})$ and the role of Mg diffusion

A. Duparchy^{1*}, J. Camut¹, A. Sankhla¹, S. Ghosh¹, B. Ryu², S. Park², S. Park², R. Deshpande¹, E. Mueller^{1,3}, J. de Boor^{1,4**}

¹ Institute of Materials Research, German Aerospace Center (DLR), D–51170 Cologne, Germany

² Energy Conversion Research Center, Electrical Materials Research Division, Korea Electrotechnology Research Institute (KERI), Changwon 51543, South Korea

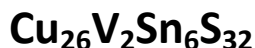
³ Institute of Inorganic and Analytical Chemistry, Justus Liebig University Giessen, Heinrich-Buff-Ring 17, D–35392 Giessen, Germany

⁴ University of Duisburg-Essen, Faculty of Engineering, Institute of Technology for Nanostructures (NST) and CENIDE, 47057 Duisburg, Germany

Corresponding Author(s): amandine.duparchy@dlr.de*, Johannes.deBoor@dlr.de**

$\text{Mg}_2(\text{Si},\text{Sn})$ is a promising thermoelectric material due to its high performance and its non-toxic, abundant, and low-cost constituents. A lot of progress has been made in optimizing its thermoelectric properties and to use it for technological application. Nevertheless, the chemical stability of these materials is a significant challenge to overcome. Temperature dependent measurements of transport properties suggests that the thermal stability of n-type $\text{Mg}_2(\text{Si},\text{Sn})$ is not only compromised at elevated temperatures but might be limited already at room temperature. In this work, integral thermoelectric properties measurement, locally resolved Seebeck analysis, scanning electron microscopy with energy dispersive X-ray spectroscopy and atomic force microscopy are introduced to assess bulk and surface microstructural changes of n-type samples stored at room temperature in ambient atmosphere for several years. The study reveals changes in carrier concentration and surface degradation for the material over time, driven by Mg diffusion which seems to be highly dependent on the Si:Sn ratio. First-principles calculations conducted by researchers at KERI (South Korea) are employed to develop a microscopic understanding which indicate that Mg diffusion occurs mainly via vacancies at the Mg site. This study elucidates a multi-step degradation mechanism for n-type $\text{Mg}_2(\text{Si},\text{Sn})$ which consists of: (i) diffusion of Mg from the matrix to the grain boundaries, (ii) diffusion of Mg along the grain boundaries towards the surface and (iii) Mg reaction with moisture, causing deterioration of the material's thermoelectric properties.

In situ diffraction study of the phase transformations occurring at high temperature in the thermoelectric colusite



Florentine Guiot,^{a,*} Abdelhamid Bourhim,^b Gabin Guélou,^b Catherine Dejoie,^c Andy Fitch,^c Emmanuel Guilmeau,^b Pierric Lemoine,^d Carmelo Prestipino.^{a,b}

^a Univ. Rennes, CNRS, ISCR-UMR 6226, F-35000 Rennes, France

^b Laboratoire CRISMAT, UMR 6508, CNRS, ENSICAEN, 14050 Caen, France

^c ID22, Structure of Materials Group ESRF - The European Synchrotron 38043 Grenoble, France

^d Institut Jean Lamour, UMR 7198, CNRS, Université de Lorraine, 54011 Nancy, France

* florentine.guiot@univ-rennes.fr

Advancements in the field of materials science, particularly those for energy conversion and storage, have progressed significantly thanks to the capabilities offered by large-scale facilities, such as synchrotrons and neutron sources, in term of *in situ* and *operando* diffraction analyses, see for example¹ and references therein. In comparison to routine laboratory analyses, these facilities provide enhanced resolution and improved sensitivity, enabling a thorough characterization of materials. Given that during operating, thermoelectric (TE) materials are exposed to temperature gradient, the understanding of their thermal properties, thermal stability and phase transitions is of prime interest. Knowledge of their thermal expansion behaviour is also crucial to develop TE devices.

