1ST JAPAN FRANCE

VIRTUAL WORKSHOP ON THERMOELECTRICS

27-30 SEPTEMBER 2021

Sunday, September 26th

Start (Fr)	End (Fr)	Start (Jp)	End (Jp)	
12:00	14:00	19:00	21:00	**Welcome reception on Gather.town**

Join us to get familiarised with Gather.town and share some drinks/thoughts in the lobby!

Monday, September 27th

Start (Fr)	End (Fr)	Start (Jp)	End (Jp)	EVENT	TALK	Page
08:15	08:30	15:15	15:30	**Reception**	**Opening comments by Emmanuel Guilmeau**	
08:30	09:00	15:30	16:00	**Session 1A** **Computational, Calculations, Transport** Chair: Jean-François Halet	**Invited 1A.** ***Phonon scattering by random and correlated disorder: beyond the single impurity approximation*****, Simon Thébaud**	1
09:00	09:15	16:00	16:15		**1A.01** *Ab initio study of intrinsic point defects in thermoelectric oxychalcogenide BiCuSeO*, Donald Goury	2
09:15	09:30	16:15	16:30		**1A.02** *Electronic conductance and thermopower of single-molecule junctions of oligo (phenyleneethynylene) derivatives*, Thomas Niehaus	3
09:30	09:45	16:30	16:45		**1A.03** *Machine-Learning-Assisted Discovery of New Thermoelectric Octahedral Transition Metal Cluster Chalcogenides*, Isaac Chantrenne	4
09:45	10:00	16:45	17:00		**1A.04** *Phonon thermal transport across heterogeneous interfaces by ab initio lattice dynamics calculation*, Yuta Hino	6
10:00	10:15	17:00	17:15		**1A.05** *Ultrafast dynamics of photoexcited carriers in bulk semiconductors and in accumulation layer: energy loss rate and screening effects*, Jelena Sjakste	8
10:15	10:45	17:15	17:45	Break		
10:45	11:15	17:45	18:15	**Session 1B** **Process and modules** Chair: Guillaume Savelli	**Invited 1B.** ***High Power Density Thermoelectric Generators with Skutterudites*****, Soufiane Eloualid**	10
11:15	11:30	18:15	18:30		**1B.01** *Electrodeposition of single crystalline Te and Ag$_2$Te nanostructures for thermoelectric conversion*, Karen Al Hokayem	11
11:30	11:45	18:30	18:45		**1B.02** *Durability testing of nanostructured PbTe-based thermoelectric elements*, Philipp Sauerschnig	12
11:45	12:00	18:45	19:00		**1B.03** *Mechanically durable thermoelectric power generation module made of Ni-based alloy for interlaboratory test*, Michihiro Ohta	14
12:00	12:15	19:00	19:15		**1B.04** *Planar-type Si phononic crystal thermoelectric generator with a top cavity structure*, Ryoto Yanagisawa	16
12:15	13:15	19:15	20:15	Discussions		

Tuesday, September 28th

Start (Fr)	End (Fr)	Start (Jp)	End (Jp)	EVENT	TALK	Page
08:30	09:00	15:30	16:00	**Session 2A** **Intermetallics I** Chair: Michihiro Ohta	**Invited 2A.** ***New intermetallic thermoelectric candidates screened by calculation*, Adrien Moll**	17
09:00	09:15	16:00	16:15		**2A.01** *Axis-dependent carrier polarity in polycrystalline $NaSn_2As_2$ for transverse thermoelectrics*, Yosuke Goto	19
09:15	09:30	16:15	16:30		**2A.02** *Growth of thermoelectric material $ZnSnSb_2$ with pseudocubic structure*, Yusuke Shigeeda	21
09:30	09:45	16:30	16:45		**2A.03** *High-Power Factor and Annealing Optimization of Fe,Ni-based Skutterudites*, Giovanna Latronico	23
09:45	10:00	16:45	17:00		**2A.04** *Impact of temperature and mode polarization on the acoustic phonon range in type-I clathrates*, Stéphane Pailhès	25
10:00	10:15	17:00	17:15		**2A.05** *Influence of nanostructuration in Fe_2VAl alloys*, Abou Diack Rasselio	27
10:15	10:45	17:15	17:45	Break		
10:45	11:15	17:45	18:15	**Session 2B** **Chalcogenides I** Chair: David Bérardan	**Invited 2B.** ***Intrinsic and extrinsic approaches to tune lattice thermal conductivity for thermoelectrics*, Naoki Sato**	28
11:15	11:30	18:15	18:30		**2B.01** *Comparisons of electronic conduction between ordered and disordered phases in quasi-ternary Cu-Zn-Sn-S sulfides*, Keita Yoshizawa	29
11:30	11:45	18:30	18:45		**2B.02** *Enhancement of the thermoelectric performances in Bi-doped and Cl-doped synthetic mineral $CuPbBi_5S_9$*, Krishnendu Maji	31
11:45	12:00	18:45	19:00		**2B.03** *First principles calculations of electronic and thermoelectric transport properties of $Pb_2Bi_2Te_5$ with different atoms sequences*, Weiliang Ma	32
12:00	12:15	19:00	19:15		**2B.04** *Polyol and Hydrothermal synthesis processes of the promising Samsonite phase*, Adam Bertrand	33
12:15	13:15	19:15	20:15	Poster Session #1		68

Wednesday, September 29th

Start (Fr)	End (Fr)	Start (Jp)	End (Jp)	EVENT	TALK	Page
08:30	09:00	15:30	16:00	**Session 3A** **Low Dimensionality** Chair: Nicolas Stein	**Invited 3A. *Nanoscale thermal transport at ceramic interfaces: a computational and machine learning approach*, Susumu Fujii**	34
09:00	09:15	16:00	16:15		**3A.01** *Anomalously low heat conduction in single-crystal superlattice ceramics lower than randomly oriented polycrystals*, Hai Jun Cho	36
09:15	09:30	16:15	16:30		**3A.02** *Growth of halide perovskite thin film for thermoelectric application*, Shrikant Saini	37
09:30	09:45	16:30	16:45		**3A.03** *Tailoring the thermoelectric properties of ScN by introducing defects*, Razvan Burcea	38
09:45	10:00	16:45	17:00		**3A.04** *Thermoelectric properties of carbon nanotubes carrier-tuned by electric double layer techniques*, Haruka Yoshida	40
10:00	10:15	17:00	17:15		**3A.05** *Tuning thermoelectric properties by epitaxial strain in p-type Sr-doped* $LaCrO_3$ *thin films*, Romain Bachelet	41
10:15	10:45	17:15	17:45	Break		
10:45	11:15	17:45	18:15	**Session 3B** **Chalcogenides II** Chair: Yuzuru Miyazaki	**Invited 3B. *Manipulation of defect structure for high performance thermoelectric chalcogenides*, Priyanka Jood**	43
11:15	11:30	18:15	18:30		**3B.01** $Cu_{26}Ti_2Sb_{6-x}Ge_xS_{32}$ *colusite with high thermoelectric performance*, Takashi Hagiwara	45
11:30	11:45	18:30	18:45		**3B.02** *Identification of resonant impurities in thermoelectric semiconductors*, Shantanu Misra	47
11:45	12:00	18:45	19:00		**3B.03** *Investigation of some niobium chalcogenides transport properties*, Hugo Bouteiller	49
12:00	12:15	19:00	19:15		**3B.04** *Ordered sphalerite derivative* $Cu_5Sn_2S_7$*: a degenerate semiconductor with high carrier mobility in the Cu–Sn–S diagram*, Ventrapati Pavan Kumar	50
12:15	13:15	19:15	20:15	Poster Session #2		68

Thursday, September 30th

Start (Fr)	End (Fr)	Start (Jp)	End (Jp)	EVENT	TALK	Page
08:30	09:00	15:30	16:00	**Session 4A** **Intermetallics II** Chair: Eric Alleno	**Invited 4A. *Point defect engineering enhances thermoelectric performance of Mg_2Si and Mg_2Sn single crystals*, Kei Hayashi**	52
09:00	09:15	16:00	16:15		**4A.01** *Strategies to Achieve High Thermoelectric Performance of n-type Mg_3Sb_2-Mg_3Bi_2 Alloys*, Kazuki Imasato	54
09:15	09:30	16:15	16:30		**4A.02** *The thermal stability of $KGaSb_4$*, Oussama El Hamouli	55
09:30	09:45	16:30	16:45		**4A.03** *Thermodynamic stability of Frenkel defect and its influence on phonon thermal conduction in Mg_3Sb_2*, Yohei Ueki	56
09:45	10:00	16:45	17:00		**4A.04** *Thermoelectric properties of n-type material, $(Mg,Y)_3(Sb,Bi)_2$*, Ryosuke Sakagami	58
10:00	10:15	17:00	17:15		**4A.05** *Thermoelectric Properties of p-Type $Ba_8Au_6Ge_{40}$ Clathrate*, Yudai Koga	59
10:15	10:45	17:15	17:45	Break		
10:45	11:15	17:45	18:15	**Session 4B** **Oxides and Silicides** Chair: Michitaka Ohtaki	**Invited 4B. *High texturization and improved thermoelectric properties using a magnetic slip casting process- the illustrative case of $CrSi_2$*, Sylvain Le Tonquesse**	60
11:15	11:30	18:15	18:30		**4B.01** *A promising multiscale approach to enhance the thermoelectric properties of β–$FeSi_2$*, Linda Abbassi	62
11:30	11:45	18:30	18:45		**4B.02** *$Ba_{1/3}CoO_2$, A Promising High-Temperature Thermoelectric Oxide*, Xi Zhang	64
11:45	12:00	18:45	19:00		**4B.03** *Electronic band structure and thermoelectric properties of $AgCoO_2$ from first principles calculations*, Hidetomo Usui	65
12:00	12:15	19:00	19:15		**4B.04** *Impact of dislocation-core structures on phonon thermal conduction in MgO by perturbed molecular dynamics*, Wataru Sekimoto	66
12:15	13:15	19:15	20:15	Closing Remarks (Koichiro Suekuni) × Drinks		

Phonon scattering by random and correlated disorder: beyond the single impurity approximation

Simon Thébaud*[1], Carlos Polanco[1], Lucas Lindsay[1], and Tom Berlijn[2,3]

[1]Materials Science and Technology Division, Oak Ridge National Laboratory – 1 Bethel Valley Road, 37830 Oak Ridge, TN, United States
[2]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory – 1 Bethel Valley Road, 37830 Oak Ridge, TN, United States
[3]Computational Sciences and Engineering Division, Oak Ridge National Laboratory – 1 Bethel Valley Road, 37830 Oak Ridge, TN, United States

Abstract

In the past decades, suppressing the lattice thermal conductivity of materials by introducing defects and disorder has been instrumental to increase the thermoelectric figure of merit. Theoretical efforts contributing to this progress have largely been based on methodologies dealing with single impurities (second-order pertubation theory and, more recently, the T-matrix approximation), with surprisingly good agreements between theory and experiments even for compounds far from the dilute limit, such as maximally-disordered alloys. In this talk, I will evaluate the validity of the single-impurity methods in alloys with strong mass differences, using simple spring-mass models and the example of Mg2(Si,Sn) with interatomic force constants derived from density functional theory. I will compare the perturbative predictions for the phonon spectrum, scattering rates and thermal conductivity with results obtained from the Chebyshev polynomials Green's function method on large disordered systems (tens of millions of atoms), in order to elucidate why pertubative approaches work so well in such compounds despite the presence of strong disorder.

In the second part of the talk, I will explore how phonon-disorder scattering can be manipulated by introducing point defects with correlations in their spatial distributions. Using simple models with mass disorder, I will discuss how the power law for low-frequency scattering rates can be changed away from Rayleigh scattering (proportional to the 4th power of the frequency), and what are the optimal correlations for minimizing the lattice thermal conductivity.

S. Thébaud, C. A. Polanco, L. Lindsay, and T. Berlijn, Phys. Rev. B 102, 094206 (2019), *Success and Breakdown of the T-Matrix Approximation for Phonon-Disorder Scattering*

Keywords: phonon transport, disorder

---

*Speaker

Ab initio study of intrinsic point defects in thermoelectric oxychalcogenide BiCuSeO

Donald Goury*[1], David Bérardan†[1], Jérôme Creuze‡[1], and Emilie Amzallag§[1]

[1]Institut de Chimie Moléculaire et des Matériaux dÓrsay – Université Paris-Saclay, Centre National de la Recherche Scientifique : UMR8182 – bat. 420 91405 ORSAY CEDEX, France

Abstract

BiCuSeO is among the best promising thermolectric materials for applications in a medium temperature range. Even if its properties are now well-known several questions remain open. Especially, it has been shown experimentally that the presence of some (yet 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 optimize the TE properties. Answering these questions requires the help of first-principles investigations. I present here a DFT study of intrinsic point defects in BiCuSeO with the CRYSTAL17 code. Firstly the study of the competing phases of BiCuSeO during the synthesis enables to plot stability diagrams in order to select the possible chemical environment that will induce different defects configurations. In a second part defects formation energies are calculated in a grand canonical approach. Finally, equilibrium Fermi energy and defects concentrations are determined in each thermodynamic limit. This study will be pursued with the study of atomic and electronic structures of pristine and defective BiCuSeO. The final step will consist in performing electrical transport calculations to obtain a quantitative study of the impact of the dominant intrinsic defects on the TE properties of BiCuSeO.

Keywords: BiCuSeO, ab initio calculations, defects

---

*Speaker

†Corresponding author: david.berardan@universite-paris-saclay.fr

‡Corresponding author: jerome.creuze@universite-paris-saclay.fr

§Corresponding author: emilie.amzallag@universite-paris-saclay.fr

sciencesconf.org:vwt2021:363977

Electronic conductance and thermopower of single-molecule junctions of oligo (phenyleneethynylene) derivatives

Thomas Niehaus*[1], Hervé Dekkiche[2], Andrea Gemma[3], Fatemeh Tabatabaei[1], Andrei Batsanov[4], Samy Merabia[5], Bernd Gotsmann[3], and Martin R. Bryce[4]

[1]Université Claude Bernard Lyon 1 – Université de Lyon, ILM UMR5306 CNRS – 43, boulevard du 11 novembre 1918, 69622 Villeurbanne cedex, France

[2]Institut de Chimie de Strasbourg (ICS) – CNRS : UMR7177, université de Strasbourg – 4, rue Blaise Pascal 67000 STRASBOURG, France

[3]IBM Zurich Research Laboratory – Säumerstrasse 4 CH-8803 Rüschlikon Switzerland, Switzerland

[4]Department of Chemistry [Durham, UK] – Stockton Road, Durham DH1 3LE, United Kingdom

[5]Institut Lumière Matière (ILM) – CNRS : UMR5306, Université Claude Bernard - Lyon I (UCBL) – UMR5306 CNRS Université Claude Bernard Lyon 1 Domaine Scientifique de La Doua Bâtiment Kastler, 10 rue Ada Byron 69622 Villeurbanne CEDEX, France, France

Abstract

We report the single-molecule transport properties of three new oligo(phenyleneethynylene) (OPE3) derivatives possessing terminal dihydrobenzo[b]thiophene (DHBT) anchoring groups and various core substituents (phenylene, 2,5-dimethoxyphenylene and 9,10-anthracenyl). Their
electronic conductance and their Seebeck coefficient have been determined using scanning tunneling
microscopy-based break junction (STM-BJ) experiments between gold electrodes. The transport properties
of the molecular junctions have been modelled using DFT-based computational methods which
reveal a specific binding of the sulfur atom of the DHBT anchor to the electrodes. The experimentally
determined Seebeck coefficient varies between –7.9 and –11.4 μV K–1 in the series and the negative sign
is consistent with charge transport through the LUMO levels of the molecules.

Keywords: DFT, NEGF, Molecular electronics

---

*Speaker

Machine-Learning-Assisted Discovery of New Thermoelectric Octahedral Transition-Metal Cluster Chalcogenides

Isaac Chantrenne*[1], Jean-Francois Halet[2], David Berthebaud[3], Fabien Grasset[4], Stephane Cordier[5], Guillaume Lambard[6], Regis Gautier[7], and Bruno Fontaine[8]

[1]Institut des Sciences Chimiques de Rennes – Centre National de la Recherche Scientifique, Universite de Rennes 1 : UMR6226 – France

[2]Institut des Sciences Chimiques de Rennes – UMR 6226 CNRS - Université de Rennes 1 - Ecole Nationale Supérieure de Chimie de Rennes – Avenue du Général Leclerc F-35042 Rennes Cédex, France

[3]CNRS-Saint Gobain-NIMS, UMI 3629, LINK – Tsukuba, Japan

[4]UMR 6226 Institut des Sciences Chimiques de Rennes (ISCR) – Université de Rennes I – 263 av. du Général Leclerc, 35042 Rennes, France

[5]Institut des Sciences Chimiques de Rennes (ISCR) – Universite de Rennes 1, CNRS : UMR6226, Ecole Nationale Supérieure de Chimie de Rennes – Campus de Beaulieu - Bât. 10 Avenue du Général Leclerc 35042 Rennes Cedex, France

[6]National Institute for Materials Science – Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

[7]Institut des Sciences Chimiques de Rennes – ISCR UMR CNRS 6226 – Campus de Beaulieu, 35000 Rennes, France

[8]Institut des Sciences Chimiques de Rennes – Institut National des Sciences Appliquées (INSA) - Rennes, Universite de Rennes 1, CNRS : UMR6226, Ecole Nationale Supérieure de Chimie de Rennes, Institut National des Sciences Appliquées [INSA] – Campus de Beaulieu - Bât. 10 Avenue du Général Leclerc 35042 Rennes Cedex, France

Abstract

Since their discovery in the earliest 70's, Chevrel-Sergent phases (MxMo6X8; 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 Mo9X11 or Mo30X32 resulting from one-dimensional *trans*-face sharing of Mo6 octahedra [4]. Some of them, such as AgxMo9Se11 (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.

References

R. Chevrel, M. Sergent, J. Prigent, *J. Solid State Chem.,* **1971**, *3*, 515-519.

---

*Speaker

T. Matthias, M. Marezio, E. Corenzwit, A.S. Cooper, H.E. Barz, *Science,* **1972**, *175*, 1465-1466.

T. Caillat, J.-P. Fleurial, G. J. Snyder, *Solid State Sci.* **1999**, *1*, 535-544.

a) S. Picard, J.-Y. Saillard, P. Gougeon, H. Noël, M. Potel, *J. Solid State Chem.*, **2000**, *155*, 417-426. b) P. Gougeon, P. Gall, A. Huguenot, R. Al Rahal Al Orabi, R. Gautier, *Inorg. Chem*, **2019**, *58*, 22, 15236-15245.

a) P. Gougeon, J. Padiou, J.Y. Le Marouille, M. Potel, M. Sergent, *J. Solid State Chem.*, **1984**, *51*, 2, 218-226. b) R. Al Rahal Al Orabi, B. Boucher, B. Fontaine, P. Gall, C. Candolfi, B. Lenoir, P. Gougeon, J.-F. Halet, R. Gautier, *J. Mater. Chem. C*, **2017**, *5*, 12097-12104. c) C. Candolfi, P. Gougeon, P. Gall, M. Potel, A. Dauscher, B. Lenoir, *Structure and Bonding*, **2019**, *180*, 125-141.

Keywords: Machine Learning, Thermoelectricity, Clusters, Chalcogenides, Chevrel phases

Phonon thermal transport across heterogeneous interfaces by ab initio lattice dynamics calculation

Yuta Hino*†[1], Susumu Fujii[1,2], Masato Yoshiya[1,2], Taiafumi Ishibe[1], and Yoshiaki Nakamura[1]

[1]Osaka University – 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
[2]Japan Fine Ceramics Center – 2-4-1, Mutsuno, Atsuta, Nagoya 456-8587, Japan

Abstract

Efforts have been made for controlling phonon thermal conduction by exploiting interface structures. In electronic devices such as integrated circuits (ICs), heat dissipation has become an issue due to downsizing of the ICs. For the heat dissipation, interfaces with higher thermal transmission are required. On the contrary, for thermoelectric conversion, low thermal conductance is required. For that, nanostructuring has attracted attention to reduce the thermal conductivity to improve the thermoelectric conversion efficiency. In either case, it is necessary to control the interface structures.

Chalcogenides such as PbTe, SnSe and GeS have attracted attention as candidates for electronic device materials or thermoelectric materials. In the case of PbTe/GeS heterogeneous interface, the interfacial thermal resistance (ITR) was found to be small although the GeS structure appears to be amorphous [1]. The origins of low ITR is discussed from a general perspective, i.e., conservations of phonon energy and crystal momentum in the unit crystal lattices at either side of the interface. However, detailed structures of the heterogeneous interface between amorphous GeS and crystalline PbTe layers are not addressed, and thus the relationship between the interface structures and thermal conductivity across the interface remains unclear. Therefore, in this study, we analyzed the atomic-level structures of heterogeneous interface and phonon properties therein.

We constructed two kinds of heterogeneous interface models: a c-PbTe/c-GeS model and a c-PbTe/a-GeS model where GeS has amorphous-like structure prepared carefully. Here, prefixes c- or a- denote crystalline or amorphous. Phonon calculations were performed by harmonic lattice dynamics method, and the lattice thermal conductivity was analyzed by calculating third-order force constants as well. The VASP [2] code was used for the structure optimization for calculating an interface energy and obtaining a starting structure for phonon calculations . The phonopy [3] and phono3py [4] codes were used for harmonic and anharmonic lattice dynamics calculations, respectively.

