

# Journées Nationales de ThermoÉlectricité 2022

## 11-13 juillet 2022 - Rennes

organisées par l'Institut des Sciences Chimiques de Rennes – UMR6226



**Projet i-Hephaistos** Innovative syntHEsis and Protection against Aging for Improved Skutteruditebased Thermoelectric generatOrS





Direction

Équipe Chimie du Solide et Matériaux

Équipe Chimie Théorique Inorganique





Depuis près de 15 ans, le colloque national consacré à la "Thermoélectricité" est annuellement organisé par un laboratoire du territoire national. Cette manifestation scientifique a été initiée par l'ancien Groupement de Recherche (GdR) "Thermoélectricité" (//gdr-thermoelectricite.cnrs.fr) et depuis 2018, elle s'adosse aux actions du **Groupement d'Intérêt Scientifique (GIS) « Thermoélectricité »** (//gis-te.univ-lyon1.fr/) et a pris le nom de Journées Nationales de Thermoélectricité (JNTE).

Suite aux éditions organisées à Grenoble en 2018, Metz en 2019 et virtuellement en 2020 et 2021 (Journée Virtuelle de la Thermoélectricité, JVT), les JNTE seront organisées en présentiel cette année par l'Institut des Sciences Chimiques de Rennes (ISCR-UMR6226) du 11 au 13 juillet 2022, à l'Ecole Nationale Supérieure de Chimie de Rennes (ENSCR). Cette manifestation nationale permettra à la communauté scientifique s'intéressant aux phénomènes physiques de conversion directe de flux thermiques en électricité et vice-versa, de présenter sous forme de présentations orales ou de posters les résultats récents en lien avec cette thématique « énergie », allant de la recherche fondamentale (théorie, matériaux, élaboration, thermique, phénomènes micro- & macroscopiques) aux applications les plus variées autour de la conversion de chaleur en électricité et de la régulation thermique.

Les JNTE 2022, s'articuleront autour (i) d'**une formation thématique** basée sur les compétences et spécificités de l'ISCR et (ii) d'**un colloque** qui s'articulera autour des sessions **« Matériaux chalcogénures », « Théorie », « Matériaux de basse dimensionnalité » et « Matériaux massifs »,** de 2 sessions posters, de 2 conférences invitées et de la remise du prix Coqblin récompensant la meilleure thèse sur la thématique thermoélectricité.

#### Comité d'organisation local:

Régis Gautier Florentine Guiot Stéphanie Lamy (logistique) Pierric Lemoine Serge Paofai (site web) Mathieu Pasturel Carmelo Prestipino Thomas Stephant Céline Teffo (gestion)

## Programme

#### Lundi 11 juillet

14h00 – 15h00	Accueil des participants à la Formation
15h00 – 16h15	Formation 1 : Bertrand Lenoir (Institut Jean Lamour, Nancy) Introduction, principes et applications de la thermoélectricité
16h30 – 17h45	Formation 2 : Mathieu Pasturel (Institut des Sciences Chimiques de Rennes) Méthodes de synthèse et mise en forme en chimie du solide
18h00 – 19h15	Formation 3 : Carmelo Prestipino (Institut des Sciences Chimiques de Rennes) Analyses structurales et spectroscopiques, apport des grands instruments
19h30 – 21h00	Dîner à la crêperie La Hublais à Cesson-Sévigné

#### Mardi 12 juillet

9h00 – 10h15	Formation 4 : Régis Gautier (Institut des Sciences Chimiques de Rennes)
	Modélisation et simulation in silico
10h30 – 11h45	Formation 5 : Pierric Lemoine (Institut des Sciences Chimiques de Rennes)
	Cristallochimie et relations avec les propriétés thermoélectriques de chalcogénures de métaux de transition

12h00 – 13h00 Déjeuner-buffet aux accents italiens

#### 13h15 – 13h45 Accueil des participants au colloque

13h45 – 14h00Mots de bienvenue :Marc Fourmigué, directeur de l'Institut des Sciences Chimiques de RennesRégis Gautier, directeur de l'Ecole Nationales Supérieure de Chimie de RennesChristophe Candolfi, directeur du GIS Thermoélectricité

 14h00 – 14h30
 Conférence invitée : Nicolas Stein (Institut Jean Lamour, Metz)

 Electrochemical synthesis and Investigations of thermoelectric SnSe films

14h30 – 15h50 Session 1 - Matériaux chalcogénures – Chairman : Mickaël Beaudhuin

Florentine Guiot (Institut des Sciences Chimiques de Rennes) Structural analyses and TE properties of Cr<sub>2</sub>Sn<sub>3</sub>S<sub>7</sub>

Hugo Bouteiller (Crismat, Caen & LINK, Tsukuba, Japon) Observation of decorrelated transport properties in a new pseudo-hollandite chalcogenide

Adéle Léon (Institut Jean Lamour, Nancy) Transport properties of the chalcogenide semiconductor Bi<sub>2</sub>Te<sub>2</sub>Se

Krishnendu Maji (Crismat, Caen) Anharmonicity induced by 6S<sup>2</sup> lone pair of Bi leads to extremely low thermal conductivity in nontoxic Cu<sub>3</sub>BiS<sub>3</sub>

15h50 – 16h30 Session Posters 1

#### **16h30 – 17h00 Conférence invitée : Sawako Nakamae (CEA, Saclay)** Recent advances in complex liquid thermoelectrics

#### 17h00 – 18h20 Session 2 – Théorie – Chairwoman : Sylvie Hébert

Raja Sen (Laboratoire des Solides Irradiés, Palaiseau) Ab initio calculations of the TE phonon drag effect in semiconductor nanostructures

Donald Goury (Institut de Chimie Moléculaire et des Matériaux d'Orsay) Ab Initio Study of the Thermodynamics of Intrinsic Point Defects and Evolution of the Equilibrium Carrier Concentration with Temperature in BiCuSeO

Runan Xie (Institut de Chimie et des Matériaux Paris-Est, Thiais) Screening quaternary Heusler by machine learning for application in thermoelectricity

Pascal Boulet (Institut Matériaux Microélectronique Nanosciences de Provence) Theoretical investigation of the Pb<sub>2</sub>Bi<sub>2</sub>Te<sub>5</sub> layered chalcogenide: electronic and TE properties