Colusites, of general formula $\text{Cu}_{26}\text{A}_2\text{E}_6\text{S}_{32}$, ($\text{A} = \text{Ti}, \text{V}, \text{Nb}, \text{Ta}, \text{Cr}, \text{Mo}, \text{W}$, and $\text{E} = \text{Ge}, \text{Sn}, \text{As}, \text{Sb}$), are considered as promising high-performance TE sulphides². Among this family, V-Sn colusite (*i.e.* $\text{Cu}_{26}\text{V}_2\text{Sn}_6\text{S}_{32}$) is characterized by a ZT value close to unity at 675K³, making this material one of the best p-type TE sulphides in this temperature region⁴. Its performances are mainly related to glasslike thermal conductivity induces by the coexistence of an ordered and a disordered form, this latter being favoured by high temperature exposure^{3,5}. However, the formation mechanism of this disordered form, supposed to be a transformation of the ordered one through sulphur volatilization, is not yet fully understood. Moreover, in some conditions of synthesis, V-Sn colusite samples can be formed by two crystallographically related phases (reported as Sn-rich and Sn-poor phases) with at least one of them being colusite^{2,6-9}. The level of caution related to the nature of the second phase, although it appears to be a second colusite phase with a slightly different unit cell parameter, stems from the difficulty to correctly identify the peak splitting for the low-angle superstructure².

In order to better understood the thermal behaviour of this promising TE material, we performed X-ray diffraction analyses on high-resolution synchrotron ID22 beamline at ESRF, Grenoble, France. The results and our conclusion, as well as the sequential method used to refine the diffraction data allowing to improve the quality of the results, will be presented in this oral presentation.

- (1) Paradis-Fortin, L et al., Time-Resolved In Situ Neutron Diffraction Study of $\text{Cu}_{22}\text{Fe}_8\text{Ge}_4\text{S}_{32}$ Germanite: A Guide for the Synthesis of Complex Chalcogenides. *Chem. Mater.* **2020**, *32* (20), 8993–9000. <https://doi.org/10.1021/acs.chemmater.0c03219>.
- (2) Guélou, G et al., Recent Developments in High-Performance Thermoelectric Sulphides: An Overview of the Promising Synthetic Colusites. *J. Mater. Chem. C* **2021**, *9* (3), 773–795. <https://doi.org/10.1039/D0TC05086E>.
- (3) Bourgès et al., High-Performance Thermoelectric Bulk Colusite by Process Controlled Structural Disorder. *J. Am. Chem. Soc.* **2018**, *140* (6), 2186–2195. <https://doi.org/10.1021/jacs.7b11224>.
- (4) Powell, A. V. Recent Developments in Earth-Abundant Copper-Sulfide Thermoelectric Materials. *J. Appl. Phys.* **2019**, *126* (10), 100901. <https://doi.org/10.1063/1.5119345>.
- (5) Candolfi, C et al., Disorder-Driven Glasslike Thermal Conductivity in Colusite $\text{Cu}_{26}\text{V}_2\text{Sn}_6\text{S}_{32}$ Investigated by Mössbauer Spectroscopy and Inelastic Neutron Scattering. *Phys. Rev. Materials* **2020**, *4* (2), 025404. <https://doi.org/10.1103/PhysRevMaterials.4.025404>.
- (6) Spry, P. G et al., New Occurrences and Refined Crystal Chemistry of Colusite, with Comparisons to Arsenosulvanite. *American Mineralogist* **1994**, *79* (7–8), 750–762.
- (7) Suekuni et al., High-Performance Thermoelectric Minerals: Colusites $\text{Cu}_{26}\text{V}_2\text{M}_6\text{S}_{32}$ ($\text{M} = \text{Ge}, \text{Sn}$). *Appl. Phys. Lett.* **2014**, *105* (13), 132107. <https://doi.org/10.1063/1.4896998>.
- (8) Bourgès et al., Structural Analysis and Thermoelectric Properties of Mechanically Alloyed Colusites. *Journal of Materials Chemistry C* **2016**, *4* (31), 7455–7463. <https://doi.org/10.1039/C6TC02301K>.
- (9) Kim, F et al., Tuning the Charge Carrier Density in the Thermoelectric Colusite. *Journal of Applied Physics* **2016**, *119* (17), 175105. <https://doi.org/10.1063/1.4948475>.

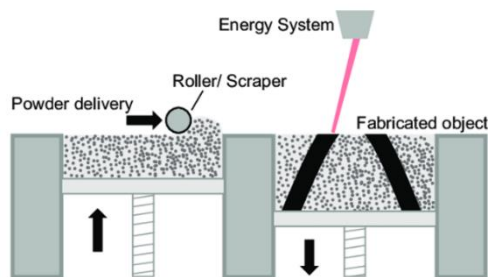
Nanostructuring of silicon germanium produced by additive manufacturing