First of all, it is found that the c-PbTe/c-GeS model showed lower interface energy than we expected. This can be attributed to the flexible rearrangement of atoms in the GeS layer due to lower elastic constant perpendicular to layers within the unitcell of SnSe structure. Surprisingly, the c-PbTe/a-GeS model showed even lower interface energy than for the c-PbTe/c-GeS model due to the more flexible arrangement of atoms in the a-GeS layer. This

---

[*] Speaker

[†] Corresponding author: yuta.hino@mat.eng.osaka-u.ac.jp

indicates that the interatomic bonding is not compromised upon forming the heterogeneous c-PbTe/a-GeS interface, and probably facilitates phonon conduction across the interface, resulting in lower ITR compared to other heterogeneous interfaces. From phonon calculations, it is found that the acoustic phonons with low frequencies dominates the thermal conduction across the heterogeneous interface.

In this study, the c-PbTe/c-GeS and c-PbTe/a-GeS heterogeneous interface models were constructed and their phonon properties were analyzed using the *ab initio* lattice dynamics. Atoms in the GeS layer are flexibly rearranged upon the formation of the heterogeneous interfaces due to the difference in elastic constants. This strengthens the interatomic bonding at the interface and promotes acoustic phonon conduction in the low frequency range, resulting in the reduction of the interfacial thermal resistance. These findings provide a new guideline for controlling heat conduction across the heterogeneous interface from the viewpoint of interface structure.

Acknowledgements: This study is in part supported by Grant-in-Aid for Scientific Research [JP19H05786, JP20H05195, JP20K05062, and JP20K15034]

References:

T. Ishibe, M. Yoshiya, Y. Nakamura et al., *Commun. Phys.*, **4** (2021) 153.

G. Kresse, J. Furthmüller, *Phys. Rev. B*, **54** (1996), 11169-11185

A. Togo, I. Tanaka, *Scr. Mater.*, **108** (2015), 1-5.

A. Togo et al., *Phys. Rev. B,* **91** (2015) 094306

Keywords: phonon, ab initio calculation, heterogeneous interface

Ultrafast dynamics of photoexcited carriers in bulk semiconductors and in accumulation layer: energy loss rate and screening effects.

Jelena Sjakste*[1], Raja Sen[2], and Nathalie Vast[3]

[1]Laboratoire des Solides Irradiés – Polytechnique - X, CNRS : UMR7642, Institut Polytechnique de Paris, CEA-DRF-IRAMIS – LSI - UMR 7642, 28 route de Saclay, F-91128 Palaiseau Cedex, France
[2]Laboratoire des Solides Irradiés – CEA-DRF-IRAMIS, Centre National de la Recherche Scientifique - CNRS, Institut Polytechnique de Paris, Polytechnique - X – LSI - UMR 7642, 28 route de Saclay, F-91128 Palaiseau Cedex, France
[3]Laboratoire des Solides Irradiés – Commissariat à l'énergie atomique et aux énergies alternatives : DRF/IRAMIS, Ecole Polytechnique, Centre National de la Recherche Scientifique : UMR7642, Institut Polytechnique de Paris – Route de Saclay, F-91128 Palaiseau Cedex, France

Abstract

Electron-phonon coupling determines the charge transport properties in pure materials as well as the relaxation dynamics of photoexcited carriers.The rapid development of the computational methods based on density functional theory, on the one hand, and of the time-energy- and momentum- resolved spectroscopy, on the other hand, allows today an unprecedently detailed insight into the role of the electron-phonon coupling [1]. A computational method based on density functional theory and on interpolation of the electron-phonon matrix elements in Wannier space allowed to successfully interpret the dynamics of photoexcited electron relaxation in several semiconductors, such as GaAs, Si, InSe, in good agreement with two-photon photoemission experiments.
In this work, we will discuss electron-phonon coupling and hot electron relaxation is several semiconductors. Recently, the dynamics of hot electron relaxation was studied in silicon, over a very large excess energy interval, from both experimental and theoretical point of view [2], and the measured relaxation times were interpreted as due to the energy transfer from electrons to the lattice. We will discuss the temperature dependence of the relaxation times related to the energy transfer in silicon, germanium and gallium arsenide, and the relative roles of different electron-phonon scattering channels in the energy transfer.

Then, we will present our results on the photoexcited electron relaxation in InSe. InSe is a quasi-2D material which was shown recently to have potential interest for optoelectronics. In this work, we will discuss our new results on the relaxation dynamics and screening of the electron-phonon interaction in doped InSe [3].

1. J. Sjakste et al, J. Phys: Cond. Mat. 30, 353001 (2018).

2. Tanimura, Kanasaki, Tanimura, Sjakste, Vast, PRB 100, 035201 (2019).

---

*Speaker

3. Chen, Sjakste et al, PNAS 117, 21962-21967 (2020).

Keywords: electron, phonon coupling, hot carrier relaxation, DFT, semiconductor

High Power Density Thermoelectric Generators with Skutterudites

Soufiane Eloualid*[1], Iurii Kogut[1], Mohamed Benyahia[2], Eugen Geczi[3], Francis Kosior[1], Philippe Masschelein[1], Christophe Candolfi[1], Anne Dauscher[1], Jan Dieter Koenig[3], Alexandre Jacquot[3], Thierry Caillat[4], Eric Alleno[2], and Bertrand Lenoir[1]

[1]Institut Jean Lamour, UMR 7198 CNRS – University of Lorraine – 2 allee Andre Guinier – Campus ARTEM, BP 50840, 54011, Nancy Cedex, France

[2]Institut de Chimie et des Matériaux Paris-Est – Université Paris-Est Créteil Val-de-Marne - Paris 12 : UMR7182, Centre National de la Recherche Scientifique : UMR7182 – 2-8, rue Henri Dunant 94320 Thiais, France

[3]Fraunhofer Institute for Physical Measurement Techniques – Heidenhofstrasse 8, 79110 Freiburg, Germany

[4]Jet Propulsion Laboratory at the California Institute of Technology – 4800 Oak Grove Drive, Pasadena, CA 91109, United States

Abstract

TEGs (thermoelectric generators) are a flexible way to transform low-grade heat into useable electrical power. While shortening the active thermoelectric legs is an effective strategy for increasing the maximum output power density, high electrical contact resistances, and thermomechanical stresses are two major issues that have so far prevented a significant reduction in the volume of thermoelectric materials integrated thus far. We show how these limitations can be overcome by employing a non-traditional leg architecture that involves the insertion of thick metallic layers. Several single-couple and multi-couple TEGs with skutterudite layers as thin as 1 mm have been produced, generating record values ranging from 3.4 to 7.6 W cm-2 at temperatures ranging from 450 to 630 K. When compared to 1-cm-long legs, the maximum achieved equates to a sixtyfold increase of skutterudites per unit volume. Thick metallic layers are established as a reliable technique for developing high-power-density TEGs in our research.

Keywords: TEG Power Density Skutterudites

---

*Speaker

Electrodeposition of single crystalline Te and Ag2Te nanostructures for thermoelectric conversion

Karen Al Hokayem[*†1], Jaafar Ghanbaja[2], Sophie Legeai[1], and Nicolas Stein[*1]

[1]Institut Jean Lamour – CNRS, Institut Jean Lamour (CNRS – Université de Lorraine) – France
[2]Institut Jean Lamour – CNRS, Institut Jean Lamour (CNRS – Université de Lorraine) – France

Abstract

Nanostructuring can be a solution to improve thermoelectric performances, as the lattice part of the thermal conductivity can be independently lowered when moving from bulk to nanostructures [**1**]. Among the thermoelectric materials, Tellurium has a high positive Seebeck coefficient (500 μV.K-1) at room temperature but with a relative high thermal conductivity (3 W.m-1K-1). Therefore efforts have been devoted in the literature to the production of low dimensional materials in the perspective of lowered thermal conductivity [**1**].
In this work, we synthesized self-standing Te nanostructures by electrodeposition technique, taking advantage of the templating properties of ionic liquids solvents (IL). Single crystalline hexagonal nanostructures were systematically obtained with a preferential orientation along the [001] direction. By varying the conditions of electrodeposition, shape and size of nanostructures can be tuned: Nanorods, nanowires and nanotubes were synthesized, with diameters that can be lowered to 50 nm. Nanostructures aspect ratio depends on the overvoltage and nanotubes can be obtained in high overpotential conditions due to mass transport effects. By changing the composition of the IL electrolyte, the speciation of TeIV can be modulated and hair-like nanowires of 70 μm long and 50±20 nm in diameter can be synthesized [**2,3**]. Finally, small rods of 70±15nm in diameter and less than 300 nm long were grown by applying a small charge density.

The Tellurium nanorods have also been used as precursors of an additional synthesis step. Indeed, by simple cementation reaction in Ag(I) aqueous solution, Te nanostructures have been transformed into Ag-rich Ag2Te. Final outstanding monoclinic single crystalline nanorods were obtained thanks to the following topotactic reaction : 2Ag + Te Ⓡ Ag2Te [**4**]. The aspect ratio is almost the same between the starting and the final nanostructures, the width being slightly increased of about 30 % (” 20 nm). The stoichiometry of Ag2Te is not influenced neither by the atomic ratio Ag/Te nor the synthesis duration. It should be underlined that the final hessite silver telluride nanostructures should behave as n type semiconductor.

Keywords: tellurium, silver telluride, nanostructures, chemical synthesis

---

[*] Speaker

[†] Corresponding author: karen.al-hokayem@univ-lorraine.fr

Durability testing of nanostructured PbTe-based thermoelectric elements

Philipp Sauerschnig*[1], Priyanka Jood[1], and Michihiro Ohta†[1]

[1]National Institute of Advanced Industrial Science and Technology – 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan

Abstract

PbTe is considered one of the prime candidates for thermoelectric energy conversion in the temperature range of 600 – 900 K thanks to its outstanding electrical and thermal properties. High zT values for both p- and n-type PbTe have been achieved through strategies such as band engineering and nanostructuring. The development of thermoelectric modules which take advantage of these high-performance materials for power generation requires overcoming several design and fabrication challenges regarding electrical contacts and mechanical stability. A critical factor for the performance and durability of thermoelectric modules is the development of a diffusion barrier layer which provides good electrical contact to minimize electrical losses. Furthermore, the diffusion barrier must be chemically and mechanically stable to ensure consistent performance under long-term operation. The mechanical properties, particularly at the intended working temperature, are an important factor for the design of durable thermoelectric modules.

In this study, we investigated the thermoelectric and mechanical properties of nanostructured PbTe-based thermoelectric materials. Furthermore, long-term durability test under continuous operation of thermoelectric legs based on these materials were conducted.

The materials, p-type Pb0.993-xNaxGe0.007Te (x=0.02, 0.04) and n-type Pb0.98Ga0.02Te were synthesized in vacuum-sealed, carbon coated quartz tubes at 1223 K, hand milled into powders and sintered with and without diffusion barrier layers (Fe or Co80Fe20 alloy) at 773 K. The thermoelectric properties (Seebeck coefficient, electrical resistivity, and thermal conductivity) and mechanical properties (thermal expansion and 3-point flexural testing) were measured in the temperature range of 300 – 900 K. The energy conversion characteristics of p-and n-type legs were simulated by finite element analysis using the measured thermoelectric properties. SEM-EDX and a resistance scanning probe were used to characterize chemical composition and internal resistance across the diffusion barrier/PbTe interface and along the thermoelectric leg. Long-term durability testing of the thermoelectric legs was performed by continuous measurement of the power generation characteristics at a hot-side temperature of approx. 773 K.

The peak zT approx. 2.0 at 773 K for p-type Pb0.973Na0.02Ge0.007Te and zT approx. 1.5 at 723 K were observed. The measurement of the linear coefficient of thermal expansion (CTE) shows consistently high values throughout the whole temperature range close to 20 ppm with only small differences between p- and n-type materials. The mechanical properties determined by 3-point flexural testing change drastically with increasing temperature.

---

*Speaker

†Corresponding author: ohta.michihiro@aist.go.jp

While both p- and n-type materials deform almost exclusively elastically until failure at room temperature, increased plastic deformation and significant reduction in flexural strength is observed towards elevated temperatures.
Thermoelectric legs with diffusion barriers with interfacial resistance values close to 10 $\mu\Omega$ cm2 were successfully prepared through direct bonding by sintering. The measurement of the power generation characteristics of the thermoelectric legs reveals high conversion efficiency, albeit still significantly lower than simulated values, the main difference being high internal resistance in the fabricated legs. The formation of cracks is observed during fabrication and leads to increased resistance and reduced mechanical stability.
The durability testing by continuous measurement of the power generation characteristics at a hot-side temperature of approx. 773 K resulted in a continuous increase in electric resistance and reduction in power output and conversion efficiency of the thermoelectric legs.

Further optimization of diffusion barrier material and fabrication process will be required to improve the performance and durability of the nanostructured PbTe-based thermoelectric device.

This work was supported by Research and Development Program for Promoting Innovative Clean Energy Technologies Through International Collaboration funded by New Energy and Industrial Technology Development Organization (NEDO)

Keywords: PbTe, lead telluride, durability, nanostructure, mechanical properties, module

Mechanically durable thermoelectric power generation module made of Ni-based alloy for interlaboratory test

Ohta Michihiro[*†1], Chetty Raju[1], Ziolkowski Pawel[2], Blaschkewitz Przemyslaw[2], Imasato Kazuki[1], Jood Priyanka[1], Muller Eckhard[2,3], and Yamamoto Atsushi[1]

[1]Global Zero Emission Research Center, National Institute of Advanced Industrial Science and Technology (AIST) – Tsukuba, Ibaraki 305-8569, Japan

[2]Institute of Materials Research, German Aerospace Center (DLR) – D-51147 Cologne, Germany

[3]Institute of Inorganic and Analytical Chemistry, Justus Liebig University Giessen – D-35392 Giessen, Germany

Abstract

A thermoelectric module made of Ni-based alloy has been developed as reference for use in interlaboratory test of the power generation characteristics. The module was fabricated with eight pairs of legs made of mechanically durable p-type Ni90Cr10 (chromel) and n-type Cu55Ni45 (constantan). To reduce thermal conductance of the module, holes were made in the p- and n-type Ni-based alloys. In testing facility developed at AIST, a maximum electrical power of _˜0.39 W and maximum conversion efficiency of _˜0.53% were obtained for the module at hot-side temperature of 773 K and cold-side temperature of 323 K. The reproducibility of power generation characteristics, including the open circuit voltage, internal resistance, and output heat flow of the module was confirmed through 12 repeated tests and _˜120 h of continuous tests at hot-side temperature of 773 K and cold-side temperature of 323 K. After tests at AIST, the Ni-based alloy thermoelectric module was sent to DLR for characterization in facility developed at DLR. The measurements at AIST and DLR were performed under nominally identical conditions. The suitability of the Ni-based alloy module as a reference for future metrological standard has been demonstrated by the interlaboratory test.

Acknowledgements: This work at AIST was supported by Research and Development Program for Promoting Innovative Clean Energy Technologies Through International Collaboration funded by New Energy and Industrial Technology Development Organization (NEDO), the International Joint Research Program for Innovative Energy Technology funded by the Ministry of Economy, Trade and Industry (METI), and the Research and Development Project for Innovative Thermal Management Materials and Technologies funded by Thermal Management Materials and Technology Research Association (TherMAT) and NEDO. This work at DLR was accomplished in the course of the project "Thermoelectric Standardization for High Temperatures" (TEST-HT, grant no. 03VP04401), which was supported by the German Federal Ministry of Education and Research. Further financial support from the Energy Efficiency & Resource Core Technology Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) was granted from the Ministry of Trade,

---

[*] Speaker

[†] Corresponding author: ohta.michihiro@aist.go.jp

Industry & Energy (MOTIE), Republic of Korea (grant no. 20188550000290).

References: [1] Chetty, R.; Nagase, K.; Aihara, M.; Jood, P.; Takazawa, H.; Ohta, M.; Atsushi Y., Appl. Energy, 2020, 260, 114443:1-9. [2] Ziolkowski, P.; Chetty, R.; Blaschkewitz, P.; Ohta, M.; Yamamoto, A.; Muller, E., Energy Technol. 2020, 8, 2000557:1-11.

Keywords: Interlaboratory test, Power generation module, Power generation characteristics, Chromel, Constantan, Thermoelectrics

Planar-type Si phononic crystal thermoelectric generator with a top cavity structure

Ryoto Yanagisawa*[1], Patrick Ruther[2], Oliver Paul[2], and Masahiro Nomura[1]

[1]IIS, The University of Tokyo – 153-8505, Tokyo, Japan
[2]IMTEK, University of Freiburg – Germany

Abstract

We developed planar-type silicon (Si) thermoelectric generator (TEG) with phononic crystal (PnC) nanostructures. 1 uW/cm2 was achieved with a temperature difference of 0.7 K in Si thermoelectric material. Planar-type TEGs were fabricated in a 300 nm thick poly-crystalline Si (poly-Si) layer doped with phosphorous at 2.0 × 10ˆ20 cm-3 carrier density on a 2.5 um thick SiO2 layer. Utilizing electron-beam lithography and reactive-ion-etching of silicon, the array of holes with a diameter of about 210 nm and a period of 300 nm is formed in the poly-Si layer. By removing a part of the SiO2 layer under the poly-Si, a bridge structure is formed to induce a temperature gradient in the poly-Si layer. In our previous work, we demonstrated the power enhancement in planar-type silicon TEG by making PnC nanostructures due to a large reduction of thermal conductivity [1]. Further improvement is expected by making a top cavity structure that helps heat to evacuate from the suspended bridge to the cold side ambient.

This work achieved 1 uW/cm2 power density of planar-type TEG with PnC nanostructures and top cavity structure. We fabricated a cavity structure on top of the poly-Si layer with a photoresist spacer and a Si wafer; the 525 um thick Si wafer is placed on the poly-Si device layer with support of a few-um-thick photoresist spacer. We measured the open-circuit voltage of TEG by applying the temperature difference between the top Si wafer and bottom Si substrate (delta T_DEV). For the TEG composed of 18 units of the device in 0.32 mm2 area, 88 uV per delta T_DEV is observed and results in 0.0056 uW/cm2/K2 power factor of TEG with an internal electrical resistance of 125 ohms; from 14 K of delta T_DEV, power density reaches 1 uW/cm2.

When the temperature difference delta T_DEV of 14 K is applied in the device, the temperature difference induced in the poly-Si PnC thin-film (delta T_TE) is 0.7 K, i.e., 5 % of delta T_DEV; this represents a 20-fold improvement over the device without top cavity structure [1]. There is an unexpected air gap of 20 um between the poly-Si layer and the top wafer. We expect a further power enhancement by improving the top cavity structure. Our simulation shows that delta T_TE reaches 20 % of delta T_DEV if the air gap becomes 3 um, which results in 10 uW/cm2 power density.

Yanagisawa, R., Tsujii, N., Mori, T., Ruther, P., Paul, O., & Nomura, M. "Nanostructured planar-type uni-leg Si thermoelectric generators," Applied Physics Express, 13(9), 095001, (2020)

Keywords: silicon, nanostructure, phononic crystal, micro generator

---

*Speaker

New intermetallic thermoelectric candidates screened by calculation

Adrien Moll*[†1], Jean-Claude Crivello[1], Jean-Marc Joubert[1], Eric Alleno[1], and Celine Barreteau[‡1]

[1]Institut de Chimie et des Matériaux Paris-Est – Université Paris-Est Créteil Val-de-Marne - Paris 12 : UMR7182, Centre National de la Recherche Scientifique : UMR7182 – 2-8, rue Henri Dunant 94320 Thiais, France

Abstract

The research of environmentally friendly, cheap and performant materials is one of the major challenges for thermoelectricity development. To make the investigation of new candidates easier and more efficient, the support of experimental work by calculations and simulation is of great importance. In this study, we combine screening calculations by DFT of a large set of compositions to highlight stable and non-metallic compounds, with the experimental study of the most promising materials. This presentation focuses on the experimental development and the physical properties of these new candidates for thermoelectricity.
Our screening calculations were applied on ternary intermetallic compounds with T-M-X composition (with T, a transition metal, a rare earth or an alkaline earth metal, M, an element from the first line of the transition metal and X, a metalloid) [1-2]. Among the stable and non-metallic compounds identified, we selected the most interesting phases for experimental study, such as SrCuSb, SrZn2P2 or VCoSn, which were never or few reported in the literature. The materials were elaborated by new and straightforward synthesis routes based on mechanical alloying or conventional melting methods.

The stability and thermoelectric properties of the phases are discussed and compared with the calculations to validate the method. Some of the new materials show promising properties which could be further improved by doping. In addition to the presentation of new materials, we propose a promising method to discover and develop novel thermoelectric compounds which can be expanded to other classes of materials.

References:

Barreteau, C., Crivello, J.C., Joubert, J.M., Alleno, E. Optimization of criteria for an efficient screening of new thermoelectric compounds: the TiNiSi structure-type as a case-study, ACS Combinatorial Sciences, 22, 813-820, (2020), https://arxiv.org/abs/1911.12027

Barreteau, C., Crivello, J.C., Joubert, J.M., Alleno, E. Looking for new thermoelectric materials among TMX intermetallics using high-throughput calculations, Computational Material Science, 156, 96-103 (2019), http://doi.org/10.1016/j.commatsci.2018.09.030

---

[*] Speaker

[†] Corresponding author: moll@icmpe.cnrs.fr

[‡] Corresponding author: barreteau@icmpe.cnrs.fr

Keywords: Ternary intermetallics, Materials synthesis, Stability, Thermoelectricity, High, throughput calculations

Axis-dependent carrier polarity in polycrystalline NaSn2As2 for transverse thermoelectrics

Yosuke Goto*†[1], Naoto Nakamura[1], and Yoshikazu Mizuguchi[1]

[1]Tokyo Metropolitan University – Japan

Abstract

Transverse thermoelectric devices consist of only one thermoelectric material, unlike conventional longitudinal thermoelectric devices that require two types of thermoelectric materials with p- and n-type polarities. However, scalable synthesis of materials that demonstrate axis-dependent carrier polarity, which is a prospective component to demonstrate the transverse thermoelectric device, is challenging. Here, we report that polycrystalline NaSn2As2, which was prepared by using uniaxial hot pressing, displayed axis-dependent carrier polarity [1].
We synthesized NaSn2As2 using Na (99.9%), Sn (99.99%), and As (99.9999%) as starting materials. The stoichiometric ratio of Na, Sn, and As was sealed in an evacuated quartz tube, heated at 700 ◦C-750 ◦C for 20 h, and cooled to 350 ◦C for 10 h, followed by furnace cooling. Uniaxial hot pressing was conducted using grinded NaSn2As2 and graphite die at 350 ◦C-450 ◦C at 70 MPa for 10 min. The size of grinded NaSn2As2 for hot pressing varied from several mm to below 100 μm (powder form).