18h30 – 20h00 Réunion du conseil scientifique du GIS Thermoélectricité

20h00 – 23h00 Dîner de gala à la Taverne de la Marine, place de Bretagne, Rennes

#### Mercredi 13 juillet

#### 8h30 – 9h50 Session 3 – Matériaux de basse dimensionalité – Chairman : Fabien Giovanelli

Sibel Nar (Laboratoire Nanotechnologies Nanosystèmes, Sherbrooke, Canada & GREMI, Orléans)

Simultaneous in-depth measurement of Seebeck coefficient and thermal conductivity of mesoporous silicon and graphenized mesoporous silicon

Rana Ghannam (Institut Charles Gerhardt, Montpellier) Impact of nanostructuring on the physical properties of SrSi<sub>2</sub>

Roderic Cravero (Institut Néel, Grenoble & Institut Lumière Matière, Villeurbanne) Understanding thermal transport in GeTe thin films and impact of nanostructuration

Marco Fabbiani (Institut Charles Gerhardt, Montpellier) Bismuth nanowires confined in zeolites and mesoporous silicas for Peltier cooling

#### 9h50-10h30 Session posters 2

#### 10h30 – 11h50 Session 4 – Matériaux massifs – Chairman : David Bérardan

Vincent Pelletier (Institut des Sciences Chimiques de Rennes) Anti-Th<sub>3</sub>P<sub>4</sub> antimonides for thermoelectric applications: experimental & theoretical investigations

Mélanie De Vos (Institut de Chimie et des Matériaux Paris-Est, Thiais) Thermoelectric properties in Fe<sub>2+x</sub>V<sub>1-x-y-z</sub>Ti<sub>z</sub>Al<sub>1+y</sub> Heusler alloys

Doaa Ali (Institut Charles Gerhardt, Montpellier) Semi-conducting complex structures Ca-Si alloys for thermoelectric applications

Emmanuel Guilmeau (Crismat, Caen) Thermoelectric sphalerite derivative sulfide

11h50 – 12h20 Remise du prix Coqblin par C. Candolfi et présentation par sa/son lauréat-e

# **Conférences invitées**

#### Electrochemical synthesis and Investigations of thermoelectric SnSe films

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Polycrystalline SnSe films have long been recognized for their appropriate optical and electrical properties for photovoltaic conversion. 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. Indeed, Zhao *et al.* [<sup>1</sup>] reported a thermal conductivity between 0.5 and 0.7 W·m<sup>-1</sup>·K<sup>-1</sup> at room temperature and a thermopower close to 500  $\mu$ V·K<sup>-1</sup> for single crystals, which results in better properties than reference materials such as Bi<sub>2</sub>Te<sub>3</sub>. Most of the thermoelectric materials are used in a bulk shape. However, decreasing the dimensionality is beneficial for the thermal conductivity, according to theoretical [<sup>2</sup>] and experimental researches [<sup>3</sup>].

In this work, we report a study of electrodeposited SnSe films. The used chemical synthesis method combines low cost, simple processing, and a moderate growth rate, enabling good crystallinity. Considering the difficulty to stabilize the baths containing Sn(II) and Se(IV) precursors, we investigated the benefits of using sodium oxalate as complexing and stabilizing agent [<sup>4</sup>]. A growth mechanism was proposed and a synthesis potential window was defined, in which the electrodeposition of SnSe films was investigated. Between -0.5 and -0.6 V vs sat. AgCl/Ag, 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. Hence we investigated the influence of the pulse potentiostatic deposition on the deposits. Thus compact and crystallized deposits were obtained with a Sn/Se ratio close to 1/1 as well as the presence of SnO<sub>2</sub>, as secondary phase.

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 [<sup>5</sup>]. This influence was verified experimentally for thicknesses below 300nm by Scanning Thermal Microscopy in  $3\omega$  configuration ( $3\omega$ -SThM) in vacuum environment [<sup>6</sup>].

The determination of the electrical resistivity and the Seebeck coefficient has been made difficult due to strong chemical bonds between the tin selenide films and the platinum substrate preventing any transfer steps. Therefore we have developed specific microdevices for the inplane thermoelectric characterization of deposited films, which are still in progress [<sup>7</sup>].

- 1. Zhao, L.-D.; et al., *Nature* **2014**, 508, (7496), 373-377.
- 2. Hicks, L. D.; Dresselhaus, M. S. *Physical Review B* **1993**, 47, (24), 16631-16634.
- 3. Rojo, M. M.;et al. ,*Nanoscale* **2017**.
- 4. De Vos, M.; et al., *Journal of the Electrochemical Society* **2020**, 167, (16), 162502.
- 5. Al-Alam, P.; et al. *Physical Review B* **2019**, 100, (11), 115304.
- 6. G. Pernot, et al., J. Appl. Phys., **2021**, 129, 5.
- 7. Osenberg, D.; et al.. *Journal of Materials Research and Technology* **2021**, 15, 1190-1200.

### **Recent advances in complex liquid thermoelectrics**

<u>S. Nakamae,</u><sup>1</sup> M. Beaughon<sup>1</sup>, K. Bhattacharya<sup>1</sup>, T. Fiuza<sup>1, 2</sup>, C. Riedl<sup>2</sup>, T. J. Salez<sup>1</sup>, B. Torres-Bautista<sup>1</sup>, M. Bonetti<sup>1</sup>, E. Dubois<sup>2</sup>, L. Jeandupeux<sup>3</sup>, E. Laux<sup>3</sup>, V. Peyre<sup>2</sup>, R. Perzynski<sup>2</sup>, P. Potty<sup>3</sup>, M. Roger<sup>1</sup>

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Thermoelectrochemical cells containing liquid electrolytes are receiving increased attention as an alternative waste-heat recovery tool, in particular, for low-power/high voltage applications. Indeed, the Seebeck coefficients (or also known as 'temperature coefficients') of liquids are one to two orders of magnitude larger than that of conventional solid-state thermoelectric materials, owing to the combined effects of the electrochemical reactions of redox agents, the thermoelectrodiffusion of charged species and the ionic double layer formation at the electrodes (see, for example [1]–[4]). Ionic liquids in particular, present many promising features such as high electrical conductivity, large temperature and electrochemical windows, low vapor pressure and toxicity, and raw material abundance [2] [5] for low-grade waste heat recovery applications. In the case of ionic nanofluids, the thermodiffusion (Soret effect) of charged nanoparticles is also known to produce non-negligible contribution to the fluid's overall Seebeck coefficient [6], [7].