M. Baudry¹, G. Savelli¹, G. Roux¹

1. CEA Liten, Université Grenoble Alpes

email: maxime.baudry@cea.fr

Among Additive Manufacturing (AM) methods, Laser Powder Bed Fusion (L-PBF), also called Selective Laser Melting (SLM), is prevalent to printing complex metal parts in small and medium series. Recent studies in L-PBF processing develops the manufacturing of new materials, including thermoelectric (TE) materials. In our previous work, we produced for the first time dense silicon germanium parts by L-PBF process. Unfortunately, mechanical cracking occurs in all samples, which hinders electrical conductivity and therefore their viability as TE materials. In this work, we present an approach with the goal to improve mechanical properties of the material while also improving phonon scattering: nanostructuring. If this strategy has already been applied to TE materials obtained by other technologies (SPS, HIP, etc.), it has never been applied to overall TE materials developed by AM. Nanostructuring in L-PBF can be accomplished by including elements that can solidify before the matrix into nanoinclusions. Then, these nanoinclusions acts as nucleation sites for matrix grains. As more grains nucleate simultaneously, grain size of the material is reduced, improving its mechanical properties. A specific study has been performed to define the best candidates for nanoparticles. Then they have been used for the p-type $\text{Si}_{85}\text{Ge}_{15}$ manufacturing. Finally, structural analyses and TE properties measurements were conducted on the nanostructured SiGe. Results of these investigations will be discussed in this presentation.



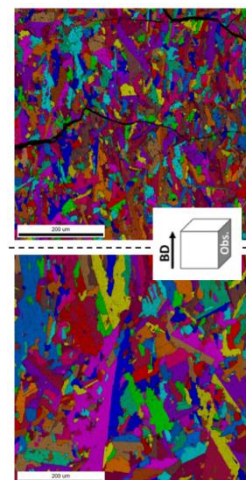
L-PBF Process



Principle and advantages of L-PBF process

SiGe + Nanoparticles
Less elongated dendrites
Grain size reduction

SiGe without nanoparticles



EBSD comparison of SiGe samples with and without nucleating agents

Posters

A p-type Semi-Conducting Copper(I)-1,3-Benzenedithiolate 2D Coordination Polymer with High Seebeck Coefficient

Andrade¹, Hawila¹, Abdallah¹, Rukemampunzi¹, Mesbah¹, Guillou², Perret³, Wuttke⁴, Niehaus⁵, Debord⁵, Boisron⁵, Pailhès*⁵ and Demessence*¹

1. UCBL, IRCELYON, UMR CNRS 5256, Villeurbanne, France.
2. Université Paris-Saclay, UVSQ, CNRS, ILV, UMR 8180, Versailles, France.
3. UCBL, CNRS-INSA Lyon-CPE Lyon, ICBMS, UMR 5246, Villeurbanne, France.
4. BCMaterials, UPV/EHU, Bilbao, Spain.
5. UBCL, CNRS, ILM, UMR 5306, Villeurbanne, France.

email: chloe.andrade@univ-lyon1.fr

During the past two decades, coordination polymers (CPs) have emerged as a highly versatile platform for wide-ranging potential applications from gas storage to separations, heterogeneous catalysis, and biomedicine, among others. These are crystalline extended networks consisting of metal ions and multidentate ligands, where metal ions act as nodes between the bridging ligands. Metal Organic Thiolates (MOT) CPs have appeared as stable and highly electrical conducting materials, with a record of 1580 S.cm^{-1} for the 2D copper-benzenehexathiolate CP [1]. Thus, conducting CPs could provide vast potential technological impacts especially because their structural complexity, which provides additional possibilities and a route for disentangling the electronic transport and the heat transport as needed for optimizing the heat conversion into electricity by the TE effects. In this poster, we will present the synthesis, the structural characterization and the transport measurements (conductivity and Seebeck) of a new p-type semi-conducting CP, the copper(I)-1,3-benzenedithiolate (Figure 1.), made of thiolate-based ligand and Cu(+I) which is stable up to 200 °C under air. While this CP has a 2D structure, our structural and theoretical studies reveal that the electronic conduction is mostly dominated by the electronic states from CuS chains embedded in the organic matrix. The 1D character of the electronic bands lead to high Seebeck values with an anomalous temperature dependence [2].