Phase purity of the samples is examined using an X-ray diffraction (XRD). It is confirmed that the obtained samples exhibit preferred orientation, as expected from its layered structure. Seebeck coefficient measurements indicate that carrier polarity depends on the measurement direction, indicating that polycrystalline NaSn2As2 shows axis-dependent carrier polarity. This is consistent with recently reported results on single crystals of NaSn2As2 [2]. Given that our sample preparation procedure is readily scalable, the present work shows the possibility for preparing transverse thermoelectric devices using polycrystalline NaSn2As2 with a preferred orientation. Furthermore, because it has been shown that NaSn2As2 exhibits superconducting transition at low-temperature [3], this work demonstrates that NaSn2As2 and the related materials can be categorized as a novel multifunctional material. In the workshop, we will discuss our recent investication for novel materials that shows axis-dependent carrier polarity.

N. Nakamura, Y. Goto, and Y. Mizuguchi, Appl. Phys. Lett. **118**, 153903 (2021).

B. He, Y. Wang, M. Q. Arguilla, N. D. Cultrara, M. R. Scudder, J. E. Goldberger, W. Windl, and J. P. Heremans, Nat. Mater. **18**, 568 (2019).

Y. Goto, A. Yamada, T. D. Matsuda, Y. Aoki, and Y. Mizuguchi, J. Phys. Soc. Jpn. **86**, 123701 (2017).

---

*Speaker

†Corresponding author: y_goto@tmu.ac.jp

Keywords: transverse thermoelectric effect, axis, dependent carrier polarity, new material, arsenide, layered structure

Growth of thermoelectric material ZnSnSb2 with pseudocubic structure

Yusuke Shigeeda*[1], Akira Nagaoka†[1], Kenji Yoshino[1], and Kensuke Nishioka[1]

[1]Faculty of Engineering, University of Miyazaki – 1-1, Gakuenkibanadainishi, Miyazaki-shi, Miyazaki-ken, 889-2192, Japan

Abstract

Introduction

In general, high thermoelectric (TE) performance materials are used the scarcity and the element toxicity. We focus on theternary II-IV-V2 group compound ZnSnSb2 as low cost and environmentally friendly TE material which has a chalcopyrite compound, which has a pseudocubic structure. When the chalcopyrite structure of lattice parameter c/a in nearly equal 2, its valence band is degeneracy with, multiple bands at same energy and achieve high power factor [1]. In fact, CuGaTe2 has chalcopyrite structure with has lattice parameter ratio c/a is 1.98, and the value of ZT is 1.4 at 950K [2]. ZnSnSb2, which lattice parameter ratio c/a is closed to 2 and the raw materials is used heavy element can be expected high TE performance. In this study, we obtained single phase of ZnSnSb2 based on the phase diagram of Zn-Sn-Sb system and investigated TE properties of ZnSnSb2 at 50-300 ℃.

Experimental procedure

We fabricated difference compositional ZnSnSb2 samples from high purity starting materials (> 99.999%). The materials were charged into quartz ampoules under 10ˆ-4 Pa and then sealed off. The ampoules were loaded into furnace and heated at 700 ℃ for 24 hours to ensure homogenization. After that, the samples were kept at each equilibrium temperature for 24 hours. The samples were allowed to cool quickly by quenching in water. Structural and compositional properties were investigated by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and different thermal analysis (DTA). The TE performance was evaluated by a commercial system (ZEM3 and LFA 457).

Result and Discussion

The growth mechanism of ZnSnSb2 shows the peritectic reaction as ZnSb + SnSb + liquid phase ↔ ZnSnSb2 for 320-360 ℃. ZnSnSb2 single phase was obtained from starting composition of Zn:Sn:Sb = 1:5:2, which atomic composition from EDX was Zn = 22.0 atm.%, Sn = 28.0 atm.%, and Sb = 50.0 atm.%. The temperature dependence of resistivity and Seebeck coefficient were showed increased with temperature, that is caused by being degenerate semiconductor due to high carrier concentration of 1019/cm3 at room temperature. The

---

*Speaker

†Corresponding author: nagaoka.akira.m0@cc.miyazaki-u.ac.jp

sciencesconf.org:vwt2021:364753

resistivity and Seebeck coefficient are 1.17 mΩcm and 51.3 μV/K at 300 ℃. The thermal conductivity decreases with increasing temperature roughly according to a T ˆ-1 relation, which means that lattice thermal conductivity is dominantly driven by phonon-phonon Umklapp scattering. As a result, the value of dimensionless figure of merit ZT for ZnSnSb2 is 0.12 at 300 ∘C.

References:

Zhang, J., Liu, R., Cheng, N., Zhang, Y., Yang, J., Uher, C., Shi, X., Chen, L., Zhang, W. High-Performance Pseudocubic Thermoelectric Materials from Non-cubic Chalcopyrite Compounds. Adv. Mater. 26, 3848–3853, (2014)

Plirdpring, T., Kurosaki, K., Kosuga, A., Day, T., Firdosy, S., Ravi, V., Snyder, G. J., Harnwunggmoung, A., Sugahara, T., Ohishi, Y., Muta, H., Yamanaka, S. Chalcopyrite CyGaTe2:A High-Efficiency Bulk Thermoelectric Material. Adv. Mater. 24, 3622-3626, (2012)

Keywords: chalcopyrite compound

High-Power Factor and Annealing Optimization of Fe,Ni-based Skutterudites

Giovanna Latronico*†[1], Paolo Mele[1], Cristina Artini[2,3], Pietro Manfrinetti[2], Carlo Fanciulli[4], Saurabh Singh[5], Tsunehiro Takeuchi[5], Cédric Bourgès[6], Takao Mori[6], and Chihiro Sekine[7]

[1]Shibaura Institute of Technology – 307 Fukasaku, Minuma-ku, Saitama-shi, 337-8570, Japan
[2]University of Genova – Via Dodecaneso, 31, 16146 Genova, Italy
[3]CNR ICMATE Genova – Via E. De Marini, 6 - 16149 Genova, Italy
[4]CNR ICMATE Lecco – Via Previati 1/E - 23900 Lecco, Italy
[5]Toyota Technological Institute – 2-12-1 Hisakata, Tempaku-ku, Nagoya, 468-8511, Japan
[6]National Institute for Materials Science – Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan
[7]Muroran Institute of Technology – 27-1 Mizumoto-cho, Muroran, Hokkaido, 050-8585, Japan

Abstract

This work relates to the synthesis and characterization of thermoelectric (TE) thin films through the Pulsed Laser Deposition (PLD) method. Rare-earth (RE) filled skutterudites denote an interesting category of TE compounds thanks to their high stability and possibility to modulate the n or p behavior by varying the composition [1]. Bulk materials of RE-filled skutterudites were deeply studied, especially by the research groups involved in the present work [2-4] while there is a lack of literature on the RE-filled skutterudites thin films. The essential properties of thin films, such as flexibility, low dimensionality, fast fabrication and control of strain at the interface with substrates, are very interesting advantages for developing TEs.

Filled skutterudite thin films of composition Smy(FexNi1-x)4Sb12 (with x = 0.70 and 0.63 being the series SKFe70 and SKFe63 respectively) were prepared by PLD on a substrate of fused silica. The PLD conditions are: laser YAG λ = 266 nm, frequency 10 Hz, *dsub-target* = 35 mm, *Tdep* = room temperature and 150 ◦C, *tdep* = 30 min, under vacuum (P = 10-4 Pa). A set of samples underwent an annealing process for 1 h at 150 ◦C as well.

Electrical conductivity σ and Seebeck coefficient S were acquired using the four-probe method with a ZEM-3 (ULVAC Advance-Riko) apparatus performing three cycles between 75 and 250 ◦C recording both heating and cooling processes. Samples required three cycles up to 250 ◦C before being stabilized exhibiting reliable data, revealing the importance of a future study regarding an adequate annealing process. In both series, the best power factor so far appears to be referable to annealed films: 323 μW/m*K2 and 466 μW/m*K2 at 250 ◦C for the samples SKFe63_2 and SKFe70_2, respectively [5]. XRD analysis clarifies how the temperature of deposition and the annealing process change the structure of the skutterudite film. For all the analyzed samples, the room temperature deposited films are amorphous, while annealing causes the formation of a crystalline structure. High-temperature deposition

---

*Speaker

†Corresponding author: na19103@shibaura-it.ac.jp

films show both skutterudite and undesired secondary phases diffraction peaks, usually Fe-Ni antimonides, or free Sb.

As aforementioned, it is clear the utmost importance of a systematic study to optimize the annealing process to enhance the thermoelectric properties of these samples. Three batches of thin films of different compositions (Smy(FexNi1-x)4Sb12 with x = 0.50, 0.63 and 0.70, being the carrier transport type n, n/p and p, respectively [3]) were deposited on fused silica under vacuum (10-4 Pa) at room temperature. Subsequently, every sample of each composition underwent an annealing process varying the temperature (150◦C, 200◦C, 250◦C, 300◦C) and the time (set a = 3 h, set b = 6 h). At the present day, room temperature S was measured by means of a PTM-3 portable device and XRD analysis were carried out as well. As a first result, the higher temperature of 300◦C is causing the degradation of the sample, while 250◦C is appearing to have the best effect on the S: the higher value is 71.2 mV/K for the x = 0.63 sample annealed at 250 ◦C for 6 hours.

References:

1) C. Artini, et al, Inorg. Chem. 55 (2016) 2574.

2) G. Latronico, et al, Metals 10 (2020) 364.

3) C. Artini, et al, Mat. Res. Bull. 139 (2021) 111261.

4) C. Artini, et al, ES Mater. Manuf. 5 (2019) 29.

5) G. Latronico, et al. in preparation
6) C. Bourgès, et al, RSC Adv. 10 (2020) 21129.

Keywords: thermoelectricity, thin films, skutterudites, power factor, annealing

Impact of temperature and mode polarization on the acoustic phonon range in type-I clathrates

Shelby Turner[1,2,3], Stéphane Pailhès[*†4], Frédéric Bourdarot[5], Jacques Ollivier[6], Thomas Keller[7], Stephane Raymond[8], Yvan Sidis[9], Pierre-Francois Lory[10], Holger Euchner[11], Michael Baitinger[12], Yuri Grin[13], Helmut Schober[14], Marc De Boissieu[15], and Valentina Giordano[16]

[1]Institut Laue-Langevin (ILL) – ILL – 6, rue Jules Horowitz BP 156 38042 Grenoble Cedex 9, France
[2]Science et Ingénierie des Matériaux et Procédés – Centre National de la Recherche Scientifique : UMR5266 – 1130 rue de la Piscine, BP 75 38402 Saint Martin DH́ères, France
[3]Institut Lumière Matière – Centre National de la Recherche Scientifique : UMR5306 – UMR5306 CNRS Université Claude Bernard Lyon 1, France
[4]Institut Lumière Matière – Centre National de la Recherche Scientifique : UMR5306 – UMR5306 CNRS Université Claude Bernard Lyon 1, France
[5]Modélisation et d'Exploration des Matériaux, Université Grenoble Alpes et Commissariat á l'Energie Atomique – CEA-INAC – 17 rue des Martyrs, 38054 Grenoble, France
[6]Institut Laue-Langevin – ILL – France
[7]Max-Planck-Institut für Festkörperforschung – Heisenbergstr. 1, D-70569 Stuttgart, Germany
[8]Laboratoire dÉlectronique et de Technologie de lÍnformation – Commissariat à l'énergie atomique et aux énergies alternatives – MINATEC 17, rue des Martyrs, 38054, Grenoble Cedex 9, France
[9]Laboratoire Léon Brillouin – LLB – CNRS, CEA, UMR-12, 91191 Gif sur Yvette, France, France
[10]Institut Laue-Langevin – ILL – 6, rue Jules Horowitz BP 156 38042 Grenoble Cedex 9, France
[11]University of Ulm – Helmholtzstraße 16, 89081 Ulm, Germany
[12]Max-Plank Institut für Chemische Physik fester Stoffe – Germany
[13]Max-Planck-Institut für Chemische Physik fester Stoffe (MPI CPfS) – Germany
[14]Institut Laue-Langevin (ILL) – ILL – 6, rue Jules Horowitz BP 156 38042 Grenoble Cedex 9, France
[15]Science et Ingénierie des Matériaux et Procédés – Centre National de la Recherche Scientifique : UMR5266 – 1130 rue de la Piscine, BP 75 38402 Saint Martin DH́ères, France
[16]Institut Lumière Matière – Centre National de la Recherche Scientifique : UMR5306 – UMR5306 CNRS Université Claude Bernard Lyon 1, France

Abstract

Crystals with a high structural complexity and chemical bonding inhomogeneity, such as tetrahedrites or type-I clathrates, often have a very low and almost temperature independent lattice thermal conductivity of about 0.5-2 W/mK in the 50-500 K range which is assumed to originate from a reduced momentum and energy space available for propagative lattice vibrations. The current understanding is that the heat conduction is mostly conveyed by

---

[*] Speaker

[†] Corresponding author: Stephane.Pailhes@univ-lyon1.fr

well-defined acoustic phonons, which exist only in a limited range of the energy and momentum phase space, delimited by a continuum of nondispersive optical phonon bands. The onset of this continuum at low energy defines the upper energy limit of the acoustic regime such that it has been associated with a phononic low-pass acoustic filter or a modified Debye energy. In the context of ab initio self-consistent phonon (SCP) theory, it has been shown that the cubic and quartic anharmonic interactions result in a temperature-induced energy renormalization of these low-lying optical branches which contributes to the anomalous behavior of the temperature dependence of the lattice thermal conductivity in structurally ordered type-I clathrates [2]. By means of inelastic neutron scattering, we provide evidence for this energy renormalization in temperature, which has been resolved for transversely and longitudinally polarized phonons in a single crystal of type-I clathrate. By mapping the neutron intensity in the momentum space, we demonstrate the coherent character of the low-lying optical phonons. The overall phonon spectrum and dynamical structure factors are satisfactorily reproduced by ab initio harmonic calculations using density functional theory with the meta-GGA SCAN functional and a fully ordered structure.

P.F. Lory, S. Pailhès et al., Nat. Comm. 8 (2017) 491

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

SR Turner, S. Pailhès et al., Physical Review Research 3 (1), 013021 (2021)

Keywords: phonons, anharmonicity, complexity, lattice thermal conductivity, clathrates

---

Influence of nanostructuration in Fe2VAl alloys

Abou Diack Rasselio*[1] and Eric Alleno†[1]

[1]Institut de Chimie et des Matériaux Paris-Est – Université Paris-Est Créteil Val-de-Marne - Paris 12 :
UMR7182, Centre National de la Recherche Scientifique : UMR7182 – 2-8, rue Henri Dunant 94320
Thiais, France

Abstract

Bi2Te3 is currently the best thermoelectric (TE) material in the market, displaying a dimensionless figure of merit $ZT = 1$ at 300 K. The Heusler alloy Fe2VAl could be considered as a substitute of Bi2Te3. Fe2VAl can either be doped as a n-type or a p-type conductor and its maximum power factor ($PFmax$) can strongly be improved by substitution to values which can be larger than that of Bi2Te3 (PFmax = 4.9 mW.m-1.K-2 at 300K) : PFmax = 4.0 – 6.0 mW.m-1.K-2 at 300 K in p-type Fe2.04V0.86Ti0.1Al [1] and n-type Fe2VTa0.05Al0.95 [2] respectively –. However, its TE performances are mainly hindered by its large thermal conductivity (λ) – λ = 10 mW.m-1.K-1 in n-type Fe2VTa0.05Al0.95 at 300K – conducting to values of ZT _˜ 0.2 at 300 K. A reduction of thermal conductivity is thus necessary for the rise of Fe2VAl.
Nanostructuring by decreasing the grain size increase the phonons scattering rate by the grain boundaries. This leads to a decrease of the thermal conductivity. In this presentation, we will focus on the influence of the grain size on the thermal properties of Fe2V1.03Al0.97. From λL _˜ 27 W.m-1.K-1 at 300K in stochiometric Fe2VAl with micron-size grains [3], this value is lowered in nanometric-size grains to values of λL _˜ 12 W.m-1.K-1 and ZT _˜ 0.1 at 300K. Secondly, we will present the influence of a heavy-element substitution such as Ta in Fe2V0.96Ta0.07Al0.97 combined with nano-grains, which yields a value of _˜ 8 W.m-1.K-1 and ZT _˜ 0.18 at 300K.

Y. Sandaiji et al., J. Japan Soc., 57, 207 (2010).

K. Renard et al., J. Appl. Phys., 115, 033707 (2014).

Nishino, Y et al., Phys. Rev. B,74, 115115 (2006)

Keywords: Fe2VAl, Heusler, Nanostructuration, Nanoscale, Bulk, Substitution

---

*Speaker

†Corresponding author: eric.alleno@icmpe.cnrs.fr

Intrinsic and extrinsic approaches to tune lattice thermal conductivity for thermoelectrics

Naoki Sato*[1]

[1]International Center for Young Scientists (ICYS), National Institute for Materials Science (NIMS) –
1-2-1 Sengen, Tsukuba, Ibaraki, Japan

Abstract

Tuning lattice thermal conductivity is one of the most crucial ways to obtain high-performance thermoelectric materials. In the past decades, various successful strategies to inhibit phonon propagation have been established, roughly classified into two classes: intrinsic and extrinsic approaches. The former, namely, strategies to search for materials with intrinsically low lattice thermal conductivity, includes complex crystal structure, resonant bonding, stereochemically active lone-pair electrons, rattling and its reminiscent anharmonic vibration, superionic transition, and bonding heterogeneity. The latter approach, such as point defects, fine grain boundary, nanoscale precipitates, and all-scale hierarchical microstructures, has been demonstrated to be effective for many classes of thermoelectric materials. In this talk, the bonding heterogeneity derived from multiple anions in local structures [1] and a layered telluride with resonant bonding inside a planar coordination environment [2] will be presented as examples for anomalous intrinsic thermal transport properties. Also, as a successful example of the extrinsic approach, I will introduce a greatly reduced lattice thermal conductivity while maintaining high carrier mobility in Mg3Sb2-based material by interstitial doping and grain boundary complexion [3].

N. Sato *et al.*, preprint: ChemRxiv (10.26434/chemrxiv.14730126.v1)

W. Zhang* and N. Sato**et al.*, Chem. Mater. **32**, 5335–5342 (2020).

Z. Liu*, N. Sato*, W. Gao**et al.*, Joule **5**, 1196–1203 (2021).

Keywords: lattice thermal conductivity, ab initio calculations, bonding heterogeneity, resonant bonding, interstitial doping

---

*Speaker

Comparisons of electronic conduction between ordered and disordered phases in quasi-ternary Cu-Zn-Sn-S sulfides

Keita Yoshizawa*†[1], Susumu Fujii[1,2], and Masato Yoshiya[1,2]

[1]Osaka University – 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
[2]Japan Fine Ceramics Center – 2-4-1, Mutsuno, Atsuta, Nagoya 456-8587, Japan

Abstract

Quasi-ternary Cu-Zn-Sn-S sulfides (CZTS) are promising candidates for thermoelectric materials because of its low thermal conductivity and high electronic conductivity, although the underlying physical mechanisms remain unclear. Elements constituting CZTS has abundant underground reserves and low toxicity, which is one of the reasons why we are focusing on this class of materials. CZTS has sphalerite-like structure, consisting of cation-ordered and cation-disordered phases, and exhibits mosaic-like meso-scale structures in the scale greater between micrometer and nanometer orders. In the ordered phase, the atomic arrangements of cations has a translational symmetry, while, in the disordered phase, the cations are randomly distributed. The previous studies[1][2] reports that thermal conductivity is decreased by the mosaic-like structure. On the other hand, high electronic conductivity is attributed to the ordered phase, because it is expected that mobility of electrons is higher in the ordered phase. However, our understanding about the relationship between the cation arrangements and electronic properties is still limited. Thus, we analyzed the mechanisms of electronic conduction in both ordered and disordered phases by ab initio calculations with an aid of calculations by Boltzmann transport equation.

Cu4ZnSn2S7, which has a sphalerite-like structure, was used as one of the model materials to start with. A supercell of the ordered phase with cations being randomly swapped is used to be a representative of the disordered phase for ease of comparison. As the Boltzmann transport equation is done in a reciprocal space, finer k-point meshes than the ones required for ordinary ab initio calculations were used for the calculations.

The calculated density of states (DOS) showed that the valence band maximum is formed mainly by Cu and S, in both ordered and disordered phases. This indicates that Cu-S bonding forms conduction pathways for electrons. Comparing the DOSes of the ordered and disordered phases, it is found that the ordered phase has a band gap while the disordered phase has not, indicating that the ordered phase is semiconductor-like while the disorder phase metallic. This suggests that the high electronic conduction is not caused by the ordered phase as reported in the previous study[1], but the disordered phase, against a fundamental understanding by Bloch's theorem. This is primarily because the electronic interaction between atoms changes with disordering cations rearrangements, resulting in semiconductor-to-metallic transition in electronic states. Consequently, electronic conductivity in the disordered phase is higher than that in the ordered phase. In addition, it is

---

*Speaker

†Corresponding author: Keita.YOSHIZAWA@mat.eng.osaka-u.ac.jp

found that electronic conductivity differs depending on crystallographic directions. This also evidences that cation arrangements modifies the electronic state, and, in turn, electronic conduction, in favor of thermoelectricity.
In this study, ab initio calculations have been performed to comprehend the differences of the electronic states of the ordered and disordered phases. It is found that the disordered phase is metallic electronic states and the ordered phase is semiconductor-like electronic states. This suggests that not only thermal conduction, but also electronic conduction can be controlled by tailoring mosaic-like nanostructure consisting of the ordered and disordered phases, which can be realized by annealing, holding the materials at a controlled temperature to take an optimized balance between enthalpy-dominating ordered phase and entropy-dominating disordered phase[3].