In this presentation, I will review the progress made in the complex liquid thermoelectric research in the past 10-15 years. The current theoretical and phenomenological understanding on the compound thermo-electro-chemical processes, as well as future research directions and technological possibilities where thermoelectric complex fluids should become advantageous will also be discussed.

- [1] M. Massetti et al., *Chemical Reviews* **121**, 12465 (2021).
- [2] W. D. G. Gonçalves et al., Curr. Opin. Green Sustain. Chem., 26, 100404 (2020)
- [3] T. J. Salez, et al., *Entropy* **20** (2018).
- [4] M. Bonetti, et al., J. Chem. Phys., 134 (2011).
- [5] V. Zinovyeva, et al., ChemElectroChem 1 426 (2014)
- [6] T. J. Salez et al., Phys. Chem. Chem. Phys., 19 9409 (2017)
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Session 1 Matériaux chalcogénures

## Structural analyses and thermoelectric properties of Cr<sub>2</sub>Sn<sub>3</sub>S<sub>7</sub>

<u>Florentine Guiot</u>,<sup>a</sup> Carmelo Prestipino,<sup>a</sup> Emmanuel Guilmeau,<sup>b</sup> Antonin Panaget,<sup>a</sup> Pierre Gaudry,<sup>a</sup> Vincent Dorcet,<sup>a</sup> Bernard Malaman,<sup>c</sup> Thierry Schweitzer,<sup>c</sup> Pierric Lemoine.<sup>a</sup>

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The design and optimization of thermoelectric (TE) materials rely on the intricate balance between thermopower (S), electrical resistivity ( $\rho$ ) and thermal conductivity ( $\kappa$ ). Perfecting such a balance is key to reach high values of the figure of merit,  $ZT = S^2T/\rho \kappa$ , necessary to improve energy recovery systems and thermoelectric cooling devices.<sup>1</sup> 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<sup>2</sup> and exhibit intrinsically low thermal conductivity.<sup>3,4</sup> Nevertheless, the TE performances of p-type copper-based sulphides are much better than those of n-type,<sup>5</sup> 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  $Cr_2Sn_3S_7$ . This compound, isotype of  $Cr_2Sn_3Se_7$ ,<sup>6</sup> 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  $Cr_2Sn_3S_7$  and some derivatives, using X-ray powder diffraction, scanning and transmission electron microscopies, magnetic measurements, spectroscopy techniques and transport measurements.

<sup>&</sup>lt;sup>1</sup> S. Hébert, D. Berthebaud, R. Daou, Y. Bréard, D. Pelloquin, E. Guilmeau, F. Gascoin, O.

Lebedev, and A. Maignan, J. Phys.: Condens. Matter 28, 013001 (2016).

<sup>&</sup>lt;sup>2</sup> O. Caballero-Calero, J.R. Ares, and M. Martín-González, Adv. Sustainable Syst. 2100095 (2021).

<sup>&</sup>lt;sup>3</sup> A.V. Powell, Journal of Applied Physics **126**, 100901 (2019).

<sup>&</sup>lt;sup>4</sup> G. Guélou, P. Lemoine, B. Raveau, and E. Guilmeau, J. Mater. Chem. C 9, 773 (2021).

<sup>&</sup>lt;sup>5</sup> P. Lemoine, G. Guélou, B. Raveau, and E. Guilmeau, Angew. Chem. Int. Ed. anie.202108686 (2021).

<sup>&</sup>lt;sup>6</sup> S. Jobic, P. Le Boterf, R. Brec, and G. Ouvrard, Journal of Alloys and Compounds **205**, 139 (1994).

### **Observation of decorrelated transport properties in a new pseudo-hollandite chalcogenide**

<u>Hugo Bouteiller</u>,<sup>1,2</sup> Bruno Fontaine<sup>3</sup>, Yoshitaka Matsushita<sup>4</sup>, Olivier Perez<sup>1</sup>, Takao Mori<sup>4</sup>, Jean-François Halet<sup>2</sup>, David Berthebaud<sup>2</sup> and Franck Gascoin<sup>1</sup>

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Transition metal chalcogenides have drawn much interest since a few decades for thermoelectric applications. This is the case for instance of the pseudo-hollandite  $A_xM_5X_8$  (A = Rb, Ba, Tl, K, Sr, In; M = Ti, V, Cr; X = S, Se, Te), the structure of which is somewhat related to that of the hollandite mineral BaMn<sub>8</sub>O<sub>16</sub>. These compounds exhibit an anionic framework made of the assemblage of face and edge-sharing M-centered MSe<sub>6</sub> octahedra forming infinite channels along the b-axis. The resulting one-dimensional channels can be fully or partially filled with mono- and/or dicationic elements that counter-balance the charge of the anionic framework and stabilize the structure (Fig.1). We focus in this work on the chromium selenides  $A_xCr_5Se_8$  (A = Rb, Ba, Tl) pseudo-hollandites. Previous studies showed that this family of compounds might present promising figure of merit (ZT = 0.5 at 800 K for Tl<sub>x</sub>Cr<sub>5</sub>Se<sub>8</sub> and ZT = 0.12 at 800 K for Ba<sub>0.5</sub>Cr<sub>5</sub>Se<sub>8</sub> for instance). In this context, charge-carrier tuning of Ba<sub>0.5</sub>Cr<sub>5</sub>Se<sub>8</sub>. Subsequent characterizations of the transport properties of this compound Rb<sub>2x</sub>Ba<sub>0.5-x</sub>Cr<sub>5</sub>Se<sub>8</sub>. Subsequent characterizations of the transport properties of this compound were performed and will be presented. In particular, an apparent decorrelation observed between the Seebeck coefficient and resistivity will be discussed.



Fig. 1. One-dimensional channel structure of the pseudo-hollandite Rb<sub>2x</sub>Ba<sub>0.5-x</sub>Cr<sub>5</sub>Se<sub>8</sub>

- [1] Takahashi et al., Chemistry of Materials, 25, 1809-1815 (2013).
- [2] Lefèvre et al., Chemistry of Materials, 27, 7110-7118 (2015).