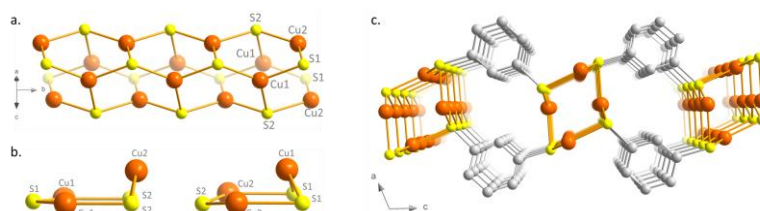


Figure 1. Structure of $[\text{Cu}_2(1,3\text{-BDT})]_n$: a. the Cu-S chain along the b axis; b. the two deformed Cu_2S_3 hexagons and c. the central projection along the b axis. Orange, yellow and gray spheres correspond to copper, sulfur and carbon atoms. Hydrogen atoms were omitted for clarity.

[1] X. Huang, H. Yao, Y. Cui, W. Hao, J. Zhu, W. Xu, D. Zhu, *ACS Appl. Mater. Interfaces* **2017**, 9, 40752-40759.

[2] C. Andrade, S. Hawila, A. Abdallah, J.-L. Rukemampunzi, A. Mesbah, N. Guillou, F. Perret, S. Wuttke, T. Niehaus, R. Debord, O. Boisron, S. Pailhès and A. Demessence, *J. Mater. Chem. C*, **2023**, <https://doi.org/10.1039/D3TC02379F>

This work was supported by the French National Agency (MOTIC ANR-21-CE08-0045).

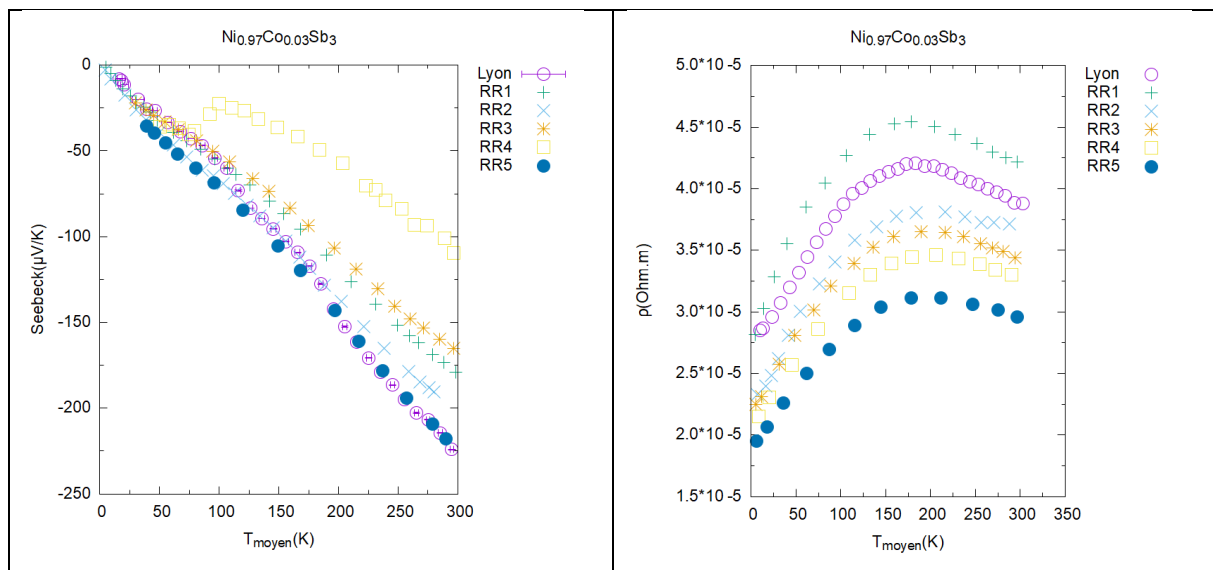
Presentation of a homemade apparatus for Seebeck coefficient and electrical resistivity measurements at low temperatures

Régis Debord¹, Stéphane Pailhès¹, Valentina Giordano¹

1. Institut Lumière Matière (ILM), UMR5306 - UCBL - CNRS, 10 rue Ada Byron, Villeurbanne CEDEX, 69622, France

email: regis.debord@univ-lyon1.fr

We will present a homemade apparatus for simultaneous measurement of Seebeck coefficient and electrical resistivity at cryogenic temperature with a Helium free compressor system that allow us to reach 10K, basic commercial electronics for measurements and thermal regulation. Thermal design and the user interface will also be discussed. The main aspects of both measurements will be resumed. We will show the ability of the bench to work on thin layer as well as bulk material. For comparison we will show the measurements on our set up with the round robin test that the GIS-TE has published few years ago on $\text{Ni}_{0.97}\text{Co}_{0.03}\text{Sb}$. [1]