Acknowledgements: This work was supported by Grants-in-Aid for Scientific Research (Grant Number: JP19H05786, JP20H05195, JP20K05062, and JP20K15034).

References:
C. Li, M. Yoshiya, S. Fujii, et al.,*ACS Applied Nano Materials* 2018 **1** (6), 2579-2588.
C. Kim, Bachelor’s Thesis, 2021, Osaka University.
T. Nakao, Master’s Thesis, 2020, Osaka University.

Keywords: electronic conduction, CZTS, ab initio, disordered, Boltzmann transport equation

Enhancement of the thermoelectric performances in Bi-doped and Cl-doped synthetic mineral CuPbBi5S9

Krishnendu Maji*[1], Christophe Candolfi[2], Pierric Lemoine[3], Adèle Renaud[3], Mathieu Pasturel[3], Xiaoyuan Zhou[4], Bin Zhang[4], and Emmanuel Guilmeau†[1]

[1]Laboratoire de cristallographie et sciences des matériaux – Centre National de la Recherche Scientifique : UMR6508, Ecole Nationale Supérieure d'Ingénieurs de Caen, Normandie Université, Université de Caen Normandie – 6 Bvd du maréchal Juin 14050 CAEN CEDEX 4, France

[2]Institut Jean Lamour – Université de Lorraine, Centre National de la Recherche Scientifique : UMR7198 – Institut Jean Lamour - CNRS - Université de Lorraine. Campus Artem 2 allée André Guinier BP 50840 54011 Nancy Cedex, France

[3]Institut des Sciences Chimiques de Rennes – Ecole Nationale Supérieure de Chimie de Rennes, Universite de Rennes 1, Université de Rennes, Institut National des Sciences Appliquées - Rennes, Institut National des Sciences Appliquées, Université de Rennes : UMR6226, Centre National de la Recherche Scientifique – Campus de Beaulieu - Bât. 10 Avenue du Général Leclerc 35042 Rennes Cedex, France

[4]Chongqing Key Laboratory of Soft Condensed Matter Physics and Smart Materials – China

Abstract

Quaternary sulfide CuPbBi5S9, commonly known as Gladite, is a naturally occurred sulfide mineral. In this work, we demonstrate the facile and highly scalable synthesis of this compound through mechanical alloying and spark plasma sintering and investigate the thermoelectric properties. It exhibits extremely low total thermal conductivities of 0.36–0.298 W m–1 K–1 in the temperature range of 300–673 K. Lattice anharmonicity, caused by the complex crystal structure, leads to low thermal conductivity which is further supported by low average sound velocity, low Young's modulus and Debye temperature, and large Grüneisen parameter. Additionally, the low thermal conductivity is further supported by density functional theory. Pristine CuPbBi5S9 shows poor n-type electrical properties due to extremely low carrier concentration (10ˆ12 cm-3 at room temperature). We have succeeded to improve the electrical properties by increasing the carrier concentration through Cl for S and Bi for Pb substitution, which acts as efficient electron donors. As a result, the maximum power factor increases from 0.2 μW cm–1 K–2 to 2.3 μW cm–1 K–2 for Cl doped sample and to 1.9 μW cm–1 K–2 for Bi-doped sample, and maximum ZT achieved of 0.43 and 0.28 for Cl and Bi-doped sample, respectively, at 700 K.

Thus, CuPbBi5S9 proves to be a promising n-type semiconductor for high-performance thermoelectric applications.

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

---

*Speaker

†Corresponding author: emmanuel.guilmeau@ensicaen.fr

First principles calculations of electronic and thermoelectric transport properties of Pb2Bi2Te5 with different atoms sequences.

Weiliang Ma*[1,2], Marie-Christine Record†[1], Pascal Boulet[2], and Jing Tian[2]

[1]Institut Matériaux Microélectronique Nanosciences de Provence – Aix-Marseille Université - AMU : UMR7334, Institut Matériaux Microélectronique et Nanosciences de Provence, Université de Toulon, Aix Marseille Univ, CNRS, IM2NP, Toulon, France : UMR7334 – 52 Avenue Escadrille Normandie Niemen, 13013 Marseille, France

[2]Matériaux divisés, interfaces, réactivité, électrochimie – Aix Marseille Université : UMR7246, Centre National de la Recherche Scientifique : UMR7246 – Campus de St-Jérome - Case MADIRELAvenue Escadrille Normandie-NiemenF-13397 Marseille Cedex 20, France

Abstract

Chalcogenide compounds such as PbTe, PbBi2Te4, PbBi4Te7 and Bi2Te3 that belong to the homologous series of ternary phases n(PbTe)·m(Bi2Te3), exhibit both excellent topological insulators and promising thermoelectric properties. For 2(PbTe)·(Bi2Te3) also read as Pb2Bi2Te5, two different possible atoms sequences have been reported: -Te-Pb-Te-Bi-Te-Bi-Te-Pb-Te- (S1) and -Te-Bi-Te-Pb-Te-Pb-Te-Bi-Te- (S2). In this paper, we performed a series of first principles calculations using density functional theory (DFT) to determine electronic and thermoelectric properties of Pb2Bi2Te5 with these 2 different atoms sequences. The related compounds PbTe and Bi2Te3 were also investigated for comparison. Different exchange-correlation functionals (LDA, PBE, EV, TB-mBJ, HSE potentials, and rev-vdW-DF2) were tested, w/o spin-orbit coupling, which has been found to have important effects. The calculated electronic bands indicate that both of the 2 sequences lead to indirect band gap semiconductors. We also calculated elastic moduli, dielectric constants, Born effective charges, and phonon dispersion within the quasi-harmonic approximation. Based on the above-mentioned calculations results, thermal conductivity has been obtained by solving the Boltzmann transport equation. Additionally, the QTAIM theory was employed to explain the differences in the properties of the 2 stackings. The most interesting compound for thermoelectric applications was found to be Pb2Bi2Te5 with the S2 sequence.

Keywords: Thermoelectric, chalcogenides, DFT, QTAIM

---

*Speaker

†Corresponding author: m-c.record@univ-amu.fr

sciencesconf.org:vwt2021:365444

Polyol and Hydrothermal synthesis processes of the promising Samsonite phase

Adam Bertrand*†1, Tristan Barbier1, Martin Leproult1, and Franck Gascoin1

1Laboratoire de cristallographie et sciences des matériaux – Centre National de la Recherche Scientifique : UMR6508, Ecole Nationale Supérieure d'Ingénieurs de Caen, Normandie Université, Université de Caen Normandie – 6 Bvd du maréchal Juin 14050 CAEN CEDEX 4, France

Abstract

Samsonite (Ag4MnSb2S6) is a mineral that can be naturally found in hydrothermal veins. Its complex crystal structure – it crystallizes in the monoclinic crystal system (space group: P21/n with a = 10.3861 Å, b = 8.1108 Å, c = 6.6637 Å, and β = 92.6390○) - together with the electron lone pair of Sb3+ atoms and the lack of research about it (never synthesized so far through lab conditions), make this phase highly promising for thermoelectric applications.[1] Indeed, authors have shown through the tetrahedrite phase, that the electron lone pair of Sb3+ may explain the ultralow thermal conductivity of Cu12Sb4S13.[2]
The objective is to synthesize Ag4MnSb2S6 through unconventional synthesis ways (**hydrothermal** synthesis and **polyol** synthesis processes) to mimic the high pressure and temperature found in natural conditions. Then, thermoelectric properties would be assessed (thermal dependence of the electrical conductivity, Seebeck coefficient and thermal conductivity).

As such, this presentation will focus on these innovative synthesis methods and compare their respective efficiency while taking into account their advantages and drawbacks. On one hand, the hydrothermal synthesis allows **highly crystalline** compounds with **simple precursors and solvent** involved but isn't easily scalable. On the other hand, the polyol synthesis is **fast** and can **easily scale up** but the crystallinity of the compound formed is rather poor, necessitating a crystal growth processing as a follow-up.

References:

L. Bindi, M. Evain, Gram-Charlier development of the atomic displacement factors into mineral structures, The case of samsonite, Ag4MnSb2S6. *American Mineralogist*, 92 (5-6), 2007, 886–891.

T. Barbier, S. Rollin-Martinet, P. Lemoine, F. Gascoin, A. Kaltzoglou, P. Vaqueiro, A.V. Powell and E. Guilmeau, Thermoelectric Materials: A New Rapid Synthesis Process for Nontoxic and High-Performance Tetrahedrite Compounds. *J. Am. Ceram. Soc.*, 99, 2016, 51-56

Keywords: Polyol, Hydrothermal, Solvothermal, Samsonite, Quaternary Sulfide

---

*Speaker

†Corresponding author: adam.bertrand@ensicaen.fr

Nanoscale thermal transport at ceramic interfaces: a computational and machine learning approach

Susumu Fujii*†[1,2], Tatsuya Yokoi[3], Atsuto Seko[4], and Masato Yoshiya[1,2]

[1]Osaka University – 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
[2]Japan Fine Ceramics Center – 2-4-1, Mutsuno, Atsuta, Nagoya 456-8587, Japan
[3]Nagoya University – Furo-chou, Chikusa, Nagoya 464-8603, Japan
[4]Kyoto University – Yoshida-Honmachi, Sakyo, Kyoto 606-8501, Japan

Abstract

Nanocrystalline materials have attracted much attention in the field of thermoelectrics, because of its very low lattice thermal conductivity that originates from the thermal resistance of grain boundaries (GBs). As the magnitude of GB thermal resistance is highly dependent on the atomic structures of individual GBs [1], elucidating GB structure-thermal conductivity relationships and their underlying mechanisms are of great importance for improving the performance of nano- or polycrystalline thermoelectric materials. Two main obstacles are as follows: (1) it is difficult to systematically observe and measure the GB structures and their thermal conductivities in experiments; (2) a method to reveal the relationships between the GB atomic structure and physical properties has not been established. In this study, we developed a method for accurately predicting GB thermal conductivities from the microscopic information of GB structures, by calculating thermal conductivities of various MgO GBs by molecular dynamics (MD) and applying machine learning (ML) techniques to the obtained data [1,2]. In addition, for more precise estimation of GB thermal conductivities, a recently developed ML potential (MLP) [3] was applied to a few Si GBs and compared with an empirical interatomic potential [4].

We calculated thermal conductivity of 92 MgO GBs and atomically decomposed thermal conductivities by perturbed MD simulations [1]. Then, local atomic environments (LAEs) of the GB atoms were converted into the structure descriptor (SOAP vector), which indicates the coordination environments of an atom. Using the SOAP vectors, LAEs in the vicinity of GBs were classified by hierarchical clustering, and structural distortion of each LAE was also quantified. It is found that classifying the LAEs into only six groups is sufficient to describe MgO GBs, namely, bulk-like, weakly strained, moderately strained, strongly strained, moderately under-coordinated, and highly under-coordinated atoms. The structural distortions significantly correlate with atomically decomposed thermal conductivities. Motivated by this correlation, we constructed a model for predicting GB thermal conductivities by multiple linear regression with input variables based on hierarchical clustering of LAEs. The model accurately predicts the thermal conductivities of tilt, twist, twin, and even high-pressure GBs, and reveals that small distortions of LAEs are sufficient to drastically reduce GB thermal conductivity [2].

In addition, we applied a MLP [3] to the structure searches and phonon analyses of a few

---

*Speaker

†Corresponding author: susumu.fujii@mat.eng.osaka-u.ac.jp

sciencesconf.org:vwt2021:365106

Si GBs. Compared with a time-honored empirical potential, the MLP exhibits superior prediction power for single-crystalline lattice thermal conductivity, GB structures, energies, and phonon properties. This feature is very important to develop a reliable GB structure-thermal conductivity relationship from high-throughput computational simulations. Then, we performed thermal conduction analyses for a few Si GBs by perturbed MD and phonon wave packet method. The latter method generates a wave packet from single phonon mode and analyzes its scattering process at the GB. The comparison of these results shows that the thermal conductivities of Si GBs are also highly dependent on their atomic structures probably due to anharmonic vibrations of the GB atoms [4].

The developments of a method to connect GB structures and properties, and MLPs accurately representing GB properties should greatly enhance our understanding of GB behavior, leading to GB engineering for thermoelectric materials.

Acknowledgments: This work was supported by JSPS Grants-in-Aid for Scientific Research (JP19H05786, JP19H05787, JP20H05195, JP19H02419, JP20K05062 and JP20K15034).

References:

S. Fujii, T. Yokoi, M. Yoshiya, *Acta Mater.* **171**, 154-162. (2019).

S. Fujii, T. Yokoi, M. Yoshiya *et al.*, *Nature Commun.* **11**, 1854 (2020).

A. Seko, arXiv: 2007.14206 (2020).

S. Fujii, A. Seko, arXiv: 2105.11959 (2021)

Keywords: thermal conductivity, grain boundaries, phonons, molecular dynamics, machine learning

Anomalously low heat conduction in single-crystal superlattice ceramics lower than randomly oriented polycrystals

Hai Jun Cho*†[1], Yuzhang Wu[1], Yuqiao Zhang[1], Bin Feng[2], Masashi Mikami[3], Woosuck Shin[3], Yuichi Ikuhara[2], Yu-Miin Sheu[4], Keiji Saito[5], and Hiromichi Ohta‡[1]

[1]Hokkaido University – Japan
[2]University of Tokyo – Japan
[3]AIST – Japan
[4]National Yang Ming Chiao Tung University – Japan
[5]Keio University – Japan

Abstract

Utilization of heat begins from achieving ultralow thermal conductivity in solids, which allows storing heat or maintaining a large thermoelectric voltage. Introducing crystal defects like grain boundaries and impurities can effectively reduce the thermal conductivity, but they also damage other important functional properties. Superlattices can provide a great prospect in this regard, as their structures can intrinsically exhibit low thermal conductivities due to the high interface density. Therefore, the thermal conductivity of superlattices is of significant interest in thermal management technologies. However, experimental studies were mostly conducted with artificially fabricated superlattices and natural superlattices in polycrystalline forms, which are not the ideal platforms for correctly addressing the intrinsic heat transportation in superlattices due to the presence of undesired defects or randomly oriented grain boundaries. In this study, we fabricated defect-free single crystalline InGaO3(ZnO)m (IGZOm) superlattice films and investigated their anisotropic thermal conductivities as a function of superlattice period (dSL). The results show that the thermal conductivity of single-crystalline IGZOm in the cross-plane direction is lower than that of IGZOm in polycrystalline forms, confirming that introducing interfaces at nanoscales is highly effective in reducing the conduction of heat. This anomalous phenomenon is attributed to the anisotropic heat conduction. According to the in-plane thermal conductivity results, the heat conduction in polycrystalline IGZOm is dominated by the in-plane component, which overwhelms the hinderance of heat transportation at grain boundaries. Interestingly, the thermal conductivity was not a monotonic function of dSL, which violates the particle-like interpretation of heat carriers and can only be explained with the wave-like properties of heat carriers. We systematically analyze the system and assess the effect of dSL on the thermal conductivity of superlattices and the nature of the overall heat conduction, which will be of significant value for the utilization of wave mechanics in thermal management technologies.

Keywords: Superlattice, Low thermal conductivity

---

*Speaker

†Corresponding author: joon@es.hokudai.ac.jp

‡Corresponding author: hiromichi.ohta@es.hokudai.ac.jp

Growth of halide perovskite thin film for thermoelectric applications

Shrikant Saini*†[1], Izuki Matsumoto[2], Sakura Kishitshita[2], Ajay Kumar Baranwal[3], Tomohide Yabuki[2], Shuzi Hayase[3], and Koji Miyazaki[4,5,1]

[1]Integrated Research for Energy and Environment Advanced Technology, Kyushu Institute of Technology, Kitakyushu, Fukuoka, Japan – Japan
[2]Department of Mechanical Engineering, Kyushu Institute of Technology, Kitakyushu, Fukuoka, Japan – Japan
[3]i-Powered Energy System Research Centre, The University of Electro-communications, Chofu, Tokyo, Japan – Japan
[4]Kyushu Insitute of Technology – 1-1 Sensui-cho, Tobata-ku, Kitakyushu, Japan
[5]Department of Mechanical Engineering, Kyushu Institute of Technology, Kitakyushu, Fukuoka, Japan – Japan

Abstract

The conversion efficiency of thermoelectric material is quantified by the figure of merit ZT (=σS2T/) where σ is electrical conductivity, S is Seebeck coefficient and is thermal conductivity. CsSnI3, halide perovskites have shown ultra-high Seebeck coefficient and ultra-low thermal conductivity. This can lead CsSnI3 to one of the best candidates for flexible coated thermoelectric materials. Mainly, CsSnI3 has been focused on solar energy applications. We optimize the growth parameters and thermoelectric properties of coated halide perovskite thin-film by a cost-effective wet printing process for large areas and near room temperature applications. Due to the freedom of shape-ability in the wet process, these films are superior to the corresponding bulks or single crystals. The base solution is prepared by CsI and SnI2 precursors. Mixing time, baking temperature, and baking time were optimized to evaluate and enhance the thermoelectric performance of CsSnI3 thin films. We measured thermoelectric properties near room temperature and found that growth parameters influence the crystal grain size further the value of the figure of merit. CsSnI3 thin films grown at solvent mixing time about 2 h, heating temperature about 130∘C and heating time 5 min show the best thermoelectric performance as Seebeck coefficient 100 μV/K, electrical conductivity 130 S/cm, thermal conductivity 0.4 W/m.K, and ZT about 0.1 near room temperature.

Keywords: thermoelectric material, halide perovskites, thermal conductivity, spin coating

---

*Speaker

†Corresponding author: saini.shrikant456@mail.kyutech.jp

sciencesconf.org:vwt2021:362943

Tailoring the thermoelectric properties of ScN by introducing defects

Razvan Burcea*[1], Lorenzo Chapel[1], Pierre-Olivier Renault[1], Thierry Girardeau[1], Fabien Paumier[1], Marc Marteau[1], Jean François Barbot[1], Fabien Giovannelli[2], Ahmad Zenji[3], Jean-Michel Rampnoux[3], Stefan Dilhaire[3], Arnaud Le Febvrier[4], and Per Eklund[4]

[1]Institut Pprime – CNRS : UPR3346 – Université de Poitiers, SP2MI, Téléport 2, 11 Boulevard Pierre et Marie Curie, F-86962 Futuroscope Chasseneuil Cedex, France

[2]Laboratoire GREMAN – CNRS : UMR7347 – IUT de Blois, 15 rue de la chocolaterie, 41029 Blois Cedex, France

[3]Laboratoire LOMA – CNRS : UMR5798 – Université de Bordeaux, 33405 Talence, France

[4]Department of Physics, Chemistry and Biology (IFM) – Linköping University, SE-581 83 Linköping, Sweden

Abstract

Transition-metal nitrides are promising candidates for thermoelectric applications [1]. As an example, ScN has a relatively high power factor $(S^2\sigma)$ of about 2.5 mW/(m.K2) at 800K, leading to ZT _˜ 0.2 [2]. However, its thermal conductivity is relatively high 10-12 W.m-1.K-1 [3] and therefore needs to be reduced for thermoelectric applications. Kerdsongpanya *et al.* theoretically demonstrated that the introduction of impurities or vacancies in ScN may influence the density of states around *EF* [4]. The presence of these defects in the matrix will create a peak close to *EF* which would maximize the ZT factor [5]. Thus, in a previous study Mg dopant were implanted at room temperature and a reduction of the thermal conductivity was reported. However, the power factor was also reduced [6].

In this work, noble gases were implanted to highlight the role of defects on the thermoelectric properties of ScN. For example, Ar ions were implanted at room temperature in a high damage regime (5-6 dpa, < 0.3% Ar concentration) and then annealed at high temperature (1500 K, 10 min). The implantation was performed on degenerate n-type ScN (111) / Al2O3 (0001) thin films, synthesized by magnetron sputtering at 800◦C. These 240 nm thick films were then characterized by different techniques such as XRD, Ellipsometry, Seebeck measurements, and the van der Pauw method for the electrical conductivity. The implanted samples show an increase in resistivity from 1.64×10-4 Ω.cm to 1.41×10-3 Ω.cm at 300K but also a decrease in carrier mobility from 16 cm^2.V-1.s-1 to 4 cm^2.V-1.s-1. Post-implant annealing allows a partial restoration of the initial electric conductivity (restored at 90%). Similarly, the Seebeck coefficient is found to increase (by a factor of 3 at 600 K) with the introduction of defects and is roughly restored by the post-implant annealing leaving the power factor almost unchanged. However, the electrical, optical and structural characterization show that several defects are still present in the film. These are expected to contribute to the reduction of the thermal conductivity and would improve the ZT value. Thermal conductivity measurements (TDTR) are under progress to determine the influence of the as-remaining defects on the thermal conductivity. Furthermore, TEM observation is planned

---

*Speaker

sciencesconf.org:vwt2021:364960

to study the as-formed defects according to the gas implanted.

P. Eklund, S. Kerdsongpanya, B. Alling, J. Mater. Chem C 4, 3905-3914 (2016)

S. Kerdsongpanya, N. V. Nong, N. Pryds, A. Žukauskaite,˙ J. Jensen, J. Birch, J. Lu, L. Hultman, G. Wingqvist, and P. Eklund, Appl. Phys. Lett. 99, 232113 (2011).

P. V. Burmistrova, J. Maassen, T. Favaloro, B. Saha, S. Salamat, Y. Rui Koh, M. S. Lundstrom, A. Shakouri, and T. D. Sands, J. Appl. Phys. 113, 153704 (2013).