## Transport properties of the chalcogenide semiconductor Bi<sub>2</sub>Te<sub>2</sub>Se

#### Adèle Léon,<sup>1</sup> Petr Levinský<sup>2</sup>, Jiří Hejtmánek<sup>2</sup>, Bertrand Lenoir<sup>1</sup>, Christophe Candolfi<sup>1</sup>

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 $Bi_2Te_2Se$ , a ternary derivative of the state-of-the-art thermoelectric compound  $Bi_2Te_3$ , exhibits topologically-protected surface states and bulk insulating properties below room temperature, characteristic of the recently discovered topological insulating behavior [1,2]. Density functional theory calculations highlighted the opportunity to create a resonant level in this compound upon Sn doping, thereby possibly inducing enhanced thermoelectric properties near room temperature [3]. However, no detailed study of the influence of various dopants has been undertaken so far.

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

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- 2. Ren, Z. et al., *Physical Review B*, **82**(24), 241306 (2010).
- 3. Wiendlocha, B., Journal of Electronic Materials, 45(7), 3515-3531 (2016).

## Anharmonicity induced by 6S<sup>2</sup> lone pair of Bi leads to extremely low thermal conductivity in nontoxic Cu<sub>3</sub>BiS<sub>3</sub>

<u>Krishnendu Maji</u>,<sup>1</sup> Pierric Lemoine,<sup>2</sup> Adèle Renaud,<sup>2</sup> Bin Zhang,<sup>3, 4</sup> Xiaoyuan Zhou,<sup>3, 4</sup> Virginia Carnevali,<sup>5</sup> Christophe Candolfi,<sup>6</sup> Bernard Raveau,<sup>1</sup> Marco Fornari,<sup>5</sup> Emmanuel Guilmeau<sup>1\*</sup>

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Keywords: wittichente, Sulfide, Thermal conductivity, Mechanical-alloying, SPS

**Abstract:** The correlation between the crystal structure and lattice dynamics in terms of phonon dispersion is the key to develop materials with extremely low thermal conductivity, which is essential for thermal barrier coating and thermoelectric energy conversion. We synthesized highly pure synthetic wittichente, Cu<sub>3</sub>BiS<sub>3</sub>, by high energy mechanochemical alloying followed by spark plasma sintering and characterized by various techniques like PXRD, SEM, and TEM etc. The bulk material shows very low thermal conductivity, 0.37–0.25 W/mK in the temperature range of 300–573 K, and a ZT value of 0.12 at 573 K. This low ZT value, caused by high resistivity and low carrier concentration ( $10^{16}$  cm<sup>-3</sup>), can be improved by optimizing carrier concentration.[1] The lattice dynamics calculation (Density Functional Theory) indicates that low energy optical phonons, basically contributed by Bi atoms, are present in the system, which interact with heat carrying acoustic phonons to lower the thermal conductivity, which is further proved by experimental data, i.e. sound velocity and low temperature heat capacity (*Cp*) measurements.

References:

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# Session 2 Théorie

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

#### Raja Sen, Jelena Sjakste, and Nathalie Vast

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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 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 do this, we solved the linearized Boltzmann equation for electronic transport in presence of non-equilibrium phonon populations introduced by a temperature gradient. Next, in our aim to understand the phonon drag effect at the nanoscale, we studied the effect of nano-structuring on the Seebeck coefficient of the pristine material. 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 nano-silicon with temperature and carrier concentrations. Our results for *n*-doped silicon not only show a good agreement with the experimental data [5] but also pave the way to further understand the contribution of phonon-drag in any semiconductor nanostructures, for example Bi<sub>2</sub>Te<sub>3</sub> [6], B<sub>4</sub>C [7], Bi [8], which still remain largely unexplored.

#### Acknowledgements

DFT calculations have been performed using the Quantum ESPRESSO software [9]. We acknowledge access to high performance computing (HPC) resources provided by the French HPC centres 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. This work was supported by the CEA ANCRE program (project Thermoint). The support from Labex Nanosaclay via ANR-10-LABX-0035 (Flagship project MaCaCQu) and from ANR via ANR-21-CE50-0008 (project Placho) is also gratefully acknowledged.

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#### Ab Initio Study of the Thermodynamics of Intrinsic Point Defects and Evolution of the Equilibrium Carrier Concentration with Temperature in BiCuSeO

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New generations of TE materials are coming up from the last decades because of the need for efficient materials for large scale applications. In this context, BiCuSeO is among the best promising materials for applications in a medium temperature range because of its quite high TE efficiency, non-toxicity, relative abundance of its elements and simple synthesis route.

Even if BiCuSeO properties are now well-known and well-documented in the literature [1], several questions remain open. Especially, it has been shown experimentally that the presence of some (unidentified) intrinsic defects could have a significant influence on the electronic and thermal transport properties. It is thus a challenge to find the nature of these defects and to take their role into account in the synthesis in order to better optimize the TE properties. Besides, extrinsic defects introduced for doping have also to be investigated as they interplay with the native intrinsic defects. As an example, n-type BiCuSeO has been obtained experimentally with Fe-doping but the evolution of the n-type nature with temperature still needs to be understood.

First, we report on the results of an ab initio study of the thermodynamics of intrinsic point defects in the thermoelectric oxychalcogenide BiCuSeO, recently published [2]. By using phase boundary mapping, we build a thermodynamic stability diagram that enables identification of several thermodynamic conditions that could be targeted experimentally in order to control the concentration of defects by tuning the chemical potential of the elements. In these conditions, the formation energies of selected intrinsic defects in their different possible charged states have been calculated. It shows that the copper vacancy dominates the other defects over the whole energy band gap, even if  $V_{Bi}$  vacancy as well as  $Cu_{Se}$  substitution can also play a role in certain thermodynamic limits.

Then, calculations of the equilibrium Fermi energy and defect concentrations show that native copper vacancies are responsible for the p-type conductivity in pristine BiCuSeO. They also give possible directions to achieve n-type conductivity in this system and to optimize the carrier concentrations in the p-type regime (Fig. 1).

Last, we investigate the influence of the temperature on the concentration of carriers using two different methods, corresponding to different experimental conditions, namely sample at thermodynamic equilibrium or rapid quenching followed by fast measurements. We show that the temperature dependence of the carriers concentration significantly depends both on the experimental condition and on the thermodynamic limit (Fig. 2.). This result can have consequences for situations corresponding to long standing applications where thermodynamic equilibrium can be reached and calls for more systematic exploration of transport properties with this temperature effect.