1.E. Alleno et al, Invited Article: A round robin test of the uncertainty on the measurement of the thermoelectric dimensionless figure of merit of $\text{Co}_{0.97}\text{Ni}_{0.03}\text{Sb}_3$, REVIEW OF SCIENTIFIC INSTRUMENTS 86, 011301 (2015)

Additive manufacturing of the full-Heusler Fe_2VAI compound by laser powder bed fusion

M. Delcroix ¹, G. Roy ¹, C. van der Rest ¹, V. Marchal-Marchant ¹, P.J. Jacques ¹

1. IMAP,IMMC, UCLouvain. Place du Levant 2, boîte L5.04.01, 1348, Louvain-la-Neuve

email: mathieu.delcroix@uclouvain.be

The digitalization of our society relies on an increased availability of electrical energy sources to power interconnected sensors, transmitters, actuators, ... Surrounding thermal energy could offer the opportunity of autonomous devices owing to thermoelectric generators (TEGs). However, widespread use of such thermoelectric generators requires both the availability of materials and the efficiency of assembled modules. This study focuses on the fabrication of TE modules based on the Heusler compound Fe_2VAI owing to Laser Powder Bed Fusion (L-PBF) manufacturing. This process allows obtaining complex and topologically optimized parts while limiting the assembly steps, bringing a significant advantage.

In this study, the printability of n-type $\text{Fe}_2\text{VAI}_{0.9}\text{Si}_{0.1}$ by L-PBF has been investigated. In the initial step, single scan tracks were examined to ensure the continuity of the melt pools and their overlapping to achieve fully dense parts. The process parameters that yielded ideal single scan tracks were used to print cubes. However, heat accumulation in the parts led to destructive warping. By reducing the laser power, it became possible to print rods with an acceptable density. It has been observed that within various ranges of process parameters, the maximum value of the Seebeck coefficient is not affected, but the electrical conductivity drops dramatically at the same level. This drop is believed to be due to the high density of cracks oriented in the building direction.

To fully characterize the TE performances of the printed materials, p- and n-type TE legs were printed. These legs were assembled into two small π -TEGs: the first with the building direction of the legs parallel to the heat flux and the second with the building direction of the legs perpendicular to the heat flux. The assembly was done through silver brazing in a hot-press. The characterization of these modules revealed unexpected results: the Seebeck coefficient of the printed legs decreased, but the electrical conductivity partially recovered after the brazing process. Moreover, the orientation of the legs with respect to the building direction appeared to have only a slight effect on the TEG performance. These results are still under investigation.

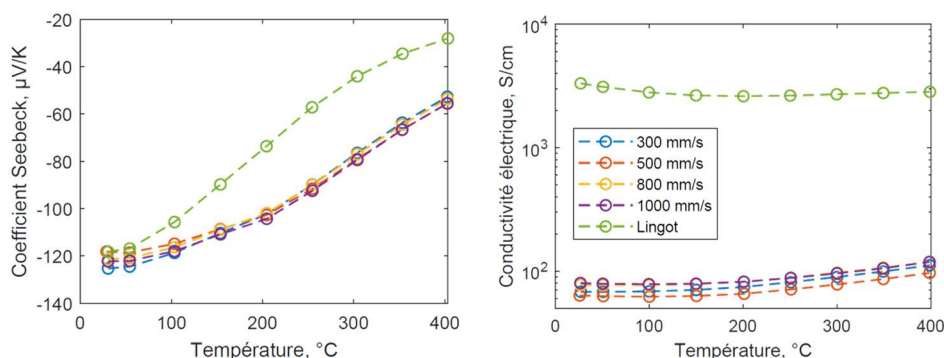


Figure 1 Seebeck coefficient and electrical conductivity measured on printed rods with different laser speeds and the original ingot.

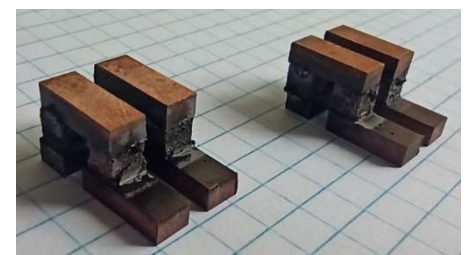


Figure 2 Picture of the two small TEGs with printed legs

Synthesis and characterization of zinc oxide (ZnO) for heat-to-electricity conversion