S. Kerdsongpanya, B. Alling, and P. Eklund, Phys. Rev. B 86, 195140 (2012).

G. D. Mahan and J. O. Sofo, Proc. Natl. Acad. Sci. USA 93, 7436 (1996).

N. Tureson, M. Marteau, T. Cabioch, N. Van Nong, J. Jensen, J. Lu, G. Greczynski, D. Fournier, N. Singh, A. Soni, L. Belliard, P. Eklund and A. le Febvrier. Phys. Rev. B 98, 205307 (2018)

Keywords: Thermoelectric, ScN, implantation, defects, power factor, electrical conductivity, thermal conductivity

Thermoelectric properties of carbon nanotubes carrier-tuned by electric double layer techniques

Haruka Yoshida*[1], Katsuaki Hashikuni[2], and Hiroaki Anno[2]

[1]Sanyo-Onoda City University, Graduate School of Engineering – 1-1-1 Daigakudori, Sanyo Onoda City, Yamaguchi Prefecture 756-0884, Japan
[2]Sanyo-Onoda City University, Department of Electrical Engineering – 1-1-1 Daigakudori, Sanyo Onoda City, Yamaguchi Prefecture 756-0884, Japan

Abstract

Nanocarbon materials, such as carbon nanotubes (CNT) and graphene, have excellent thermoelectric properties as well as lightweight and flexible mechanical properties and have been actively studied for device applications such as sensors, transistors, solar cells, etc.
To utilize super-growth carbon nanotubes (SG-CNTs) [1] as a thermoelectric material, we fabricated ionic liquid-based electric double-layer transistor (EDLT) [2] and investigated the pn-type control by carrier injection into SG-CNTs and their thermoelectric properties.

For the EDLT fabrication method, SG-CNT film was fabricated on a 25×25 mm^2 quartz glass substrate by spin coating method. Then, gold electrodes were formed by sputtering method and ionic gel was applied on the electrodes.

As the gate voltage VG changed from −2.0 V to 2.4 V, the Seebeck coefficient S changed from 84 μV/K to −144 μV/K, which were higher than S = 41.6 μV/K at VG = 0 V. In other words, pn control with electron doping for $VG >$ 0 and hole doping for $VG <$ 0 was realized, consistent with the EDLT principle. Furthermore, the electrical conductivityσ increased from 1.4 S/cm to 141 S/cm by applying VG.

As a result, it was found that the carrier injection of electrons and holes into SG-CNTs could be controlled by changing VG of EDLT, and that the power factor of SG-CNTs was enhanced by carrier doping. We will discuss the relationship between thermoelectric properties and the amount of charge injected into SG-CNTs by the EDLT technique.

K. Hata, et al., Science, **306**, 1362–1364 (2004).
K. Yanagi, et al., Nano Lett., **14**, 6437–6442(2014).

Keywords: thermoelectric properties, carbon nanotube, electric double layer technique, carrier injection

---

*Speaker

Tuning thermoelectric properties by epitaxial strain in p-type Sr-doped LaCrO3 thin films

Romain Bachelet*†[1], Dong Han[2], Rahma Moalla[2], Ignasi Fina[3], Valentina M. Giordano[4], Marc D'esperonnat[2], Claude Botella[2], Geneviève Grenet[2], Regis Debord[4], Stéphane Pailhès[4], and Guillaume Saint-Girons[2]

[1]Institut des Nanotechnologies de Lyon – CNRS : UMR5270 – INL, UMR CNRS 5270, Ecole Centrale de Lyon, 36 avenue Guy de Collongue, 69134 Ecully Cedex, France
[2]Institut des Nanotechnologies de Lyon – UMR CNRS 5270 – France
[3]Institut de Ciencia de Materials de Barcelona – Spain
[4]Institut Lumière Matière – UMR CNRS 5306 – France

Abstract

Thermoelectric perovskite oxides of general formula ABO3 are appealing because of their chemical flexibility, property tunability by doping, structural compatibility and thermal stability, which can be obtained with abundant and low toxicity elements [1]. Indeed, the well-known *n*-type thermoelectric ABO3, especially the SrTiO3-based solid solutions, exhibit large thermoelectric power factors (PF _˜40 μW cm-1 K-2) [2-3], and can be elaborated in epitaxial films with single-crystal quality [4-5]. However, the counterpart *p*-type ABO3 are much less known. Sr-doped LaCrO3 is one of the few *p*-type thermoelectric ABO3 exhibiting optimal PF around 25 at.% Sr (La0.75Sr0.25CrO3) [6-7].

In this communication, we will first show that high-quality Sr-doped LaCrO3 epitaxial films can be elaborated by solid-source molecular beam epitaxy (MBE) [8], and secondly that the electronic and thermoelectric properties of La0.75Sr0.25CrO3 can be largely tuned by epitaxial strain within ± 2% range (see Figure) [9]. In particular, the electric conductivity can be controlled over two orders of magnitude, ranging from ∼0.5 S cm-1 (tensile strain) to ∼35 S cm–1 (compressive strain). Consistently, the Seebeck coefficient can be finely tuned by a factor of almost two from ∼127 μV K–1 (compressive strain) to 208 μV K–1 (tensile strain). The thermoelectric power factor can consequently be tuned by almost two orders of magnitude. The compressive strain yields a remarkable enhancement by a factor of three for 2% compressive strain with respect to almost relaxed films.

Figure: In-plane electrical conductivity and Seebeck coefficient of La0.75Sr0.25CrO3 epitaxial thin films as a function of in-plane strain and corresponding stress.

References

J. He *et al.*, J. Mater. Res. 26, 1762 (2011); https://doi.org/10.1557/jmr.2011.108

---

*Speaker

†Corresponding author: romain.bachelet@ec-lyon.fr

T. Okuda *et al.*, Phys. Rev. B 63, 113104 (2001); https://doi.org/10.1103/PhysRevB.63.113104

G. Bouzerar *et al.*, Europhys. Lett. 118, 67004 (2017); https://doi.org/10.1209/0295-5075/118/67004

B. Jalan and S. Stemmer, Appl. Phys. Lett. 97, 042106 (2010); https://doi.org/10.1063/1.3471398

M. Apreutesei *et al.*, Sci. Technol. Adv. Mater. 18, 430 (2017); https://doi.org/10.1080/14686996.2017.1336055

D.P. Karim and A.T. Aldred, Phys. Rev. B 20, 2255 (1979); https://doi.org/10.1103/PhysRevB.20.2255

K.H.L. Zhang *et al.* Adv. Mater. 27, 5191 (2015); https://doi.org/10.1002/adma.201501959

D. Han *et al.*, J. Appl. Phys. 126, 085304 (2019); . https://doi.org/10.1063/1.5101049

D. Han *et al.*, ACS Appl. Electron. Mater., *accepted* (2021) ; https://doi.org/10.1021/acsaelm.1c00425

Keywords: Thermoelectric oxides, perovskite ABO3, thin film, epitaxy, strain

Manipulation of defect structure for high performance thermoelectric chalcogenides

Priyanka Jood*†[1] and Michihiro Ohta[1]

[1]Global Zero Emission Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan – Japan

Abstract

Defect engineering is one of the key approaches in enhancing the thermoelectric performance of the materials. In this talk, the defect-related physical effects on the thermoelectric transport in Ag2Se and PbTe systems will be presented.
Ag2Se is considered as a potential candidate for use in room-temperature thermoelectric applications owing to its unique transport properties, such as glass-like thermal conductivity and narrow band gap. In this study, a correlation between composition (Ag/Se ratio), defect structure, and transport properties was established, to optimize its figure of merit zT. In-depth microscopic analysis revealed the coexistence of a metastable (monoclinic) structure and the main orthorhombic crystal structure in stoichiometric Ag2Se. Successfully inhibiting the metastability and stabilizing the orthorhombic structure through anion excess resulted in a $> 50\%$ increase in carrier mobility. A nearly flat zT of $\sim$1 over the 300–375 K temperature range was achieved [1,2].

PbTe has long been of interest to the thermoelectric community due to its outstanding performance in mid temperature range (600-900 K) [3,4]. Na+1 has been the most conventional dopant for p-type PbTe with a history of practical application in RTGs on several of NASA space missions in the 1960s. Despite great efforts of optimizing Na doping in PbTe, Na solubility and doping efficiency remained low. In this work we show that, enhanced Na solubility can be achieved at high temperatures by fixing the equilibrium to Te-rich. The higher Na concentration leads to band convergence between the light (L) and heavy valence (Σ) bands in PbTe, increasing the Seebeck coefficient and suppressing the bipolar thermal conductivity. Maximum zT nearing 2 is achieved which is $\sim$25% higher than traditionally reported values for pristine PbTe-Na [5].

At AIST, the work was supported by Research and Development Program for Promoting Innovative Clean Energy Technologies Through International Collaboration funded by the New Energy and Industrial Technology Development Organization (NEDO), Development of Thermal Management Materials and Technology funded by the NEDO, The Thermal & Electric Energy Technology Foundation (TEET) of Japan, and the International Joint Research Program for Innovative Energy Technology funded by the Ministry of Economy, Trade and Industry (METI). Acknowledgements to R. Chetty of AIST, G. J. Snyder and M. G. Kanatzidis of Northwestern University, and Y. Matsushita and Y. Takagiwa of NIMS for their respective contributions to this work.

---

*Speaker

†Corresponding author: p.jood@aist.go.jp

sciencesconf.org:vwt2021:365121

References

1. P. Jood, R. Chetty, M. Ohta, *J. Mater. Chem. A* (2020) 8, 13024.

2. P. Jood, M. Ohta, *ACS Appl. Energy Mater.* (2020) 3, 2160.

3. X. Hu, P. Jood, M. Ohta, M. Kunii, K. Nagase, H. Nishiate, M. G. Kanatzidis, and A. Yamamoto, *Energy Environ. Sci.* (2016) 9, 517

4. P. Jood, M. Ohta, A. Yamamoto, and M. G. Kanatzidis, *Joule* (2018) 2, 1339.
5. P. Jood, J. P. Male, S. Anand, Y. Matsushita, Y. Takagiwa, M. G. Kanatzidis, G. J. Snyder, and M. Ohta, *J. Am. Chem. Soc.* (2020) 142, 36, 15464.

Keywords: PbTe, Silver selenide, defects, band engineering, room temperature material, Thermoelectrics

Cu26Ti2Sb6–xGexS32 colusite with high thermoelectric performance

Takashi Hagiwara*[1], Koichiro Suekuni†[1,2], Pierric Lemoine[3], Andrew R. Supka[4], Raju Chetty[5], Emmanuel Guilmeau‡[6], Bernard Raveau[6], Marco Fornari[4], Michihiro Ohta[5], Rabih Al Rahal Al Orabi[4], Hikaru Saito[7], Katsuaki Hashikuni[1], and Michitaka Ohtaki[1,2]

[1]Interdisciplinary Graduate School of Engineering Sciences, Kyushu University – Kasuga, Fukuoka 8168580, Japan

[2]Transdisciplinary Research and Education Center for Green Technologies, Kyushu University – Kasuga, Fukuoka 816-8580, Japan

[3]Université de Rennes 1 – CNRS, ISCR-UMR 6226 – F-35000 Rennes, France

[4]Department of Physics and Science of Advanced Materials Program – Central Michigan University, Mt. Pleasant, Michigan 48859, United States

[5]Global Zero Emission Research Center, National Institute of Advanced Industrial Science and Technology (AIST) – Tsukuba, Ibaraki 305-8569, Japan

[6]CRISMAT – CNRS, Normandie Université, ENSICAEN, UNICAEN – 14000 Caen, France

[7]Institute for Materials Chemistry and Engineering, Kyushu University – Kasuga, Fukuoka 816-8580, Japan

Abstract

Cu–S-based compounds with sphalerite-derived structures have attracted increasing attention as thermoelectric (TE) materials over the last decade. [1, 2] Examples include colusites Cu26T2M6S32 (T = V, Nb, Ta, Cr, Mo, W and M = Ge, Sn), which exhibit degenerate semiconducting properties and low thermal conductivity. [3, 4] In this work, we designed and synthesized a new member of colusite Cu26Ti2Sb6S32, and investigated the TE properties of Ge-substituted series, Cu26Ti2Sb6–xGexS32 (x = 1–3), up to 673 K. [5] The crystal structure was determined by powder X-ray diffraction and confirmed by high-angle annular dark-field scanning transmission electron microscopy. Cu26Ti2Sb6S32 exhibited a semiconducting character and low thermal conductivity of 0.6 W K^{-1} m^{-1}. The former character is consistent with the electronic structure obtained by the density functional theory. The substitution of Ge for Sb increased the hole carrier concentration to _˜10^{21} cm^{-3}. As a result, the power factor (PF) reached as high as 1.2 mW K^{-2} m^{-1} at 673 K for x = 2. Degenerated heavy/light electron bands at the top of the valence band are probably responsible for the high PF. Due to the high PF and low thermal conductivity, ZT reaches 0.9 for x = 2 at 673 K.

This work was financially supported by JSPS KAKENHI Grant No. JP20H02440 (K. S.), and grants from the International Joint Research Program for Innovative Energy Technology funded by METI and Research and Development Program for Promoting Innovative Clean

---

*Speaker

†Corresponding author: suekuni.koichiro.063@m.kyushu-u.ac.jp

‡Corresponding author: emmanuel.guilmeau@ensicaen.fr

Energy Technologies Through International Collaboration funded by NEDO. E.G. and P.L. acknowledge the financial support of CNRS through the International Emerging Actions program (EXPRESS project).

K. Suekuni, T. Takabatake, APL Mater., **4**, 104503 (2016).

A. V. Powell, J. Appl. Phys., **126**, 100901 (2019).

G. Guélou, P. Lemoine, B. Raveau, E. Guilmeau, J. Mater. Chem. C, **9**, 773 (2021).

K. Suekuni, M. Ohta, T. Takabatake, E. Guilmeau, Thermoelectric Energy Conversion, 197–216, (2021).

T. Hagiwara, K. Suekuni, P. Lemoine, A. R. Supka, R. Chetty, E. Guilmeau, B. Raveau, M. Fornari, M. Ohta, R. Al Rahal Al Orabi, H. Saito, K. Hashikuni, M. Ohtaki, Chem. Mater. **33**, 3449 (2021).

Keywords: sulfide, colusite

Identification of resonant impurities in thermoelectric semiconductors

Shantanu Misra*†[1], Bartlomiej Wiendlocha[2], Anne Dauscher[3], Bertrand Lenoir[4], and Christophe Candolfi[1]

[1]Institut Jean Lamour (IJL) – CNRS : UMR7198, Univesité de Lorraine – Campus Artem 2 allée André Guinier BP 50840 54011 Nancy Cedex, France

[2]Faculty of Physics and Applied Computer Science, AGH University of Science and Technology – Al. Mickiewicza 30, 30-059 Krakow, Poland

[3]Institut Jean Lamour (IJL) – Université de Lorraine, Centre National de la Recherche Scientifique : UMR7198 – Campus Artem 2 allée André Guinier BP 50840 54011 Nancy Cedex, France

[4]Institut Jean Lamour (IJL) – CNRS : UMR7198, Université de Lorraine – Campus Artem 2 allée André Guinier BP 50840 54011 Nancy Cedex, France

Abstract

The dimensionless thermoelectric figure of merit, *ZT*, that governs the efficiency of the thermoelectric devices, has been successfully improved through the increase of the power factor, the decrease in the lattice thermal conductivity or the synergistic effect of both strategies. One possible way of optimizing the power factor of semiconductors is through the introduction of an impurity that gives rise to a resonant level (RL) at the edge of either the valence or conduction bands [1,2]. The impurity atoms distort locally the electronic band structure beyond the rigid-band model. A significant increase in the thermopower and, hence, in the power factor is observed when the chemical potential resides in this distortion due to the increased Density of States (DOS). So far, the main experimental strategy to unravel the resonant nature of a given impurity in semiconductor was tied to the variation of the thermopower as a function of the charge carrier concentration, known as the Ioffe-Pisarenko plot. However, Pisarenko plots can remain inconclusive in many practical cases, since the impurity may affect the thermopower of the material due to various non-rigid-band effects.

In this work, we propose a novel method which allows to distinguish between resonant and non-resonant impurities in semiconductors. Using a combination of experimental data and theoretical calculations based on the Kubo-Greenwood formalism, we show that an analysis of the low-temperature electrical resistivity and carrier mobility allows to unambiguously conclude on the character of a given impurity, even when the Ioffe-Pisarenko plot is inconclusive. Our findings are based on a detailed analysis of the canonical SnTe system doped with resonant In [3].

References

1. Heremans, J. P., Jovovic, V., Toberer, E. S., Saramat, A., Kurosaki, K., Charoenphakdee, A., Yamanaka, S. & Snyder, G. J. Enhancement of Thermoelectric Efficiency in PbTe by

---

[*] Speaker

[†] Corresponding author: shantanu.misra@univ-lorraine.fr

Distortion of the Electronic Density of States. *Science* 321, 554 (2008).

2. Heremans, J. P., Wiendlocha, B. & Chamoire, A. M. Resonant levels in bulk thermoelectric semiconductors. *Energy Environ. Sci.* 5, 5510 (2012).
3. Wiendlocha, B., Misra, S., Dauscher, A., Lenoir, B. & Candolfi, C. Residual resistivity as an independent indicator of resonant levels in semiconductors. *Materials Horizons* 8, 1735–1743 (2021).

Keywords: Thermoelectrics, Resonant level, semiconductors, Thermopower, residual resistivity

Investigation of some niobium chalcogenides transport properties

Hugo Bouteiller*[1], David Berthebaud[2], Sylvain Le Tonquesse[2], Amélie Galodé[1], Louise Goodwin[1], and Franck Gascoin†[1]

[1]Laboratoire de cristallographie et sciences des matériaux (CRISMAT) – Centre National de la Recherche Scientifique : UMR6508, Ecole Nationale Supérieure d'Ingénieurs de Caen, Normandie Université, Université de Caen Normandie – 6 Bvd du maréchal Juin 14050 CAEN CEDEX 4, France
[2]CNRS-Saint Gobain-NIMS, Laboratory for Innovative Key Materials and Structures (LINK), National Institute for Materials Science – Tsukuba, Japan

Abstract

Since the discovery of new transition metal chalcogenides presenting interesting features in previous studies, the exploration of other chalcogenides has highly concentrated our efforts. Niobium chalcogenides were previously studied for their Seebeck coefficient anomalies at very low temperature resulting from charge-density waves phenomena. We propose here to present our latest results on the synthesis and characterization of the transport properties of these materials to evaluate their thermoelectric performance, especially at very high temperatures. The structure of these chalcogenides presents quasi-one dimensional large infinite channels that might be interesting regarding the scattering of phonons. The non-stoichiometric composition of the materials will also be discussed.

Keywords: Chalcogenides, Selenides, Tellurides, New materials, Synthesis

---

*Speaker

†Corresponding author: franck.gascoin@ensicaen.fr

Ordered sphalerite derivative Cu5Sn2S7: a degenerate semiconductor with high carrier mobility in the Cu–Sn–S diagram

Ventrapati Pavan Kumar*†[1], Pierric Lemoine[2], Virginia Carnevali[3], Gabin Guélou[4], Oleg Lebedev[1], Philippe Boullay[1], Bernard Raveau[1], Rabih Al Rahal Al Orabi[5], Marco Fornari[6], Christophe Candolfi[7], Carmelo Prestipino[8], Denis Menut[9], Bernard Malaman[7], Jean Juraszek[10], Koichiro Suekuni[11], and Emmanuel Guilmeau‡[4]

[1]Laboratoire CRISMAT – CNRS : UMR6508, Normandie Univ, ENSICAEN, UNICAEN, CNRS, CRISMAT, 14000 Caen – France

[2]Institut des Sciences Chimiques de Rennes-UMR 6226 CNRS – Université de Rennes : UMR6226 – France

[3]Department of Physics and Science of Advanced Materials Program, Central Michigan University – Mt. Pleasant, MI 48859, USA, United States

[4]Laboratoire CRISMAT – CNRS : UMR6508, Normandie Univ, ENSICAEN, UNICAEN, CNRS, CRISMAT, 14000 Caen – France

[5]Department of Physics and Science of Advanced Materials Program, Central Michigan University – Mt. Pleasant, MI 48859, USA, United States

[6]Department of Physics and Science of Advanced Materials Program, Central Michigan University – Mt. Pleasant, MI 48859, USA, United States

[7]Institut Jean Lamour – Université de Lorraine, Centre National de la Recherche Scientifique : UMR7198 – Institut Jean Lamour - CNRS - Université de Lorraine. Campus Artem 2 allée André Guinier BP 50840 54011 Nancy Cedex, France

[8]Institut des Sciences Chimiques de Rennes-UMR 6226 CNRS – Université de Rennes – France

[9]Synchrotron SOLEIL – CNRS : UMRUR1 – L'Orme des Merisiers Saint-Aubin - BP 48 91192 GIF-sur-YVETTE CEDEX, France

[10]Groupe de physique des matériaux (GPM) – Université de Rouen Normandie, Institut national des sciences appliquées Rouen Normandie, Centre National de la Recherche Scientifique, Normandie University, UNIROUEN – Avenue de l'Université, BP12, 76801 Saint-Etienne-du-Rouvray Cedex, France

[11]Interdisciplinary Graduate School of Engineering Sciences, Kyushu University – Kasuga, Fukuoka 8168580, Japan

Abstract

Regardless of the complexity of the phase diagram of the Cu–Sn–S system, several compositions near the prototypical mohite Cu2SnS3 have arisen as potential non-toxic, earth-abundant and cost-efficient photovoltaic and thermoelectric materials [1-2]. In this work, we

---

*Speaker

†Corresponding author: pavanudaya@gmail.com

‡Corresponding author: emmanuel.guilmeau@ensicaen.fr

revisited the Cu2+xSn1-xS3 system and discovered two new members with in the short range of x value, namely a monoclinic ($C2$) ordered sphalerite derivative member, Cu5Sn2S7 and a semi-ordered cubic sphalerite derivative member, Cu22Sn10S32. Using a combination of synchrotron diffraction and spectroscopy, transmission electron microscopy, precession-assisted electron diffraction tomography, Mossbauer spectroscopy, first principles calculations and transport properties measurements, we discuss the structure–thermoelectric properties relationships and clarify the interesting crystal chemistry in these systems. The ternary sulfide Cu5Sn2S7 exhibits a degenerate semiconducting behavior with exceptionally high hole mobility originating from the interplay between atomic ordering and charge delocalization [3]. In addition, the structural characterization and transport properties of the semi-ordered cubic phase, Cu22Sn10S32, will be discussed in detail during the presentation [4].