 $\epsilon_F$  (eV) Fig. 1. Formation energies of the dominant intrinsic point defects in BiCuSeO for a Cu-rich thermodynamic limit in function of the Fermi energy.

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Fig. 2. Temperature dependence of the hole carrier concentration for Cu-poor and Cu-rich thermodynamic limits.

## Screening quaternary Heusler by machine learning for application in thermoelectricity

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Heusler alloys, full and half-, thanks to their high versatility of compositions as well as their very interesting properties, are good candidates for thermoelectric applications. In the Heusler family, quaternary alloys also exist and allow to further increase the chemical diversity and so one to achieve more complex properties. However, due to the high number of combinations, traditional screening methods are not effective to target relevant compounds. To accelerate this research, it is advantageous to use machine learning methods [1].

In our project, we are looking for new promising quaternary Heusler compounds screened within a dataset of 24 selected elements [2]. First, a database of calculated thermodynamic, electronic and magnetic properties, obtain from DFT calculations (Density Functional Theory) on binary and ternary compounds was constructed. Then, a supervised learning with the neural network model was built to predict the enthalpy of formation and the density of state at the Fermi level (metallic or semiconductor character) of quaternary Heusler compounds. Our model presents comparable or superior performance than the state of art and allow to identify promising compounds among the 24<sup>4</sup> possible configurations of our dataset.

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## Theoretical investigation of the Pb<sub>2</sub>Bi<sub>2</sub>Te<sub>5</sub> layered chalcogenide : electronic and thermoelectric properties

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Owing to their low lattice thermal conductivity, compounds of the  $n(PbTe)-m(Bi_2Te_3)$  homologous series (Fig. 1, left) have been reported in the literature with good thermoelectric (TE) properties [1]. Among these layered chalcogenides, the  $Pb_2Bi_2Te_5$  compound has been evidenced with two stacking sequences termed A and B [2,3] (Fig. 1, right). To understand the differences in their properties, we have determined the electronic and thermoelectric properties of this compound for the two different stacking sequences from a series of first principles calculations using density functional theory.

The most interesting compound for thermoelectric applications has been found to be  $Pb_2Bi_2Te_5$  with the stacking B sequence. To get a comprehensive set of thermoelectric properties and explain the low lattice thermal conductivity observed in these compounds, a full theoretical investigation of the electronic structures, transport behaviour, and lattice dynamic properties of the compound has been conducted. Depending on the doping and temperature conditions a ZT value as high as 4.0 is predicted. The details on how this value has been obtained will be presented.

The band engineering approach has then been implemented by applying biaxial tensile and compressive strains on  $Pb_2Bi_2Te_5$  to improve the TE properties. The strain effects on the electronic structure will be presented and we will show that, under certain constrains, the TE properties can be improved.



Fig. 1. Layered chalcogenides. Left: Structures of (PbTe)<sub>m</sub>(Bi<sub>2</sub>Te<sub>3</sub>)<sub>n</sub> for (m,n) = (1,2), (1,1) and (2,1); Right: A and B stacking of Pb<sub>2</sub>Bi<sub>2</sub>Te<sub>5</sub>

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# Session 3 Matériaux de basse dimensionalité

## SIMULTANEOUS IN-DEPTH MEASUREMENT OF SEEBECK COEFFICIENT AND THERMAL CONDUCTIVITY OF MESOPOROUS SILICON AND GRAPHENIZED MESOPOROUS SILICON

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Mesoporous silicon, obtained by electrochemical etching, from an electrolytic solution of HF and CH<sub>3</sub>CH<sub>2</sub>OH, is a promising material for tuning the thermoelectric properties [1] [2] (Seebeck coefficient, thermal and electrical conductivity) in order to maximize the figure of merit, ZT. Depending on the thickness of mesoporous silicon (named membrane in the present work with thickness varying from 30  $\mu$ m until 160  $\mu$ m) the properties of the membrane will be different. A graphene insertion is also made to increase the electrical conductivity of this type of material, which decrease drastically by the creation of a porous layer. [3]

Thanks to a homemade device (ZT-meter), it is possible to measure directly the in-depth Seebeck coefficient as well as the thermal conductivity. The operating principle and working steps of the set of measurements will be specifically detailed in this paper. Additionally, the ZT-meter was calibrated using typical membranes as 3 mm thickness  $Bi_2Te_3$  (S= -175±15  $\mu$ V/K) and 0.45 mm thickness Cu (S = 1.5±0.5  $\mu$ V/K) very close to the work respectively of *Wu et al* [4] and *Dörling et al* [5]. Thermal conductivity is determined using the hot plate method, which includes heat fluxmeters (direct measurement of heat flux and temperature interface). In the case of this work, properties of mesoporous silicon (MePSi) and graphenized mesoporous silicon (MePSi-Gr) have been evaluated with S (MePSi) = 700±20  $\mu$ V/K and S(MePSi-Gr) = 100±20  $\mu$ V/K for the same porous thickness of 0.135 mm.

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### Impact of nanostructuring on the physical properties of SrSi<sub>2</sub>

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Today thermoelectric materials are mainly made of chalcogen or pnictogen atoms with the drawbacks of scarcity and toxicity. To overwhelm these problems, many trials have been made to improve the thermoelectric performance of new materials based on silicides. Optimizing these materials seems to be very competitive due to their economic and ecological advantages[1].

Alkaline earth silicides have been very useful in thermoelectricity due to the abundance of their precursors, their non toxicity and their performances comparable to conventional thermoelectric materials such as PbTe in the mid-temperature range. In the lower temperature range (200-500K) efforts must be performed to be competitive with  $Bi_2Te_3$  alloys.  $SrSi_2$  alloys could be a promising thermoelectric material despite the lack of research. This cubic semiconducting alloy with a narrow band gap has a power factor comparable to  $Bi_2Te_3$ . The performances are limited by the phonon contribution to the thermal conductivity (about 6 Wm<sup>-1</sup>K<sup>-1</sup> at RT) which lead to a maximum ZT about 0.05 for pure  $SrSi_2$  at 300K[2]. Thus, reducing the thermal conductivity should permit to improve the phonon diffusion and thus the ZT. Several routes can be investigated such as the scattering by mass defect or the nanostructuring.

In our work, we will present the effect of the nanostructuring on the lattice dynamic and thermoelectric properties of  $SrSi_2$  alloys.