N. DRAME

1. ULCO, UDSMM, MREI-1, 59140 Dunkerque, France

email: nouhadrame85@gmail.com

This thesis is in the field of energy. It deals with the conversion of heat that can be recovered and transformed into electricity from a material subjected to a temperature difference. This phenomenon, known as the thermoelectric effect, opens up the possibility of energy conversion applications using low-cost materials. The first involves preparing zinc oxide (ZnO) and doping it with aluminum, iron or nickel, with the aim of optimizing its thermoelectric parameters. The second part of the work consists in measuring these thermoelectric parameters and assessing the material's conversion efficiency by calculating the ZT figure of merit. The last part of the work concerns the realization of a device for recovering waste heat for conversion into electricity using a doped ZnO ceramic. As part of the National Thermoelectricity Day, we will present the initial results of the synthesis of pure ZnO by the Pechini method and aluminum-doped ZnO. We will also present the electrical and dielectric parameters of ZnO.

Lattice dynamics study of thermoelectric cubic SrSi₂ by Raman scattering experiments and ab initio calculations

R. Ghannam¹, J. Rouquette¹, M. Beaudhuin^{1*}, R. Viennois^{1*}

1. Institut Charles Gerhardt Montpellier, CNRS-UM-ENSCM, Montpellier, France

email: mickael.beaudhuin@umontpellier.fr, romain.viennois@umontpellier.fr

Thermoelectric materials (TEM) attract high interest from many fields of science as a potential green energy resource. For a few decades the TEM community has been on the quest for more efficient and environment friendly compounds. At present, the drawback of the best-performing TEM compounds is their toxicity, rareness, and/or costs of the chemical elements they are synthesized from. For this reason, silicides have attracted high interest because they are made of abundant, cheap, and non-toxic elements.

Among silicides, cubic SrSi₂ has attracted the attention because of its good thermoelectric properties at the vicinity of the room temperature. A ZT of 0.15 was obtained for undoped SrSi₂ at 300 K [1] and ZT as large as 0.4 was reached for yttrium-doped SrSi₂ at 300 K [2] thanks to its moderate thermal conductivity ($\kappa = 4\text{-}5\text{ W/m.K}$) [1-2] compared to most of the silicides [3] and despite its simple cubic crystal structure containing 12 atoms. This suggests higher anharmonicity in SrSi₂ than in other silicides. Recent theoretical works suggested that cubic SrSi₂ could be a topological Weyl semimetal [4] and the presence of quadratic double-Weyl phonons [5], making this material very attractive for topological science. However, despite the interest of this material, until now there is no experimental study of the lattice dynamics and the DFT study in ref. 5 was limited to the phonon dispersion curves of SrSi₂. We have therefore began to study the lattice dynamics of SrSi₂ both theoretically and experimentally.

In the present work, we present a combined pressure dependent Raman scattering study and ab initio study of the lattice dynamics of cubic SrSi₂. We find 5 of the 8 Raman-active modes predicted by the theory, but one of the missing mode is overlapping another observed mode. Good agreement is found for the frequencies and the calculated Grüneisen parameters follow qualitatively the experimental trend. We notably show that the phonons in the intermediate range $150\text{-}300\text{ cm}^{-1}$ have low Grüneisen parameters (less than 1) whereas moderate Grüneisen parameters (above 1) were found above 300 cm^{-1} . However, we found that the low energy optical mode predicted at 7.5 meV, which is optically silent, has large Grüneisen parameter (about 2.5) and its interaction with the acoustical phonons could explain the rather low lattice thermal conductivity of SrSi₂ compared to most of the silicides.

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

Arige Hodroj¹, V. Bouquet¹, C. Prestipino², V. Demange¹, R. Lebullenger¹, M. Pasturel¹

1. Univ Rennes, CNRS, Institut des Sciences Chimiques de Rennes – UMR6226, 35042 Rennes, France
2. Univ Normandie, CNRS, Laboratoire de Cristallographie et Sciences des Matériaux – UMR6508, 14050 Caen, France

In the realm of thermoelectric materials, Skutterudites derived from CoSb_3 have gained prominence as mid-temperature range candidates due to their unique properties. They exhibit interesting electronic properties, including elevated hole mobility and a large Seebeck coefficient. Moreover, their thermal conductivities can be significantly diminished through the incorporation of 'rattlers' within their large structural voids, enabling them to attain impressive performances with figure-of-merit values nearing 2 [1,2].

The synthesis of skutterudites using conventional melting and solidification methods presents challenges, primarily due to their slow double-peritectic formation at "low" temperatures, necessitating prolonged annealing processes. As a response, alternative approaches have been explored, with recent developments in magnesiothermic synthesis showing promise in simplifying and expediting the process [3,4].