References:

Shen, Y.; Li, C.; Huang, R.; Tian, R.; Ye, Y.; Pan, L.; Koumoto, K.; Zhang, R.; Wan, C.; Wang, Y. Eco-Friendly p-Type Cu2SnS3 Thermoelectric Material: Crystal Structure and Transport Properties. *Sci. Rep.* **2016**, *6*, 32501.

Lokhande, A. C.; Babar, P. T.; Karade, V. C.; Gang, M. G.; Lokhande, V. C.; Lokhande, C. D.; Kim, J. H. The Versatility of Copper Tin Sulfide. *J. Mater. Chem. A* **2019**, *7* (29),17118–17182.

Pavan Kumar, V.; Lemoine, P.; Carnevali, V.; Guélou, G.; Lebedev, O. I.; Boullay, P.; Raveau, B.; Al Rahal Al Orabi, R.; Fornari, M.; Prestipino, C.; Menut, D.; Candolfi, C.; Malaman, B.; Juraszek, J.; Guilmeau, E. Ordered Sphalerite Derivative Cu5Sn2S7: A Degenerate Semiconductor with High Carrier Mobility in the Cu-Sn-S Diagram. *J. Mater. Chem. A.* **2021**, *9*, 10812–10826.

Pavan Kumar, V.; Lemoine, P.; Carnevali, V.; Guélou, G.; Lebedev, O. I.; Raveau, B.; Al Rahal Al Orabi, R.; Fornari, M.; Prestipino, C.; Menut, D.; Candolfi, C.; Malaman, B.; Juraszek, J.; Suekuni, K.; Guilmeau, E. Local disorder-induced low thermal conductivity in degenerate semiconductor Cu22Sn10S32. *Inorg. Chem.* **2021** *(Accepted).*

Keywords: Sphalerite derivative, degenerate semiconductor, high carrier mobility

Point defect engineering enhances thermoelectric performance of Mg2Si and Mg2Sn single crystals

Kei Hayashi*†1

1Department of Applied Physics, Graduate School of Engineering, Tohoku University – 6-6-05,
Aramaki-Aza-Aoba, Aoba, Sendai, Miyagi 980-8579, Japan, Japan

Abstract

Mg2Si and Mg2Sn have attracted much attention as highly efficient thermoelectric (TE) materials which can be used at mid-temperature. In most research, Mg2(Si,Sn) polycrystals (PCs) were prepared to enhance TE performance by reducing lattice thermal conductivity lat. In contrast, we focused on Mg2Si and Mg2Sn single crystals (SCs), because SCs generally show high electrical conductivity σ than PCs. However, the lat of SCs is also expected to be higher than that of PCs. Thus, we utilized point defect engineering to reduce lat of Mg2Si and Mg2Sn SCs. To induce point defects in the Mg2Si and Mg2Sn SCs, physical and chemical pressure were applied: for the former, the Mg2Si and Mg2Sn SCs were prepared under an Ar atmosphere, whereas elemental doping was performed for the latter. Obtained results are listed below.
(1) The prepared Mg2Si and Mg2Sn SCs contained Si vacancy (VSi) and Mg vacancy (VMg), respectively [1,2]. With increasing the Ar pressure, the VMg fraction in the Mg2Sn SC increased [2].

(2) By doping boron (B) to the Mg2Si and Mg2Sn SCs, the VSi and VMg fraction both increased accompanied by the decrease of lattice constant, i.e., the increase of chemical pressure [3].

(3) Owing to the presence of VSi and VMg, the lat of the non-doped and B-doped Mg2Si/Mg2Sn SCs were found to be lower than that of non-doped and B-doped Mg2Si/Mg2Sn PCs [3]. In particular, the 0.5% B-doped Mg2Sn SC exhibited the lowest lat at 650 K, which reached the minimum lat predicted theoretically [4].

Next, we examined whether the point defect engineering can be combined with a conventional doping method [5]. Sb was selected as a doner dopant for the Mg2Sn SC to enhance σ. With increasing the Sb concentration, the electron carriers increased, leading to the enhancement of σ. The σ of the Sb-doped Mg2Sn SCs was higher than that of the Sb-doped Mg2Sn PCs. Although the VMg fraction decreased by the Sb doping, the Sb-doped Mg2Sn SCs contained VMg. Thus, the lat of the Sb-doped Mg2Sn SCs was lower than that of Sb-doped Mg2Sn PCs. The evaluated dimensionless figure-of-merit zT reached 0.72 at 650 K for the 1% Sb-doped Mg2Sn SC, which is higher than that of Sb-doped Mg2Sn PC.

In the workshop, we will demonstrate the effectiveness of point defect engineering for the

---

*Speaker

†Corresponding author: kei.hayashi.b5@tohoku.ac.jp

sciencesconf.org:vwt2021:364925

enhancement of TE performance of Mg2Si and Mg2Sn SCs.

This work was partly based on collaborative research between Sumitomo Metal Mining Co., Ltd. and Tohoku University, which is part of the Vision Co-creation Partnership, and was also supported in part by the Grant-in-Aid for JSPS Fellows, Grant-in-Aid for Scientific Research, Grant-in-Aid for Scientific Research on Innovative Areas, and Grant-in-Aid for Transformative Research Areas from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

K. Hayashi et al., AIP Adv., 10(2020)035115

W. Saito, K. Hayashi, et al., Sci. Rep. 10 (2020) 2020.

W. Saito, K. Hayashi, et al., ACS Appl. Energy Mater. 4 (2021) 5123.

Y. Jin et al., RSC Adv. 6 (2016) 48728.

W. Saito, K. Hayashi, et al., ACS Appl. Mater. Interfaces 12 (2020) 57888.

Keywords: Mg2Si, Mg2Sn, single crystal, point defect

Strategies to Achieve High Thermoelectric Performance of n-type Mg3Sb2-Mg3Bi2 Alloys

Kazuki Imasato*[1,2], Michihiro Ohta[1], and Gerald Jeffrey Snyder[2]

[1]Global Zero Emission Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan – Japan
[2]Northwestern University [Evanston] – 633 Clark Street, Evanston, IL 60208 Evanston, United States

Abstract

There has been significant interest in type Mg3Sb2-Mg3Bi2 alloys since the demonstration of high zT in the n-type Mg3Sb1.5Bi0.5. Considering the limited number of state-of-art n-type thermoelectric materials for the low-grade heat recovery and cooling technology, the further development of Mg3Sb2-Mg3Bi2 alloys is a significant step towards the commercial application of thermoelectric materials. In this talk, I will present the strategies to achieve a high thermoelectric performance of Mg3Sb2-Mg3Bi2 alloys from the perspective of defects, composition, microstructure, and electronic band structure. The thermoelectric performance of n-type Mg3Sb2-Mg3Bi2 alloys was systematically investigated and significantly improved with thorough experimental characterizations. The main mechanisms of the improvement are optimization of the band structure and microstructure. The substitution of the atomic site such as alloying, and doping is an effective way to tune the thermoelectric performance by changing effective mass and mobility, in addition to the reduction of lattice thermal conductivity. The best composition can be determined based on the operating temperature with tunable band gap. Also, the electrically-resistive grain boundary can significantly decrease the mobility of the charge carrier especially around room temperature. By removing the grain boundary effect by using high temperature press or saturation annealing technique, the thermoelectric performance of the material can be increased by more than 200 %. Without those detailed insights into the underlining mechanisms of emerging thermoelectric properties, the acquisition of such a high performance could be challenging. These results were compiled to establish foundational methodologies to fully take advantage of the potential of this material system.

References

K. Imasato et al., Energy Environ. Sci., 2019,12, 965-971

K. Imasato et al., Advanced Materials 2020, 32 (16), 1908218

Keywords: Mg, Alloying, Grain Boundary, Doping, Bi

---

*Speaker

The thermal stability of KGaSb4

Oussama El Hamouli*[1], Müjde Yahyaoğlu[2], Umut Aydemir[2], Shantanu Misra[1],
Christophe Candolfi[1], and Bertrand Lenoir[1]

[1]Institut Jean Lamour (IJL) – CNRS : UMR7198, Univesité de Lorraine – Campus Artem 2 allée André
Guinier BP 50840 54011 Nancy Cedex, France
[2]Koç University – Rumelifeneri Yolu, 34450 Sarıyer-İstanbul, Turkey

Abstract

The rise of high-throughput calculations has led to the discovery of new promising thermoelectric materials in recent years, that notably include Zintl phases. Most of these phases are p-type, with only few n-type Zintl phases discovered so far. Confirming theoretical predictions, KGaSb4 has been recently identified to be n-type dopable through substituting Ba for K, leading to peak ZT of 0.9 at around 673 K. In this work, we explore in detail the stability of this phase prepared by ball-milling using a combination of high-temperature powder X-ray diffraction and differential scanning calorimetry. Our results show that this phase starts to decompose around 473 K, whose speed increases as the temperature increases. The decomposition consists mainly of the formation of Sb as a secondary phase, which keeps growing in proportion until it becomes the major phase.

Keywords: Thermoelectric, Zintl, Stability

---

*Speaker

Thermodynamic stability of Frenkel defect and its influence on phonon thermal conduction in Mg3Sb2

Yohei Ueki*†1, Susumu Fujii2,1, Masato Yoshiya2,1, Hiromasa Tamaki3, and Tsutomu Kanno3

1Osaka University – 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
2Japan Fine Ceramics Center – 2-4-1, Mutsuno, Atsuta, Nagoya 456-8587, Japan
3Panasonic Corporation – Hikaridai 3-4, Seika, Kyoto 619-0237, Japan

Abstract

Mg3Sb2, classified as a Zintl phase compound, has been attracting attention due to its high electrical conductivity and low thermal conductivity. Recently, it has been reported that Mg3Sb2 has a high density of Frenkel defects and it reduces the lattice thermal conductivity without deteriorating electronic properties, thereby increasing efficiency of thermoelectric conversion(1). However, many of details of the Frenkel defects remain unclear, e.g., how the pairs of vacancies and interstitials are distributed in the crystal lattice of Mg3Sb2. Possible influence of the Frenkel defects onto thermal conduction also needs to be quantitatively evaluated, in order to further exploit this kind of ubiquitous point defects for better transport and thermoelectric properties.

Thus, in this study, we have attempted to clarify the thermodynamic stability of Frenkel defect and the reduction mechanism of thermal conductivity in Mg3Sb2, through analyzing the phonon properties using first-principles lattice dynamics calculations. Formation energy of the Frenkel defect was also calculated for the CaMg2Sb2 for comparison, as it has the same crystal structure as Mg3Sb2.

The Mg3Sb2 models containing a Frenkel defect was constructed and their internal energies were evaluated by first-principles calculations . First-principles lattice dynamics calculations were then performed for these models to analyze the phonon properties and compared with the perfect crystal of Mg3Sb2 . The VASP(2) code was used for electronic structures calculations and structure optimization.

When compared with CaMg2Sb2, the formation energy of a Frenkel defect pair in Mg3Sb2 was smaller at 0K. It can be attributed to the smaller size of cations around the interstitial Mg atom. Considering vibrational entropy at finite temperature by harmonic lattice dynamics calculations, the formation free energy of a Frenkel defect decreased with increasing temperature. This suggests that the Frenkel defects become thermodynamically more stable at high temperature in Mg3Sb2. This result is consistent with the fact that Mg3Sb2 experimentally forms a high density of Frenkel defects under finite temperature(1). The anharmonic lattice dynamics calculations showed that phonons in low frequency region mainly contribute to thermal conductivity in the perfect crystal of Mg3Sb2. By introducing a pair of Frenkel defect, the group velocity of phonons in a wide frequency range was reduced drastically, which would lead to decrease in thermal conductivity even if phonon mean free

---

*Speaker

†Corresponding author: Yohei.UEKI@mat.eng.osaka-u.ac.jp

path or its relaxation time is put aside. This can be attributed to the local disorder of the crystal structure caused by the introduction of a Mg interstitial atom and a Mg vacancy of the Frenkel defect.

In this study, it is found that the Frenkel defects become thermodynamically more stable at high temperature in Mg3Sb2 compared with CaMg2Sb2, due to the smaller size of cations surrounding the Frenkel defect. It is also found that the thermal conductivity of Mg3Sb2 is reduced because of formation of Frenkel defect, which drastically decreases phonon group velocities in a wide frequency range. These findings may be applied to other materials including Mg3(Sb,Bi)2, which shows favorable thermoelectric conversion performance.

Acknowledgements:
This work was supported by Grants-in-Aid for Scientific Research (Grant Number: JP19H05786, JP20K05062).

References:
(1) T. Kanno, H. Tamaki, M. Yoshiya, H. Uchiyama, S. Maki, M. Takata, Y. Miyazaki, "High-Density Frenkel Defects as Origin of N-Type Thermoelectric Performance and Low Thermal Conductivity in Mg3Sb2-Based Materials " *Adv Funct Mater.*, 2008469 (2021).
(2) G. Kresse and J. Furthmüller, "Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set", *Phys. Rev. B*, **54**(1996), 11169-11185

Keywords: Mg3Sb2, phonon, frenkel defect

Thermoelectric properties of n-type material, (Mg,Y)3(Sb,Bi)2

Ryosuke Sakagami*†[1,2], Kunihiro Kihou[1], Mizuki Nagata[1,3], Hirotaka Nishiate[1], and Chul-Ho Lee[1]

[1]National Institute of Advanced Industrial Science and technology (AIST) – Japan
[2]Keio University – Japan
[3]Tokyo University of Science – Japan

Abstract

Mg3Sb2-based compounds are one of promising n-type thermoelectric materials exibiting high thermoelectric performance. Recently, we succeeded to synthesize Te free Y-doped Mg3(Sb,Bi)2 compounds using melting method that is applicable for mass production [1]. In this study, we tried to enhance their carrier mobility by enlarging grain size for further improvement. We optimized the conditions of hot pressing and Mg-vapor annealing. The obtained maximum dimensionless figure-of-merit (ZT) was 1.32 at 674 K in Mg3.3Y0.01Sb1.5Bi0.5 samples. [1] K. Kihou, H. Kunioka, H. Nishiate, and C.H. Lee, J. Mater. Res. Technol. **10**, 438 (2021).

Keywords: Mg3Sb2, based compounds, Mg, vapor anneal, grain growth, carrier mobility

---

*Speaker

†Corresponding author: sakagami-ryosuke@aist.go.jp

Thermoelectric Properties of p-Type Ba8Au6Ge40 Clathrate

Yudai Koga*[1], Katsuaki Hashikuni[2], and Hiroaki Anno†[2]

[1]Graduate School of Engineering, Sanyo-Onoda City University – 1-1-1 Daigakudori, Sanyo Onoda City, Yamaguchi Prefecture, 756-0884, Japan

[2]Department of Electrical Engineering, Sanyo-Onoda City University – 1-1-1 Daigakudori, Sanyo Onoda City, Yamaguchi Prefecture, 756-0884, Japan

Abstract

Semiconducting clathrates are attracting attention as one of the thermoelectric materials that realize the concept of Phonon Glass Electron Crystal. Most of the thermoelectric clathrates reported so far, however, are n-type. The development of high-performance p-type clathrates for application as thermoelectric element materials has become an important issue. In the previous study, Zhang et al. reported that Ba8Au5.3Ge40.7 was p-type [1]. Therefore, in this study, Ba8Au6Ge40 was synthesized as part of the search for p-type clathrate and investigated its thermoelectric properties, intending to find a better p-type clathrate.
Polycrystalline samples were prepared by a spark plasma sintering technique. The crystal structure and chemical composition were determined by X-ray diffraction and an electron probe microanalysis, respectively. In addition, the Seebeck coefficient and electrical conductivity were measured in the range of 300–900 K. Hall measurements were conducted at 300 K.

From the XRD results, it was confirmed that the main phase of the sample was clathrate. In addition, the diffraction peak of the (320) plane of the XRD pattern decreased greatly, suggesting the preferential occupation of Au in the 6c site. A trace amount of the BaAu2Ge2 phase was, however, observed at the same time.

The maximum Seebeck coefficient and the electrical conductivity were 133 μV/K and 823 S/cm at 900 K, respectively. The power factor was calculated as 14.6 μW/(cmK^2) at 900 K. The temperature at the maximum power factor for the sample was 900 K, which was about 200 K higher than that for Ba8Au5.3Ge40.7 [1]. The thermal conductivity was estimated to be 1.90 W/(mK) at 900 K. The thermoelectric figure of merit was estimated to be 0.68 at 900 K. The Hall carrier mobility of the sample was 3.7 cm^2/Vs, and the carrier concentration was 2.5×10^{21} cm^{-3}, at 300 K. On the other hand, the carrier concentration of the previous study was 7.14×10^{19} cm^{-3} at 300 K [1].

In the future, we will estimate the optimum carrier concentration that maximizes thermoelectric performance and clarify the optimum Au composition value.
H. Zhang et al., Inorg. Chem., **50,** 1250–1257 (2011).

Keywords: Germanium clathrate, Au, p type

---

*Speaker

†Corresponding author: anno@rs.socu.ac.jp

High texturization and improved thermoelectric properties using a magnetic slip casting process - the illustrative case of CrSi2

Sylvain Le Tonquesse*†[1], Wenhao Zhang[2], Takao Mori[3], Jean-François Halet[4], David Berthebaud[5], and Tohru Suzuki[6]

[1]CNRS-Saint Gobain-NIMS, Laboratory for Innovative Key Materials and Structures (LINK), National Institute for Materials Science – Tsukuba, Japan
[2]National Institute for Materials Science – Tsukuba, Japan
[3]National Institute for Materials Science – Tsukuba, Japan
[4]CNRS-Saint Gobain-NIMS, Laboratory for Innovative Key Materials and Structures (LINK), National Institute for Materials Science – Tsukuba, Japan
[5]CNRS-Saint Gobain-NIMS, Laboratory for Innovative Key Materials and Structures (LINK), National Institute for Materials Science – Tsukuba, Japan
[6]National Institute for Materials Science – Tsukuba, Japan

Abstract

CrSi2 is a promising p-type thermoelectric material for industrial application because it is low cost and has low toxicity, high oxidation resistance and good mechanical properties [1]. As a bulk polycrystal, it shows an high power factor (> 1 mW m-1 K-2) but the maximum ZT remains moderate (_˜ 0.13 at 800 K) due to its relatively high thermal conductivity (12 W m-1 K-1 at 298 K). For this reason, most of the researches aims at reducing its thermal conductivity via alloying with heavy (and often expensive) elements or by nanostructuration/nanocomposite [2]. An alternative approach to enhance ZT of hexagonal CrSi2 is via crystallographic texturization along the preferential c direction. However, conventional texturization methods such as the thermomechanical rolling and hot-forging processes are not well adapted to most transition metals silicides due to their purely elastic mechanical behavior.

Here, an alternative and efficient texturization process will be presented which consists in slip casting a dispersion of CrSi2 particles under a strong magnetic field (up to 12 T). This process takes advantage of the anisotropic susceptibility of diamagnetic materials to orient the freely moving particles inside the suspension along their easy magnetization axis. After slip casting, the obtained highly textured green body that can further densified by Cold Isostatic Pressing and Spark Plasma Sintering. In this presentation, this synthesis method, which can certainly be applied to other types of high performance thermoelectic materials, will be described in details. A combined structural and texture analyses realized using X-Ray Diffraction [3] and Electron Back-Scattered Diffraction show a strong {001} texture along the magnetic field direction. As a result, the directional thermoelectric properties measured

---

*Speaker

†Corresponding author: sylvain.letonquesse@cnrs.fr

on the synthesized textured materials were found to compete with those measured on single crystals. To conclude this talk, a theoretical study based on bands structure calculations and aiming at better understanding the origin of the large anisotropy of the transport properties in CrSi2 will be presented.

References :

S. LeBlanc et al. Renew. Sust. Energ. Rev. 84 (2014) 313
M. Khalil et al. J. Appl. Phys. 126 (2019) 135103
D. Chateigner, Combined Analysis (2010) Wiley

Keywords: Texturation, Slip, casting, Silicide

A promising multi-scale approach to enhance the thermoelectric properties of β–FeSi2

Linda Abbassi*[1,2], David Mesguich[3], David Berthebaud[4], Bhuvanesh Srinivasan[5,6],
Sylvain Le Tonquesse[4], Takao Mori[7], Geoffroy Chevalier[8], Claude Estournès[9],
Emmanuel Flahaut[10], Romain Viennois[2], and Mickaël Beaudhuin[2]

[1]CIRIMAT – CNRS : UMR5085, Université Paul Sabatier (UPS) - Toulouse III – Université de Toulouse, France
[2]ICGM – UMR CNRS 5253, Montpellier – Université de Montpellier, France
[3]CIRIMAT – CNRS : UMR5085, Université Paul Sabatier [UPS] - Toulouse III, Université Paul Sabatier (UPS) - Toulouse III – France
[4]CNRS-Saint Gobain-NIMS, IRL 3629, LINK – Tsukuba, Japan
[5]WPI-MANA, NIMS – Tsukuba, Japan
[6]CNRS-Saint Gobain-NIMS, IRL 3629, LINK – Tsukuba, Japan
[7]National Institute for Materials Science – Tsukuba, Japan
[8]CIRIMAT – CNRS : UMR5085, Université Paul Sabatier (UPS) - Toulouse III – Université de Toulouse, France
[9]CIRIMAT – CNRS : UMR5085, Université Paul Sabatier (UPS) - Toulouse III – Université de Toulouse, France
[10]CIRIMAT – CNRS : UMR5085, Université Paul Sabatier (UPS) - Toulouse III – Université de Toulouse, France

Abstract

Iron disilicide β-FeSi2 can be considered as an outstanding candidate for thermoelectric application as it is composed of abundant and non-toxic chemical elements.
However, its performances are limited and its thermal conductivity reaches 10.3 W/m.K at 440 K [1]. After alloying with Al (n-type) or Co (p-type) its power factor is similar to the best thermoelectric materials in the mid-temperature range [2]. However its thermal conductivity remains high, about 4.3 W/m.K [3], and 6.2 W/m.K [3] at 425 K respectively.