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## Understanding thermal transport in GeTe thin films and impact of nanostructuration

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Heat management in microelectronics and energy recycling is a challenge in today's society. The study of the thermal properties of chalcogenide phase-change materials (PCMs) such as the prototypical GeTe compound will allow to improve and optimize their thermoelectric properties. To achieve this improvement, reducing the thermal conductivity to increase the thermoelectric figure of merit of the semiconducting PCM is a key strategy [1]. Obtaining a polycrystalline PCM with a thermal conductivity as low as possible, without affecting electronic properties, can be achieved by nanostructuring the PCM in order to increase phonon scattering and hinder heat propagation.

In this experimental work, we first investigate thermal transport in polycrystalline GeTe thin films, providing an upper limit for the thermal conductivity of nanostructured GeTe. Second, we study amorphous GeTe, whose thermal conductivity should represent the lowest limit: the phonon mean free path is expected to be the smallest possible and can be calculated using the kinetic formula for thermal conductivity and literature values for this latter, giving an approximate value of 1.5 nm. Between these two limits, should fall the thermal conductivity of nanocomposites made of nanocrystalline GeTe grains embedded in amorphous carbon, where it is possible to finely control the phonon mean free path (MFP) by tuning the GeTe grain size between approximatively 50 and 20 nm. The elastic contrast between the two materials is expected to strongly affect phonon propagation and thus mean free path [2].

To the purpose of our study, we have developed a sensitive differential 3-omega method adapted for thermal measurements on electrically conductive thin films [3,4]. Our results for crystalline GeTe (k~3.0 W.m<sup>-1</sup>.K<sup>-1</sup> $\pm$ 0.7 W.m<sup>-1</sup>.K<sup>-1</sup> at RT) and amorphous GeTe (k~0.30 W.m<sup>-1</sup>.K<sup>-1</sup>  $\pm$  0.08 W.m<sup>-1</sup>.K<sup>-1</sup> at RT) are in nice agreement with recent literature results [5]. Their temperature dependence allows to identify the dominant phonon scattering mechanism (see figure 1). We show that GeTe-C nanocomposites with a grain size 20nm exhibit a greatly reduced thermal conductivity (k~1.39 W.m<sup>-1</sup>.K<sup>-1</sup> $\pm$  0.07 W.m<sup>-1</sup>.K<sup>-1</sup> at RT), with a temperature dependence dominated by the electronic contribution.



Figure 1: Thermal conductivity versus temperature for crystalline GeTe (in red), and amorphous GeTe (in blue). The green area indicates the region where thermal conductivity of nanocomposites is expected to fall.

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## Bismuth nanowires confined in zeolites and mesoporous silicas for Peltier cooling

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The creation of novel functional materials is a technological need and a scientific challenge for the production of innovative systems able to face the requirements of many application fields. Cooling technologies are useful in many fields related to daily life (domestic refrigeration, computer cooling, air conditioning ...) as well as high technology (cooling of optoelectronic devices, superconducting devices, thermal management of electronic devices ...) In this, all-solid technologies based on the thermoelectric effect such as Peltier cooling devices represent a real alternative, as they have no moving parts, are compact and reliable. Despite the technological advance of the system, large-scale applications of Peltier cooling devices have been limited so far, mainly due to their insufficient performance and their rather high cost. Because of better performance at the lowest temperature and of the absence of tellurium present in  $Bi_2Te_3$ ,  $Bi_{1-x}Sb_x$  alloys have a strong potential for cooling applications. Moreover, nano-structuring the TE phase from a bulk material to a nanometric sized mono-dimensional wire has the potential for obtaining original and improved properties. The specific aims are the decrease of thermal conductivity and the increase of the Seebeck coefficient by exploiting the quantum confinement of the metal phase.

Therefore, the insertion of the metallic Bi or Bi alloys inside of a porous structure, such as zeolite channels and silica pores, could improve the thermoelectrical properties with respect to the bulk materials. Among the many parameters, the channel arrangement and dimensionality are of crucial importance in obtaining metal nanowires affecting the outcome performances of the composite. Here, we introduced Bi metal under pressure from melt into ordered porous alumina and silica with 4 - 10 nm pores. Electron microscopy confirms the full filling of the pores and the negative variation of the electrical resistivity coefficient observed for a reduced range of temperatures suggest a confinement effect on electrons. In contrast, the absence of change in the Raman spectra indicate the absence of confinement effect on phonons.



Fig. 1. Representation of the metal-zeolite nanocomposite synthesis process.

# Session 4 Matériaux massifs

### Anti-Th<sub>3</sub>P<sub>4</sub> Antimonides for Thermoelectric Applications: Experimental & Theoretical Investigations

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Thermoelectric materials with potential industrial applications at very high temperature, from 600°C to 1000°C and possibly higher, are needed to harvest waste heat and convert it into usable energy. This particular temperature range targets the steel, non-ferrous, ceramics and glass industries that use a lot of energy, 50% of which being lost during the production process.

Materials based on the cubic structure  $Th_3P_4$  are good candidates for applications at such high temperatures. Indeed, in this family of intermetallics, *n*-type La<sub>3</sub>Te<sub>4-x</sub> is already known as a good thermoelectric material with ZT superior to unity above 1000°C [1-2]. These compounds have been developed by NASA for the past 10 years or so and will be implemented in their next generation radioisotope thermoelectric generators. There is a need to develop a *p*-type counterpart of the same structure type, e.g, rare-earth antimonides crystallizing in the anti-Th<sub>3</sub>P<sub>4</sub> structure, making it easier to fabricate *p*-*n* thermoelectric couples. However, there is only scarce information about the *p*-type counterparts, even if a few reports have shown very promising thermoelectric properties and stability at high temperature, with, for instance a ZT of 0.75 reported for La<sub>0.5</sub>Yb<sub>3.5</sub>Sb<sub>3</sub> at 1000°C [3].

With the development of powerful methods to compute the electronic band structure of solids and the increasing complexity of the formulations of advanced thermoelectric materials, quantum chemical calculations based on density functional theory (DFT) are helpful tools for the optimization of thermoelectric material properties. To gain further information in the electronic transport properties, Boltzmann transport theory can be combined with band structure calculations assuming a constant relaxation time.