The magnesiothermic method consists in the reduction of metal oxides by magnesium. This method offers several advantages over traditional ones, including the use of stable oxide precursors, which are cost-effective and stable in air. Additionally, it operates at lower temperatures and shorter reaction times, thanks to the high reducing power of magnesium. Importantly, it also holds the potential to scale up the synthesis process due to its simple straightforward experimental setup.

In this poster presentation, we discuss preliminary findings regarding the scalability of the magnesiothermic method for both n-type skutterudites ($\text{In}_{0.22}\text{Co}_4\text{Sb}_{12}$) and p-type skutterudites ($\text{Ce}_{0.8}\text{Fe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$). These results hold promise for streamlining the synthesis of skutterudites and advancing their potential for thermoelectric applications.

References

- [1] G. & P. Rogl, *Cur. Op. Green Sust. Chem.*, 4 (2017) 50-57
- [2] G. Rogl *et al.*, *Acta Mater.*, 95 (2015) 201-211
- [3] S. Le Tonquesse *et al.*, *J. Alloys Compd.*, 796 (2019) 176-184
- [4] S. Le Tonquesse *et al.*, *Mat. Today Chem.*, 16 (2020) 100223

Thermo-osmosis on graphitic surfaces: the influence of enthalpy excess

Mehdi Ouadfel

1. Institut Lumière Matière (ILM)

Université Claude Bernard Lyon 1, Centre National de la Recherche Scientifique

UMR5306 CNRS Université Claude Bernard Lyon 1 Domaine Scientifique de La Doua Bâtiment Kastler, 10 rue Ada Byron 69622 Villeurbanne CEDEX, Franc - France

email: mehdi.ouadfel@univ-lyon1.fr

Nanofluidic system offer great promises for energy conversion. In particular, thermo-osmosis, a phenomenon in which a thermal gradient along an interface sets a fluid in motion, can be used to convert waste heat into electricity. Thermoosmosis largely depends on two parameters: the slip length and the enthalpy excess.

Here we used MD simulations to study the thermo-osmosis of an aqueous electrolyte confined between graphitic surfaces. In particular, we showed that calculating the enthalpy excess is sufficient to predict the direction and the amplitude of the flow generated. We also revealed the great impact of the surface charge density and the charge distribution on thermo-osmosis,

Implantation effects on the thermoelectric properties of scandium nitrides thin films.

C. Poterie¹, R. Burcea¹, H. Bouteiller¹, P. Eklund², A. le Febvrier², and J.-F. Barbot¹.

1. Institut PPRIME, CNRS, Université de Poitiers–ENSMA, UPR 3346, SP2MI, TSA 41123, 86073 Poitiers cedex 9, France

2. Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden

email: charlotte.poterie@univ-poitiers.fr

Ion implantation is widely used in the semiconductor industry to control electrical conductivity (dopant incorporation), but also to introduce specific defects such as platelets in the smart cut™ process. In our work we show that this process can be used to manage both the electrical (σ) and thermal conductivity (k) as well as the Seebeck coefficient (S) of thermoelectric materials. To this purpose, n-type degenerated ScN thin films grown by magnetron sputtering were implanted with different types of ions (noble gases or others) and their physical properties are being studied in relation with the microstructural modifications. As example, the figure below shows the effect of argon implantation (5 dpa, RT) on the microstructure of the film and on its TE properties. As depicted Fig. 1, thermal conductivity at RT is divided by 4 after implantation, highlighting the enhanced phonon scattering by the as-introduced defects. In addition, the value of the Seebeck coefficient measured over a wide temperature range also increases. Experiments are underway to better understand the role of different types of defects on the observed changes in properties.

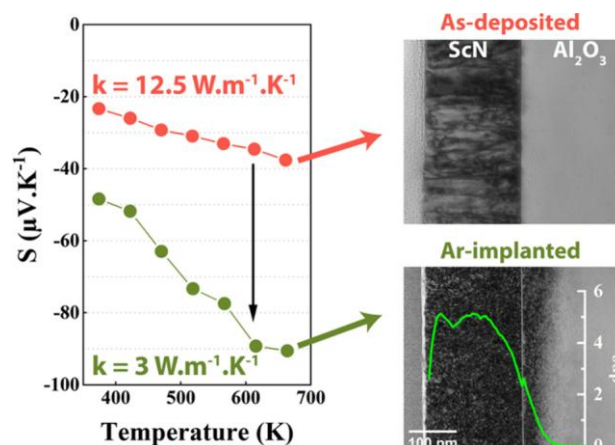


Figure 1 - Effects of Ar-implantation on the structural and TE properties of ScN films [1]