To decrease this value, it is possible to follow the multi-scale approach where a large spectrum of phonons can be scattered using different length scales. As most of the phonons are scattered below several hundreds of nm, we focused this work on the nanostructuring, stacking faults and point defects. To achieve our goal, we investigated both top-down and bottom-up approaches to obtain nanostructured β-FeSi2 pellets by spark plasma sintering. Both strategies enabled us to obtain pellets with high relative density (> 93%). The decrease in the crystallite size (as low as 50 nm) enabled us to reduce significantly the lattice component of the thermal conductivity.

We will discuss the advantages of both top-down and bottom-up approaches to obtain

---

*Speaker

nanostructured β-FeSi2. We will also present the impact of this multi-scale approach on the thermoelectric performances of β-FeSi2.

References:

Waldecker, H. Meinhold, U. Birkholz, Physica Status Solidi (A), 1973, 15(1), 143–149.

Rowe, D. M., 2006, CRC,Taylor & Francis.
Hesse, Zeitschrift Fur Angewandte Physik, 1969, 28, 133.

Keywords: Thermal conductivity, Spark Plasma Sintering, β, FeSi2, Nanostructuring

Ba1/3CoO2, A Promising High-Temperature Thermoelectric Oxide

Xi Zhang*†[1], Yuqiao Zhang[1], Liao Wu[2], Hai Jun Cho[1], and Hiromichi Ohta[1]

[1]Research Institute for Electronic Science, Hokkaido University – Japan
[2]Graduate School of Information Science and Technology, Hokkaido University – Japan

Abstract

Several electrical conducting oxides such as electron doped-SrTiO3, Na3/4CoO2, and Ca3Co4O9 have been expected as thermoelectric materials because of their good environmental compatibility against metal tellurides and selenides. However, reported *ZT*s (reliable values) of conducting oxides are too low (< 0.1 at room temperature, -˜0.3 at 1000 K) for the practical applications due to their high thermal conductivity. In order to reduce the thermal conductivity of oxide with keeping high power factor, we substituted heavier ions to layered Na3/4CoO2 with Sr and Ba. As the result, we found that Ba1/3CoO2 exhibits rather high *ZT* of 0.11 at room temperature[1]. Here we report the thermoelectric properties of Ba1/3CoO2 at high-temperatures in air. We fabricated Ba1/3CoO2 epitaxial films by the R-SPE method (Na3/4CoO2)[2] followed by the ion exchange treatment with Ba2+. The resultant Ba1/3CoO2 films showed excellent thermal stability in air at high temperatures up to 600 ◦C in air, while Na3/4CoO2 films was unstable above -˜350 ◦C. The power factor (in-plane) of Ba1/3CoO2 films was similar to Na3/4CoO2 films at room temperature (-˜1 mW m–1 K–2), and it did not show clear temperature dependence above room temperature. Room temperature thermal conductivity (in-plane) of Ba1/3CoO2 films was -˜3 W m–1 K–1, which was -˜55% of that of Na3/4CoO2 (-˜5.5 W m–1 K–1). The thermal conductivity (in-plane) of Ba1/3CoO2 films showed clear decreasing tendency and it reached a low value of -˜1.7 W m–1 K–1. *ZT* of Ba1/3CoO2 films was -˜0.1 at room temperature and it gradually increased with temperature. The *ZT* at 300 ◦C was -˜0.33, which is the highest among layered cobalt oxides (reliable values). Our results suggest that Ba1/3CoO2 would be a promising high-temperature thermoelectric oxide.

References

Y. Takashima *et al.*, *J. Mater. Chem. A* **9**, 274 (2020).

H. Ohta *et al.*, *Cryst. Growth Des.* **5**, 25 (2005).

Keywords: Layered cobaltite, Epitaxial thin film, Thermoelectric, Low thermal conductivity, Thermal stability

---

*Speaker

†Corresponding author: zhangxielle@gmail.com

Electronic band structure and thermoelectric properties of AgCoO2 from first principles calculations

Hidetomo Usui*[1]

[1]Department of Physics and Materials Science, Shimane University – Matsue, Shimane 690-8504, Japan

Abstract

The discovery of large thermopower in NaxCoO2[1] and the findings in cobaltates/cobaltites[2, 3, 4] that followed have suggested that CdI2-type hexagonal CoO2 layer is an important factor for realizing high thermoelectric performance. It has been proposed that the "pudding-mold-type" band of NaxCoO2 gives rise to a coexistence of large Seebeck coefficient and small resistivity.[5] In 2011, The thermoelectric performance of p-type AgCoO2 crystallized in the R-3m and P63/mmc space groups has been reported.[6] AgCoO2 is expected to exhibit high thermoelectric performance because of the crystal structure composed of the CdI2-type hexagonal CoO2 layer. However, small power factor has been observed, indicating that the samples were not well optimized.

Given this background, we investigate the thermoelectric properties of AgCoO2 using first principles calculations. We calculate the Seebeck coefficient and the power factor *PF* divided by the constant relaxation time

tau within the Boltzmann transport theory. It is found that *PF/*

tau of AgCoO2 is 2-3 times larger than that of NaxCoO2. Large *PF/*

tau of AgCoO2 originates form the band degeneracy and the band shape around the Fermi level. The Co *a1g* and *eg* bands are almost degenerate for AgCoO2, whereas the *eg* band sinks below the Fermi level for NaxCoO2. Moreover, the *a1g* band forms pudding mold like structure, which results in large density of states and large group velocity around the Fermi level. These features of the electronic band structure can give rise to the coexistence of large Seebeck coefficient and small resistivity. We therefore conclude that AgCoO2 can be a promising thermoelectric material.

This work was supported financially by JSPS KAKENHI Grant JP19K15436, Japan.

Keywords: First principles band calculations, cobaltates

---

*Speaker

Impact of dislocation-core structures on phonon thermal conduction in MgO by perturbed molecular dynamics

Wataru Sekimoto*†1, Susumu Fujii1,2, and Masato Yoshiya1,2

1Osaka University – 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
2Japan Fine Ceramics Center – 2-4-1, Mutsuno, Atsuta, Nagoya 456-8587, Japan

Abstract

To improve thermoelectric figure of merit, it is necessary for materials to simultaneously achieve high electrical conductivity and low thermal conductivity. To control these conflicting properties, it is important to understand the origin of electrical and thermal conduction and their dominant factors. Among lattice defects which can reduce the thermal conductivity, dislocations, linear lattice defects, has been studied many years from the viewpoint of mechanical properties as dislocations are responsible for plastic deformations. However, most of these findings are confined to controlling of the mechanical properties. For various properties other than the mechanical properties, dislocations have been understood as a detrimental factor. Recently, increasing attention has been paid to dislocations as a means of manipulating those other functional properties including thermal conduction because dislocations are ubiquitous in materials.
The influence of dislocations on the thermal conductivity has been studied both experimentally and theoretically. In experiments, the reduction in the thermal conductivity due to the complex dislocation textures were evaluated[1]. It is difficult to quantitatively understand the underlying mechanisms behind the observed phenomena because there are interactions among dislocations and with other lattice defects in real materials. On the other hand, through analytical theories based on theory of nonlinear elasticity and discrete lattice model[2], it is possible to grasp its influence onto thermal conduction. However, this analytical model has shortcomings upon applying it to real materials in exchange for generality. Consequently, our understanding about the impact of dislocation core structures on thermal conduction is still limited. Thus, we aim at clarifying how local atomic coordination in the vicinity of dislocation core modifies thermal conduction.

In this study, perturbed molecular dynamics calculations[3, 4] have been carried out in order to calculate the overall thermal conductivity and also to elucidate the mechanisms how dislocations affect thermal conduction at the atomic level. MgO with rocksalt structure was chosen as a model material as O atoms have an FCC sublattice. Because this sublattice is common in many materials, especially oxides, the findings of this study would be applied to a variety of technologically important materials. A pair of edge dislocations with the opposite Burger's vector was introduced in a supercell to satisfy the three-dimensional periodic boundary conditions upon modelling of edge dislocations used for calculations.

---

*Speaker

†Corresponding author: Wataru.Sekimoto@mat.eng.osaka-u.ac.jp

It is found that the overall thermal conductivity decreases with introducing the dislocations and its magnitude of decrease in thermal conductivity differs between different slip systems or dislocation core structures. Analysis of the atomic-level thermal conductivity shows that the phonon properties in the vicinity of the dislocation cores vary significantly depending on bond strains. Especially, the influence of the bond strain field becomes non-linear at the nearest neighbor atoms to the dislocation core. It accompanies the substantial spatial variations in the atomic-level thermal conductivity. With more detailed analysis, it is found that the bond-strain field due to the dislocation triggers anisotropic atomic vibrations, thereby scattering phonons and reducing thermal conductivity [5].

These findings suggest that careful introduction of dislocations and control of spatial distribution of the dislocations by applying external stress would facilitate tailoring thermal conduction.

Acknowledgements:

This work was supported by Grants-in-Aid for Scientific Research (Grant Number: JP19H05786, JP20H05195, JP20K05062 and JP20K15034).

References:

H. Zhao, et al., *Adv. Energy Mater.*, **7**, 1700446 (2017).

P. G. Klemens, *P. Phys. Soc. A*, **68**, 1113-1128 (1955).

M. Yoshiya, et al., *Mol. Simulat.*, **30**, 953-961 (2004).

S. Fujii, M. Yoshiya, *J. Electron. Mater.*, **45**, 1217–1226 (2016).

W. Sekimoto, S. Fujii, M. Yoshiya, *Scr. Mater.*, **202**, 113991 (2021).

Keywords: Dislocation, Thermal conductivity, Molecular dynamics

POSTERS

Thermal conductivity of Bi2Se3 from bulk to thin films: Theory and experiment

Lorenzo Paulatto[*,1]

[1]Institut de minéralogie, de physique des matériaux et de cosmochimie (IMPMC) – Museum National d'Histoire Naturelle, Université Pierre et Marie Curie - Paris 6 : UM120, Institut de recherche pour le développement [IRD] : UR206, Centre National de la Recherche Scientifique : UMR7590 – Tour 23 - Barre 22-23 - 4e étage - BC 115 4 place Jussieu 75252 PARIS, France

Abstract

We calculate the lattice-driven in-plane () and out-of-plane ($\perp$) thermal conductivities of Bi2Se3 bulk, and of films of different thicknesses, using the Boltzmann equation with phonon scattering times obtained from anharmonic third order density functional perturbation theory.
We compare our results for the lattice component of the thermal conductivity with published data for on bulk samples and with our room-temperature thermoreflectance measurements of $\perp$ on films of thickness (L) ranging from 18 nm to 191 nm, where the lattice component has been extracted via the Wiedemann-Franz law.

Ab initio theoretical calculations on bulk samples, including an effective model to account for finite sample thickness and defect scattering, compare favorably both for the bulk case (from literature) and thin films (new measurements). In the low-T limit the theoretical in-plane lattice thermal conductivity of bulk Bi2Se3 agrees with previous measurements by assuming the occurrence of intercalated Bi2 layer defects.

We show that the decrease of room-temperature $\perp$ in Bi2Se3 thin films as a function of sample thickness can be explained by the incoherent scattering of out-of-plane momentum phonons with the film surface. Our work outlines the crucial role of sample thinning in reducing the out-of-plane thermal conductivity.
Phys. Rev. B 101, 205419 (2020)

Keywords: thermal conductivity abinitio bi2se3 anharmonicity

---

[*] Speaker

Fabrication and Thermoelectric Properties of Boron Carbide Based Hard Materials Sintered by SPS

Ryuichiro Koyama*[1] and Satofumi Maruyama*†[1]

[1]Tokyo City University – 1-12-14 Tamadutumi Setagaya Tokyo, Japan

Abstract

Boron carbide materials possess excellent mechanical properties such as high hardness, light weight, and wear resistance. Therefore, it can apply various applications like cutting and grinding tools, ceramics bearing, etc. In addition, boron carbide, so-called B4C, has a relatively wide range of solid solutions, B4.3C to B10.6C, and exhibits attractive thermoelectric properties depending on the composition. However, boron carbide has a problem in sintering, especially in the boron rich region in boron carbide because of the low self-diffusion coefficient in boron and boron carbide caused by the strong covalent bonding of boron. Due to this reason, it must be sintered at temperatures exceeding 2273K or under high pressure sintering. A few decades ago, Takagi et al. proposed for new sintering method called "reaction boronizing sintering" for complex boride based hard materials. In the mechanism of reaction boronizing sintering, boronizing reaction is occurred by solid state diffusion between metal and boron first, and the metal boride is generated. After the boronizing reaction, the eutectic liquid phase is appeared by the pseudo binary eutectic reaction between boride and metal. In this method, a eutectic liquid phase has important roles in chemical reactions and the densification of the boride material. In this study, we applied the "reaction boronizing sintering" method to the sintering for boron carbide materials. Ni, which undergoes eutectic reaction with boron, was composited with boron carbide, and the sintering behavior and thermoelectric properties were investigated.

The boron carbide materials with Ni were prepared by powder metallurgy method using spark plasma sintering (SPS) from Ni powders, amorphous B powder and C powder. The obtained samples were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), mechanical properties by Vickers hardness test, electrical conductivity σ and Seebeck coefficient S.

The results of X-ray diffraction experiments showed that boron carbide was the main phase and Ni-based borides such as the NiB phase appeared as the second phase.

The sample density of the sintered boron carbide was increasing with the increase in the Ni contents. SEM observation results also showed that the pores were disappearing and became denser with the increase of Ni contents. As Ni promoted sample densification, the results of Vickers hardness also showed enhancement with the Ni contents. This suggests that compositing with Ni is effective for the sintering of boron carbide compacts.

The Seebeck coefficients increased with the increase of Ni contents, reaching a maximum value around 300 μV/K at $x = 0.05$ in B6.5C-xNiB, which was attributed to the accelerated

---

*Speaker

†Corresponding author: smaruyam@tcu.ac.jp

reaction of the starting materials B and C, with the addition of Ni and the increase of the boron carbide phase. The Seebeck coefficient decreased above $x = 0.10$ due to the increase of metallic NiB phase.

Keywords: Boron carbide SPSLiquid, phase sintering

Thermal stability and phase decomposition of the thermoelectric Cu5Sn2S7 by in situ synchrotron X-ray powder diffraction

Thomas Stéphant*[1], Marie Augereau[2], Carmelo Prestipino[3], Gabin Guélou[4], Erik Elkaim[5], Bernard Raveau[6], Emmanuel Guilmeau[7], and Pierric Lemoine†[8]

[1]Institut des Sciences Chimiques de Rennes – Universite de Rennes 1, CNRS : UMR6226 – Campus de Beaulieu - Bât. 10 Avenue du Général Leclerc 35042 Rennes Cedex, France

[2]Laboratoire de cristallographie et sciences des matériaux – Centre National de la Recherche Scientifique : UMR6508, Ecole Nationale Supérieure d'Ingénieurs de Caen, Normandie Université – 6 Bvd du maréchal Juin 14050 CAEN CEDEX 4, France

[3]CNRS, Université de Rennes 1, SCR – CNRS, Université de Rennes 1 – Campus de Beaulieu - Bâtiment 10B, 263 avenue du Général Leclerc, 35042 Rennes Cedex, France, France

[4]Laboratoire de cristallographie et sciences des matériaux (CRISMAT) – Centre National de la Recherche Scientifique : UMR6508, Ecole Nationale Supérieure d'Ingénieurs de Caen, Normandie Université, Université de Caen Normandie – 6 Bvd du maréchal Juin 14050 CAEN CEDEX 4, France

[5]Synchrotron SOLEIL (SOLEIL) – CRISTAL beamline, Synchrotron SOLEIL – France

[6]CRISMAT – CNRS, Normandie Université, ENSICAEN, UNICAEN – 14000 Caen, France

[7]Laboratoire CRISMAT – CNRS : UMR6508, Université de Caen Basse-Normandie, Ecole Nationale Supérieure d'Ingénieurs de Caen – France

[8]Institut des Sciences Chimiques de Rennes (ISCR) – Universite de Rennes 1, CNRS : UMR6226, Ecole Nationale Supérieure de Chimie de Rennes – Campus de Beaulieu - Bât. 10 Avenue du Général Leclerc 35042 Rennes Cedex, France

Abstract

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 Cu2+xSn1-xS3 system has revealed the existence of a new phase for x = 0.15, Cu5Sn2S7, crystallising in a monoclinic structure of space group with unit cell parameters a = 12.0580(5) Å, b = 5.4063(2) Å, c = 8.5026(3) Å, and β = 98.163(3)$\circ$ [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-1 K-1 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 Cu5Sn2S7 studied by synchrotron X-ray powder diffraction on the CRISTAL beamline at the SOLEIL synchrotron, France.

---

*Speaker

†Corresponding author: pierric.lemoine@univ-rennes1.fr

Keywords: Copper Tin Sulphide, In situ X, ray diffraction, crystal structure, thermal stability

Resolution of the cationic distribution in synthetic germanite Cu22Fe8Ge4S32 by an experimental combinatorial approach based on synchrotron resonant powder diffraction data: A case study and guidelines for analogous compounds

Paradis-Fortin Laura*[1,2,3], Pierric Lemoine†[2], Carmelo Prestipino‡[2], Bernard Malaman[4], Erik Elkaim[5], Vivian Nassif[6], Stephane Cordier[2], and Emmanuel Guilmeau[1]

[1]Laboratoire CRISMAT – UMR 6508, CNRS, ENSICAEN – 6 Boulevard du maréchal Juin, 14050 Caen, France

[2]Univ. Rennes 1 – CNRS, ISCR, UMR 6226 – 263 Avenue Général Leclerc, 35700 Rennes, France

[3]Institute of atomic and molecular sciences, National Taiwan University – No. 1, Section 4, Roosevelt Rd, Da'an District, Taipei City, 106, Taiwan

[4]Institut Jean Lamour – Centre National de la Recherche Scientifique : UMR7198, Université de Lorraine – Institut Jean Lamour, 2 allée André Guinier, 54000 Nancy, France

[5]Synchrotron SOLEIL – CRISTAL beamline, Synchrotron SOLEIL – L'Orme des Merisiers, 91190 Saint-Aubin,, France

[6]Institut NEEL, CNRS, University of Grenoble Alpes – CNRS : UPR2940 – 25 Avenue des Martyrs, 38042, Grenoble, France

Abstract

Here we present a method for the cationic distribution determination of sulfur materials, which represents a promising class of material with important perspective for thermoelectric generator. The method is based on the use of neutron and X-ray resonant diffraction with a combinatorial approach, *i.e.* all possible cationic configurations respecting periodicity are tested automatically with respect to a group of patterns with alternative set of scattering function/length. In order to illustrate this approach, the case of synthetic Germanite (Cu22Fe8Ge4S32), a Cu-rich sulfide mineral, structurally related to high performances thermoelectric colusites, is presented. Its cationic distribution is still the object of debate due on one hand, to the similarity of Cu, Fe and Ge elements for X-rays, and to the other hand, to the number, symmetry equivalence and mix occupation of the cationic sites. Using of such method and its complementarity with single crystal X-rays diffraction and 57Fe Mössbauer spectroscopy it was possible to propose only 2 structural models, among the almost 18 000 possible, compatibles with all experimental results. This result is of prime interest to explain the different thermoelectric properties encountered in germanite and colusite systems, and to correlate them to their corresponding crystal structure. This approach can be in principle extent to other class of compounds if certain symmetry prerequisite are satisfied.