Theoretical and experimental investigations were carried out in order to better understand the differences in the transport properties of La<sub>4</sub>Sb<sub>3</sub> and Yb<sub>4</sub>Sb<sub>3</sub>, and to improve the thermoelectric performance of these antimonides by doping Yb<sub>4</sub>Sb<sub>3</sub> with various rare-earth and/or group 15 atoms.

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## Thermoelectric properties in Fe<sub>2+x</sub>V<sub>1-x-y-z</sub>Ti<sub>z</sub>Al<sub>1+y</sub> Heusler alloys

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Applications such as the "Factory 4.0" or the "connected home" require the implementation of wireless autonomous sensors. Powering these sensors with thermoelectric generators is an elegant way of solving the question of their maintenance. Nevertheless, Bi<sub>2</sub>Te<sub>3</sub>, the commercialized material, displays a large figure of merit ZT = 1 at 300 K but it contains rare and expensive tellurium. Fe<sub>2</sub>VAl could be an alternative to Bi<sub>2</sub>Te<sub>3</sub> if its figure of merit could be increased. Its chemical elements are abundant, cheap, eco-friendly and its power factor can reach values as large as  $PF = 9 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$  for *n*-type conduction [1]. However, its thermal conductivity is more than ten times larger in its pristine form ( $\kappa = 29 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ) and even when substituted, its figure of merit is smaller than ZT = 0.2 at 300 K. Its lattice thermal conductivity thus requires to be decreased to improve its performances.

Prior to the reduction of the thermal conductivity, the power factor must be optimized, more specifically for *p*-type Fe<sub>2</sub>VAl, which exhibit smaller power factor than in *n*-type compositions. Indeed, the power factor does not exceed 3.2 mW·m<sup>-1</sup>·K<sup>-2</sup> at 300 K in *p*-type Fe<sub>2</sub>V<sub>0.99</sub>Al<sub>1.01</sub> whereas  $PF = 6.8 \text{ mW·m}^{-1} \text{ K}^{-2}$  is reached for *n*-type Fe<sub>2</sub>V<sub>1.03</sub>Al<sub>0.97</sub> [A. Diack-Rasselio et al., submitted]. In the literature, Sandaiji et al. [2] reported (in Japanese)  $PF = 4.0 \text{ mW·m}^{-1} \text{ K}^{-2}$  in Fe<sub>2.04</sub>V<sub>0.86</sub>Ti<sub>0.1</sub>Al and ascribed this power factor enhancement to the Fe over-stoichiometry. This scenario is compatible with their (incomplete set of) data, but an alternate scenario should be envisaged: the combined effect of Ti-doping with Fe excess. Moreover, this high value of power factor in *p*-type Fe<sub>2</sub>VAl has not been optimized.

We thus initially synthesized the  $Fe_{2.03}V_{0.97-x}Ti_xAl$  alloy series. Every sample crystallize in the cubic L2<sub>1</sub> structure with a solubility limit larger than 0.15 for Ti.  $PF = 4.0 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$  was also obtained at 300 K in  $Fe_{2.03}V_{0.87}Ti_{0.1}Al$  as well as in  $Fe_{2.03}V_{0.92}Ti_{0.05}Al$ . Hall effect measurements allowed a plot of the Seebeck coefficient versus the hole concentration (Pisarenko's plot), which indicate that the power factor and Seebeck coefficient enhancements are caused by an increased effective mass ( $m^* = 8.9 \times 9.31 \times 10^{-31}$  kg) of the charge carriers. We then synthesized the  $Fe_{2+x}V_{1-x-y-z}Ti_zAl_{1+y}$  and  $Fe_{2+x}V_{1-x-y}Al_{1+y}$  alloy series, to disentangle the respective effect of Ti-doping and Fe excess on the electronic transport. We also synthesized  $Fe_{2+x}V_{0.93-x-y-z}Ti_zTa_{0.07}Al_{1+y}$  to combine the power factor enhancement with a reduction of thermal conductivity by alloying with the heavy Ta atom. We will present the results of these three series.

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### Semi-conducting complex structures Ca-Si alloys for thermoelectric applications

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A drawback of the best-performing thermoelectric materials (TEM) is their toxicity, scarcity, and/or costs of the chemical elements they are synthesized from. For this reason, alkaline-earth silicides have attracted high interest as they are made of abundant, cheap and non-toxic elements. Among their many compounds, hexagonal Ca<sub>3</sub>Si<sub>4</sub> [P6<sub>3</sub>/m, No 176] and orthorhombic Ca<sub>14</sub>Si<sub>19</sub> [R-3c, No 167] meet all the requirements to be the next generation TEMs [1]. Their carrier concentrations is within the semi-conducting regime, and their narrow energy bandgaps are favorable for large power factors, a requirement for good TEMs. According to the "phonon glass-electron crystal" concept, their complex structures should also favor very low thermal conductivities and thus facilitate even more an exceptionally high thermoelectric figure of merit. Ab initio studies of thermoelectric transport in Ca<sub>3</sub>Si<sub>4</sub> also conjectured that large anharmonic motions of Ca chains could contribute additionally to reduce thermal transport [2]. Despite these promising prerequisite properties for excellent TEMs, so far only few experimental studies have been carried out to shed light on the phonon properties of Ca<sub>3</sub>Si<sub>4</sub> and Ca<sub>14</sub>Si<sub>19</sub>.

In the present study, we investigate the structure-function relationship of these compounds on a microscopic scale by ab initio lattice dynamics calculations, neutron and x-ray diffraction, and inelastic neutron scattering experiments. We examined the structural and phonon properties over a wide temperature range (2-950 K) to establish their ground state properties and in particular their dynamical response to heat treatment in the temperature regime of potential applications. The experimental data are supported by density functional theory calculations to scrutinize the microscopic origin of the vibrational properties and thus the reduced heat transport. The final goal of the work is to identify modifiable microscopic properties for improving their performance as TEMs.