References

- [1] R. Burcea, J.-F. Barbot, P. O. Renault, D. Eyidi, T. Girardeau, M. Marteau, F. Giovannelli, A. Zenji, J.-M. Rampoux, S. Dilhaire, P. Eklund, and A. le Febvrier, ACS Appl. Energy Mater. 5, 11025 (2022)

Screening New Quaternary Semiconductor Heusler Compounds By Machine-Learning Methods

R. Xie¹, J.-C. Crivello¹, C. Barreteau³

1. Univ Paris Est Creteil, CNRS, ICMPE, UMR 7182, 2 rue Henri Dunant, 94320 Thiais, France

email: runan.xie@cnrs.fr

The following work presents a theoretical workflow to accelerate the discovery of new quaternary Heusler compounds for thermoelectric applications. The process consists of several steps: (i) construction of a consistent home-made DFT learning database with a limited set of compounds mainly involving unary, binary, and ternary configurations; (ii) machine-learning regression to estimate the heat of formation for all possible arrangements of atoms in the 4 crystallographic sites of the Heusler phase; (iii) classification learning to predict the semiconductor (SC) feature; (iv) verification of stable SC compounds through a convex hull analysis of the ground state for each quaternary system; and (v) phonon calculation to check the mechanical stabilities of the final candidates. From a selection of 24 chemical elements, 13 272 unique DFT calculations were performed among all $24^4 = 331\,776$ configurations. The learning and screening process led to predict the properties of all quaternaries ($24 \times 23 \times 22 \times 21 = 255\,024$) along with the discovery of 8 new stable semiconducting compounds (TaAlCoMn, TaSiFeMn, NbAlCoMn, NbSiFeMn, ...), promising potential interest in thermoelectric properties.

Design and use of membranes suspended on silicon as nanothermogenerators

Florentin Chambettaz

MOIZ

Avec l'émergence de protocoles de communications basse consommation dédiés aux réseaux de capteurs sans fils, il existe désormais une réelle demande pour des micro-sources d'énergie capables d'alimenter les batteries. Cette plage de puissance peut être obtenue à partir d'un thermogénérateur (TEG) standard avec un gradient de température de quelques degrés dans des conditions de fonctionnement stationnaires. Cependant, ces conditions d'utilisation ne sont pas forcément adaptées aux petits capteurs sans fil notamment lorsque la source d'énergie est intermittente et/ou le volume disponible trop limité pour contenir le TEG macroscopique. Pour cette raison, un intérêt croissant a émergé concernant la conception de nouveaux micro-thermogénérateurs utilisant une configuration planaire et suspendue. L'avantage majeur de cette configuration est qu'elle permet d'évacuer la chaleur qui n'est pas convertie par le TEG sans avoir besoin d'un dissipateur thermique tout en conduisant à la formation d'un gradient de température utilisable. La plupart de ces dispositifs ont déjà été utilisés comme capteurs, le défi majeur reste désormais de les utiliser comme générateur d'énergie en remplacement des piles.

Dans ce poster nous discuterons du fonctionnement d'une de ces nanoTEGs développés à l'institut Néel et dont la technologie a été transférée à la start-up MOIZ. Nous aborderons les différentes étapes de fabrications de cette structure suspendue sur silicium et les procédés de fabrication correspondant en salle blanche. Les problématiques liées à l'industrialisation de cette technologie innovante seront également évoqués.

With the emergence of low-power communications protocols dedicated to wireless sensor networks, there is now a real demand for micro-energy sources capable of powering batteries. This power range can be obtained from a standard TEG with a temperature gradient of a few degrees under stationary operating conditions. However, these conditions of use are not necessarily suitable for small wireless sensors, particularly when the energy source is intermittent and/or the available volume is too limited to contain the macroscopic TEG. For this reason, increasing interest has emerged regarding the design of new micro and nano thermoelectric generators using a planar and suspended configuration. The major advantage of this configuration is that it allows the heat that is not converted by the TEG to be evacuated without the need for a heat sink while leading to the formation of a usable temperature gradient. Most of these planar thermoelectric devices have already been used as sensors, the major challenge now remains to use these as an energy generator. In this poster we will discuss of the nanoTEG technology that has been developed in Institut Néel and that is now used in MOIZ start-up to power autonomous sensors. The different steps of manufacturing nanoTEGs by using clean room processes will be reviewed. We will discuss as well as the issues related to the industrialization of this innovative technology.