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### **Thermoelectric Sphalerite Derivative Sulfides**

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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 Cu<sub>5</sub>FeS<sub>4</sub>, germanite derivative Cu<sub>22</sub>Fe<sub>8</sub>Ge<sub>4</sub>S<sub>32</sub>, stannoidite Cu<sub>8</sub>Fe<sub>3</sub>Sn<sub>2</sub>S<sub>12</sub>, colusites Cu<sub>26</sub>T<sub>2</sub>M<sub>6</sub>S<sub>32</sub> (T = V, Cr, Nb, Mo, Ta, W; M = Sn, Ge), synthetic Cu<sub>2</sub>SnS<sub>3</sub>, kesterite Cu<sub>2</sub>ZnSnS<sub>4</sub>, and tetrahedrites Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>. In this poster, recent advances in synthetic minerals and new copper-based sulphide compounds will be presented. Some peculiar structural features in connection with order/disorder phenomena, were carefully examined to establish rules and correlations between the crystal structures, electronic structures, vibrational and thermoelectric properties.[1-4]

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## **Posters**

### A Tunable Structural Family with Ultralow Thermal Conductivity: Copper-Deficient Cu<sub>1-x</sub>□<sub>x</sub>Pb<sub>1-x</sub>Bi<sub>1+x</sub>S<sub>3</sub>

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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 ( $\kappa$ ), for thermoelectric and thermal barrier applications, and requires the study of highly pure materials. We synthesized the n-type sulfide CuPbBi<sub>5</sub>S<sub>9</sub> with an ultralow  $\kappa$  value of 0.6–0.4 W m<sup>-1</sup> K<sup>-1</sup> in the temperature range 300–700 K.<sup>1</sup> In contrast to prior studies, we show that this synthetic sulfide does not exhibit the ordered gladite mineral structure but instead forms a copperdeficient disordered aikinite structure with partial Pb replacement by Bi, according to the chemical formula  $Cu_{1/3} \square_{2/3} Pb_{1/3} Bi_{5/3} S_3$ .<sup>1</sup> By combining experiments and lattice dynamics calculations, we elucidated that the ultralow  $\kappa$  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  $\kappa$  values.<sup>1</sup> A drastic improvement in the carrier concentration and thermoelectric figure of merit have been obtained upon Cl for S and Bi for Pb substitution. The  $Cu_{1-x} \square_x Pb_{1-x} Bi_{1+x} S_3$  series provides a new, interesting structural prototype for engineering n-type thermoelectric sulfides by controlling disorder and optimizing doping.

<sup>1.</sup> Maji, K.; Lemoine, P.; Renaud, A.; Zhang, B.; Zhou, X.; Carnevali, V.; Candolfi, C.; Raveau, B.; Al Rahal Al Orabi, R.; Fornari, M.; Vaqueiro, P.; Pasturel, M.; Prestipino, C.; Guilmeau, E. J. Am. Chem. Soc. **2022**, 144 (4), 1846–1860.

## Thermal stability and phase decomposition of the thermoelectric Cu<sub>5</sub>Sn<sub>2</sub>S<sub>7</sub> by in situ synchrotron X-ray powder diffraction

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Copper tin sulphides (CTS) have been extensively studied for their promising photovoltaic and thermoelectric properties. They are recognised 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 Cu<sub>2+x</sub>Sn<sub>1-x</sub>S<sub>3</sub> system has revealed the existence of a new phase for x = 0.15, Cu<sub>5</sub>Sn<sub>2</sub>S<sub>7</sub>, crystallising in a monoclinic structure of space group *C*2 with unit cell parameters *a* = 12.0580(5) Å, *b* = 5.4063(2) Å, *c* = 8.5026(3) Å, and  $\beta$  = 98.163(3)° [1]. This *p*-type ternary phase exhibits a degenerate semiconducting behaviour with exceptionally high hole mobility originating from the interplay between atomic ordering and charge delocalisation. Despite a relatively high thermal conductivity ( $\approx$  4 W m<sup>-1</sup> K<sup>-1</sup> at 700 K), this compound is characterised by promising figure of merit ZT reaching 0.16 at 700 K.

The understanding of the thermal stability is fundamental for large-scale applications, especially regarding thermoelectric materials. In this work, we report on the thermal stability as well as the structural evolution of  $Cu_5Sn_2S_7$  studied by synchrotron X-ray powder diffraction on the CRISTAL beamline at the SOLEIL synchrotron, France.

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## In situ diffraction study of the phase transformations occurring in the thermoelectric colusite Cu<sub>26</sub>V<sub>2</sub>Sn<sub>6</sub>S<sub>32</sub>

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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<sup>1</sup> and exhibit intrinsically low thermal conductivity.<sup>2,3</sup> Derivatives of the natural mineral colusite, with general formula  $Cu_{26}A_2E_6S_{32}$ , (A = V, Nb, Ta, Cr, Mo, W; E = Ge, Sn, As, Sb), are an emerging class of excellent thermoelectric materials.<sup>4</sup> As example, the ZT value of the colusite  $Cu_{26}V_2Sn_6S_{32}$  rises to near unity at 675K, making this material one of the best p-type TE in this temperature region.<sup>5</sup> Its performances are mainly related to the coexistence of an ordered (*P*-43*n*) and a disordered (*F*-43*m*) forms obtained after sintering at 1023 K (i.e. sample H), leading to a very low thermal conductivity.<sup>5,6</sup> In addition, colusite  $Cu_{26}V_2Sn_6S_{32}$  is known to exhibit an intrinsic exsolution phenomenon supposed to be related to the coexistence of Sn-rich and Sn-poor colusites.<sup>7,8</sup>

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  $Cu_{26}V_2Sn_6S_{32}$ . 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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### Machine-Learning-Assisted Discovery of New Thermoelectric Octahedral Transition-Metal Cluster Chalcogenides

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Since their discovery in the earliest 70's, Chevrel-Sergent phases ( $M_xMo_6X_8$ ; M = Ag, Sn, Ca, Sr, Ba, Sn, Pb, 3d elements or lanthanides; X = S, Se, or Te; x = 0–4) [1] have been extensively studied, mainly for their superconducting properties [2], but also for other various applications in magnetic devices, catalysis, batteries or thermoelectricity [3]. Later, some derivative phases were found, containing larger clusters such as  $Mo_9X_{11}$  or  $Mo_{30}X_{32}$  resulting from one-dimensional *trans*-face sharing of  $Mo_6$  octahedra [4]. Some of them, such as  $Ag_xMo_9Se_{11}$  (x = 3.6 – 3.8), show outstandingly low lattice thermal conductivity, giving rise to promising thermoelectric properties [5]. With these results in mind, electronic structure and electronic transport DFT calculations and machine learning approaches are used for the design of new cluster species which could display interesting thermoelectric properties. The first results will be presented.

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