---

*Speaker

†Corresponding author: pierric.lemoine@univ-rennes1.fr

‡Corresponding author: carmelo.prestipino@univ-rennes1.fr

sciencesconf.org:vwt2021:365863

Keywords: structure resolution, complexe structure, synchrotron, Rietveld, sulfur, thermoelectrics

---

Time-resolved in situ neutron diffraction study of Cu22Fe8Ge4S32 germanite: a guide for the synthesis of complex chalcogenides

Pierric Lemoine*†[1], Laura Paradis-Fortin[2,3], Carmelo Prestipino[4], Ventrapati Pavan Kumar[5], Bernard Raveau[6], Vivian Nassif[7], Stephane Cordier[8], and Emmanuel Guilmeau[9]

[1]Université de Rennes 1 – CNRS, ISCR-UMR 6226 – F-35000 Rennes, France
[2]Institut des Sciences Chimiques de Rennes (ISCR) – Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) UMR 6226, F-35000 Rennes, France – France
[3]Laboratoire de cristallographie et sciences des matériaux (CRISMAT) – Normandie Univ, ENSICAEN, UNICAEN, CNRS, CRISMAT, 14000 Caen – France
[4]Institut des Sciences Chimiques de Rennes – Universite de Rennes 1, Centre National de la Recherche Scientifique : UMR6226, Centre National de la Recherche Scientifique : UMR6226 – Campus de Beaulieu - Bât. 10 Avenue du Général Leclerc 35042 Rennes Cedex, France
[5]Laboratoire de cristallographie et sciences des matériaux (CRISMAT) – Normandie Univ, ENSICAEN, UNICAEN, CNRS, CRISMAT, 14000 Caen – France
[6]CRISMAT – CNRS, Normandie Université, ENSICAEN, UNICAEN – 14000 Caen, France
[7]Institut NEEL, CNRS, University of Grenoble Alpes (Institut NEEL) – CNRS : UPR2940 – 38042 Grenoble, France
[8]Groupe Chimie du Solide et Matériaux, Institut des Sciences Chimiques de Rennes – Universite de Rennes 1 – UMR-CNRS 6226, 35042 Rennes Cedex, France
[9]Laboratoire CRISMAT – CNRS : UMR6508, Université de Caen Basse-Normandie, Ecole Nationale Supérieure d'Ingénieurs de Caen – France

Abstract

Solid-state synthesis in a sealed silica tube is one of the most popular methods for the production of inorganic materials. Nevertheless, the determination of the best synthesis conditions is a trial-and-error process that generally requires many experiments, varying temperature and duration time. In this poster presentation will be described the results of the in situ synthesis of a polycrystalline sulfide in a sealed silica tube, monitored by time-resolved neutron powder diffraction [1]. This technic has allowed to analyse in detail all successive crystallization/decomposition sequences and intermediate products and has revealed that sealed tube synthesis is highly dynamic, with reaction times shorter than expected. These results, combined with ex situ X-ray powder diffraction and thermal analyses on crystallized samples, have revealed the primordial role of the cooling conditions on the secondary phase formation and stability of the thermoelectric synthetic germanite Cu22Fe8Ge4S32. Beyond

---

*Speaker

†Corresponding author: pierric.lemoine@univ-rennes1.fr

new data on the complex crystal chemistry of germanite, our study demonstrates the compelling benefits of time-resolved in situ neutron powder diffraction in the optimization of the synthesis process for a wide range of complex chalcogenide materials. [1] L. Paradis-Fortin, P. Lemoine, C. Prestipino, V. Pavan Kumar, B. Raveau, V. Nassif, S. Cordier, E. Guilmeau, Chem. Mater. 2020, 32, 8993.

Keywords: thermoelectric sulfide, germanite, neutron powder diffraction, in situ analysis, crystal structure, chemical reaction

---

Thermoelectric properties of RbZn4As3

Keigo Ono*[1,2], Kunihiro Kihou[1], Ryosuke Sakagami[1], Tsutomu Iida[2], and Chul-Ho Lee†[1]

[1]National Institute of Advanced Industrial Science and Technology – Central 2, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan
[2]Tokyo University of Science – Katsushika, 125-8585,, Japan

Abstract

Zintl phase compounds are one of the most famous systems of thermoelectric materials. In particular, Sb-based 122-Zintl compounds have been intensively explored, resulting in finding many new thermoelectric materials that the dimensionless figure-of-merit (ZT) exceeds the value of 1. On the other hand, we have found high performance thermoelectric materials in As-based Zintl compounds [1,2]. Although lighter atomic mass of As than Sb is a disadvantage in terms of the lattice thermal conductivity, those exhibit low thermal conductivity plausibly due to the existence of lone pairs. Recently, we have found that As-based 143-Zintl compounds of NaZn4As3 exhibit extremely low lattice thermal conductivity [3]. Because it consists of double conduction layers, higher carrier mobility than 122 compounds could be expected.

In this study, we synthesized Rb(Zn,Cu)4As3 by solid-state reaction. We found that RbZn4As3 exhibits extremely low thermal conductivity of 1.2 W/mK and 0.63 W/mK at T = 301 K and 574 K, respectively. We found that hole carriers were successfully doped by Cu doping. Details will be discussed in the conference.

K. Kihou, et al., Inorg. Chem. 56, 3709 (2017).

H. Kunioka et al., Dalton Trans. 47, 16205 (2018).

A. Yamashita et al., J. Solid State Chem. 291, 121588 (2020).

Keywords: Thermoelectric materials, Zintl phase compounds

---

*Speaker

†Corresponding author: c.lee@aist.go.jp

Development of High performance pi Type Thermoelectric Device Using Flexible Ag2(S,Se) Material

Saurabh Singh*[1], Keisuke Hirata[2], Masaharu Matsunami[2], and Tsunehiro Takeuchi[2]

[1]Toyota Technological Institute – 2-12-1 Hisakata, Tempaku-ku, Nagoya, 468-8511, Japan
[2]Toyota Technological Institute – Hisakata 2-12-1, Tempaku, Nagoya 468-8511, Japan

Abstract

The development of thermoelectric generators for an alternate source of energy is currently a major focus as devices capable of supplying an input power (mW to mW) to many sensors, electronic gadgets, and wearable devices in the low-temperature range around 300 – 400 K. Improvement of the figure of merit, *ZT*, of the thermoelectric materials used in such device are very important. Besides, if these materials are flexible, the number of applications would be significantly enlarged. Recently, Ag2S is found to be an interesting material, as near room temperature, it possesses good flexible properties with very low thermal conductivity (_˜ 0.5 W/m K) and large Seebeck coefficients (_˜ -900 mV/K). However, due to large electrical resistivity (_˜ 10ˆ6 mohm cm), the value of *ZT* was found to be very low. To improve the *ZT,* the substitutions of Se andTe at the sulfur site are investigated. Although significant enhancement in *ZT* is achieved, but, limited to *n*-type only. Also, the major focus in the literature is on the development of prototype devices, which obviously have small output. To achieve the high-performance, p-type TE device has more advantage, where both *n* and *p*-type materials with high *ZT* are used to generate better output power. Here, we have utilized the Bi-Sb-Te based *p*-type materials together with flexible Ag2S and Ag2S/Se in the development of the p-type device, and achieve the maximum output power density of _˜1.525 mW/cm2.

In the present work, Polycrystalline samples were prepared by using the standard melting method. Structural characterization of as-prepared powder sample was carried out by using Bruker D8 Advance Cu Ka source and found to be in a single phase. Chemical composition and grain structure analyses were performed using Scanning Electron Microscope-Energy Dispersive X-ray spectroscopy (SEM-EDX), HITACHI SU 6600. Heat and electron transport properties were measured on hot-pressed bulk samples. Thermal conductivity measurement was done by using Laser flash analysis (NETZSCH LFA 457); whereas for Seebeck coefficient and electrical resistivity measurement, experimental systems developed in our laboratory were used [4].

Further, by using the synthesized materials showing high *ZT,* we developed the optimization conditions of the stacked devices using an integrated sintering process, where single pair, two leg and three-leg devices were made. The output performance of these devices at different temperature gradient (deltaT= 10 – 50 K) was tested using homemade TE device testing equipment interfaced with LabVIEW program. We succeeded in developing the stacked thermoelectric devices, where the issue of cracks formation at boundary of *p* and *n* layer

---

*Speaker

due to brittle nature of Bi-Sb-Te are effectively manage by use of highly flexible and insulating Ag2S inter-layers. These devices can be fabricated easily using the simple hot-press technique, have very compact in size, and exhibit maximum output power of 1678 μW at deltaT = 50 K. The maximum power density of 1.525 mW/cm2 of a mechanically robust device is very useful for commercial applications. In this workshop, discuss in more detail the fabrication, and high-performance output achieved in silver chalcogenides based TE devices.

Keywords: Thermoelectrics, Chalcogenides, Devices

Possibility of n-type doping in CaAl$_2$Si$_2$-type Zintl phase compound CaZn$_2$X$_2$ (X = As, P)

Kazutaka Nishiguchi*†[1], Masayuki Ochi[1], Chul-Ho Lee[2], and Kazuhiko Kuroki[1]

[1]Department of Physics, Osaka University – 1-1 Machikaneyama-cho, Toyonaka-shi, Osaka, 560-0043, Japan

[2]National Institute of Advanced Industrial Science and Technology (AIST) – Central2, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

Abstract

In an attempt to search for high-performance thermoelectric materials, the possibility of n-type doping of CaAl$_2$Si$_2$-type Zintl phase compound CaZn$_2$X$_2$ (X = As, P) is explored using first-principles calculations based on the density functional theory. We consider n-type (electron carrier) doping of CaZn$_2$X$_2$ with the following two situations: interstitial-site doping of alkaline earth metals AE (= Mg, Ca, Sr, Ba) and group 3 elements G3 (= Sc, Y, La), and G3 substitutional doping for the Ca site. To see this, the defect formation energy of these charged states is evaluated within the generalized gradient approximation using the supercell approach. Our study reveals that the interstitial-site doping of AE = Ca, Mg or G3 = Sc, Y and G3 = La, Y substitutional doping are favorable in terms of energy stability for both X = As and P, and that each of these defect formation energies of both doping cases for X = As is smaller than that for X = P. Therefore, our study suggests that the addition of excess AE = Ca, Mg and G3 = Sc or G3 = La, Y substitutional doping for the Ca site is favorable for realizing n-type CaZn$_2$X$_2$ as high-performance thermoelectric materials.

Keywords: CaAl$_2$Si$_2$ type Zintl phase compound, n type doping, formation energy, first principles calculations

---

*Speaker

†Corresponding author: nishiguchi@presto.phys.sci.osaka-u.ac.jp

Electronic structure modification for increasing the Seebeck coefficient of Cu2Ti4S8

Katsuaki Hashikuni*†[1,2], Koichiro Suekuni[2,3], Hidetomo Usui[4], Raju Chetty[5], Michihiro Ohta[5], Toshiro Takabatake[6], and Michitaka Ohtaki[2,3]

[1]Department of Electrical Engineering, Faculty of Engineering, Sanyo-Onoda City University – Sanyo Onoda, Yamaguchi 756-0884, Japan

[2]Interdisciplinary Graduate School of Engineering Sciences, Kyushu University – Kasuga, Fukuoka 816-8580, Japan

[3]Transdisciplinary Research and Education Center for Green Technologies, Kyushu University – Kasuga, Fukuoka 816-8580, Japan

[4]Department of Physics and Materials Science, Shimane University – Matsue, Shimane 690-8504, Japan

[5]Global Zero Emission Research Center, National Institute of Advanced Industrial Science and Technology (AIST) – Tsukuba, Ibaraki 305-8569, Japan

[6]Department of Quantum Matter, Graduate School of Advanced Science and Engineering, Hiroshima University – Higashi-Hiroshima, Hiroshima 739-8530, Japan

Abstract

Cu2Ti4S8 is an n-type metallic thiospinel that shows a relatively high power factor (PF) of 0.23 mWK^{-2}m^{-1} at 673 K. The electronic properties are governed by a conductive network composed of edge-shared TiS6 octahedra (dominated by the Ti-3d and S-3p orbitals). [1] Partial substitution of Co for Ti increases the PF up to 0.6 mWK^{-2}m^{-1}. [2,3] Electronic structure calculations suggest that the Co-3d orbitals are superimposed on the Ti-3d orbitals near the Fermi energy (EF). [2,3] However, effects of the electronic structure modification on the electronic properties have not been studied so far. In this work, we focus on the contribution of the Co substitution to the high PF by comparing the thermoelectric properties and electronic structures of Cu2CoyTi4–yS8 and Cu2ScyTi4–yS8. [4]

We have prepared the samples of Cu2CoyTi4–yS8 (y = 0–1.5) and Cu2ScyTi4–yS8 (y = 0–2) by the direct reaction of the constituent elements followed by pulsed-electric-current sintering. For both substituted systems, the electrical resistivity ρ and Seebeck coefficient —S— increased with increasing y, being consistent with a decrease in the electron carrier concentration (n). At the equivalent n levels, —S— for the Co-substituted samples was significantly larger than that for the Sc-substituted counterpart, leading to the doubled PF for the former. Analyses of the relationship between —S— and n gave the electron effective mass m* of 6–9m0 and 3–4m0 for the Co- and Sc-substituted samples, respectively. The first-principles calculations for Cu2ScTi3S8 and Cu2CoTi3S8 indicated that the Sc-3d orbitals are located at higher energy above the EF, but the Co-3d orbitals lie near the EF. The density of states (DOS) at EF for Cu2CoTi3S8 was found to be twice as high as that for Cu2ScTi3S8. These experimental and computational results demonstrated that the electronic structure modification due to the Co substitution increases m* (DOS) to enhance

---

*Speaker

†Corresponding author: k-hashikuni@rs.socu.ac.jp

—*S*— in Cu2Ti4S8.

This work was supported financially by JSPS KAKENHI Grant JP19J12916 (to K.H.) and JP17H04951 (to K.S.), grant from the International Joint Research Program for Innovative Energy Technology by METI, and CREST JST Grant JPMJCR16Q6, Japan.

K. Hashikuni *et al.*, Inorg. Chem. **58**, 1425 (2019).

K. Hashikuni *et al.*, Appl. Phys. Lett. **109**, 182110 (2016).

C. Bourgés *et al.*, J. Alloys Compd. **781**, 1169 (2019).

K. Hashikuni *et al.*, J. Alloys Compd. **871**, 159548 (2021).

Keywords: Thermoelectric materials, Sulfide, Spinel, Electronic structure

Freely attachable broadband camera sheet based on series photo-thermoelectric coupling structure

Kou Li*[1,2] and Kawano Yukio[1,2,3]

[1]Laboratory for Future Interdisciplinary Research of Science and Technology, Tokyo Institute of Technology – Japan
[2]Department of Electrical and Electronic Engineering, School of Engineering, Tokyo Institute of Technology – Japan
[3]Department of Electrical, Electronic, and Communication Engineering, Faculty of Science and Engineering, Chuo University – Japan

Abstract

Introduction

Recent thermoelectric (TE) conversion techniques play indispensable roles in industrial sectors. TE conversion also enables imaging measurements based on the photo-thermoelectric (PTE) effect[1]. This phenomenon advantageously functions as uncooled broadband imaging. Despite that, optimization of PTE device design, based on photo-absorbent channels and electrodes which exhibit good TE properties for high-sensitive imaging, is yet to be fully achieved. To this end, this work presents a series composite PTE coupling structure between p-type carbon nanotube (CNT) film channels and Bi thin-film electrodes. Mechanical flexibility of the CNT film channel facilitates free-form three-dimensional (3D) imaging configurations, and the use of Bi electrodes governs sensitive device operation which is well comparable with solid-state photo-detectors.

Result

Fig. 1b presents the operating mechanism of the proposed device, so-called the photo-thermoelectric (PTE) effect. Light irradiation on the device induces the Seebeck effect, and DC voltage signals can be obtained as photo-responses. The photo-responses depend on effective Seebeck coefficients at the photo-detection area; CNT film-series electrode interfaces. Based on the fact that CNT films are originally p-type, the use of metal electrodes, which show negative Seebeck coefficients such as Ni or Bi, enhances the effective Seebeck coefficient and associated photo-detection sensitivity (Fig. 1c). The above device design strategy enables uncooled broadband photo-detection with a minimum noise equivalent power of 5 pWHz–1/2. The obtained sensitivity equals over 110 times sensitivity enhancement than that of the conventional CNT film PTE imager, and is well comparable with those of cutting-edge solid-state devices including bolometers. By incorporating the above findings, Fig. 1d demonstrates non-destructive and 3D monitoring of a complicatedly bend target object with the freely attachable, multi-pixel, and highly-sensitive PTE camera sheet. The target conceals tiny breakages and a metallic impurity on its curvature under an opaque coating. The omni-directional 3D IR sensing allowed clear visualization of these defects based on local changes of transmission PTE signals.

---

*Speaker

In conclusion, the photo-thermoelectric device design based on CNT films-Bi electrodes series composite structure develops the multi-functional and versatile imager, resulting in the demonstration of free-form 3D non-destructive inspection. The concept and technology achieved here potentially contribute to establishing a ubiquitous social safety monitoring platform.

Reference

B.C. St-Antoine, et al. *Nano Res.* **5**, 73–81 (2012).
K. Li, et al. *Adv. Photon. Res.* **2**, 2000095 (2021).

Keywords: carbon nanotube, photo, thermoelectric effect, non, destructive imaging inspections

Growth of n-type thermoelectric material (Cu1-xAgx)ZnSnS

Kouichi Okamoto*†[1], Akira Nagaoka[1], Yusuke Shigeeda[1], Kenji Yoshino[1], and Kensuke Nishioka[1]

[1]University of Miyazaki – 1-1,Gakuenkibanadainishi,Miyazaki-shi,Miyazakiken, Japan

Abstract

Introduction

The multinary kesterite CuZnSnS (CZTS) and related material are candidates as high-performance thermoelectric materials [1]. Cu on the Zn antisite (CuZn) is the dominant acceptor defect in stoichiometric CZTS because it is easy to switch Cu and Zn positions, causing its high population for p-type conduction. This intrinsic Cu/Zn distorted structure in CZTS would effectively increase scattering of the heat-carrying phonons, which decreases thermal conductivity without adding a potential barrier to carrier transport such as grain boundaries or a nanocomposite structure. Thus, CZTS could maintain both high electrical conductivity and low thermal conductivity while remaining environmentally friendly. Considering CZTS based thermoelectric application, n-type conduction of CZTS is required. AgZnSnS (AZTS) indicates the n-type because First-principle calculations predict that Zn on the Ag antisite (ZnAg) defect plays an important role in determining the n-type conduction [2]. In this study, we investigated growth and thermoelectric properties of (Cu1-xAgx)ZnSnS (CAZTS) for n-type thermoelectric material.

Experimental procedure

We fabricated different compositional CAZTS samples from high purity starting materials ($>$ 99.99%). The materials were charged into quartz ampoules under 10 Pa and then sealed off. The ampoules were loaded into furnace and heated at 1050 $\circ$C for 24 hours to ensure homogenization. The ampoule was then allowed to cool to room temperature naturally. Structural and compositional properties were investigated by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX). Conduction type were evaluated by Hall effect measurement and commercial thermoelectric system (ZEM3).

Result and Discussion

We investigated the Seebeck coefficient of CAZTS($0.1 \leq$ x ≤ 0.5)solid solutions as functions of temperature for 373-723 K. The conversion of p-type to n-type can be observed at Ag composition x = 0.4, which Seebeck coefficient at ambient temperature was negative value of 100 μV/K. Negative Hall coefficient can be also observed from CAZTS (x = 0.4), which indicates the carrier concentration of 10^{1}cm^{3}.

---

*Speaker

†Corresponding author: hk17012@student.miyazaki-u.ac.jp

References:

Nagaoka, A., Masuda, M., Yasui, S., Taniyama, T., Nose, Y., The single-crystal multinary compound CuZnSnS as an environmentally friendly high-performance thermoelectric material. Appl. Phys. Express **11**, 051203, (2018)

Liang, X., Wang, P., Huang, B., Zhang, Q., Wang, Z., Liu, Y., Zheng, Z., Qin, X., Zhang, X., Dai, Y., Effects of Ag Incorporation on the Band Structures and Conductivity Types of (Cu1-xAgx)ZnSnS Solid Solutions. ChemPhotoChem. **2**, 811–817, (2018)

Keywords: kesterite compounds

Synthesis and characterisation of lead-doped Bi2Te2Se

Adèle Léon*[1], Shantanu Misra[2], Anne Dauscher[3], Bertrand Lenoir[4], and Christophe Candolfi†[2]

[1]Institut Jean Lamour (IJL) – Université de Lorraine, Centre National de la Recherche Scientifique : UMR7198 – Institut Jean Lamour - CNRS - Université de Lorraine. Campus Artem 2 allée André Guinier BP 50840 54011 Nancy Cedex, France

[2]Institut Jean Lamour (IJL) – Institut Jean Lamour (UMR-CNRS 7198), Université de Lorraine – France

[3]Institut Jean Lamour (IJL) – Université de Lorraine, Centre National de la Recherche Scientifique : UMR7198 – Institut Jean Lamour - CNRS - Université de Lorraine. Campus Artem 2 allée André Guinier BP 50840 54011 Nancy Cedex, France

[4]Institut Jean Lamour (IJL) – CNRS : UMR7198, Université de Lorraine – Ecole Nationale Supérieure des Mines de Nancy, Parc de Saurupt, 54042 Nancy, France, France

Abstract

The state-of-the-art thermoelectric material Bi2Te3 has been widely studied over the last few decades and recently revisited for its non-trivial topological character [1,2]. Attempts to enhance its thermoelectric properties through the introduction of a resonant level showed that tin distorts the valence bands of Bi2Te3, leading to an increased Seebeck coefficient [3]. The ternary derivative kawazulite Bi2Te2Se has raised interest for its topologically-protected surface states and bulk insulating properties [4,5]. However, no detailed study of its thermoelectric properties and on the influence of various dopants has been undertaken so far.

We report on the synthesis of polycrystalline samples of Bi2-xPbxTe2Se ($0 \leq x \leq 0.05$). The samples were synthetized by using a conventional powder metallurgy route in sealed silica tubes followed by spark plasma sintering at 400 ◦C for 20 minutes. The transport properties of the obtained dense samples were measured over a wide range of temperatures (300 – 700 K), both parallel and perpendicular to the pressing direction, in order to assess the influence of Pb. The results evidence that Pb acts as an acceptor impurity, leading to p-type, heavily-doped semiconducting properties. The solubility limit of Pb in Bi2Te2Se was found to be around $x = 0.03$. Combined with low thermal conductivity values, the beneficial influence of Pb on the electrical properties results in a high thermoelectric figure of merit ZT of ˜ 0.94 at 424 K.

References

- Heremans, J. P. et al., 2017. *Nature Reviews Materials*, *2*(10), 17049.

---

*Speaker

†Corresponding author: christophe.candolfi@univ-lorraine.fr

- Wright, D. A., 1958. *Nature*, *181*(4612), 834-834.
- Jaworski, C. M. et al., 2009. *Physical Review B*, *80*(23), 233201.
- Jia, S. et al., 2011. *Physical Review B*, *84*(23), 235206.
- Wiendlocha, B., 2016. *Journal of Electronic Materials*, *45*(7), 3515-3531.

Keywords: Tetradymite, Doped Semi, conductors, Anisotropy

Theoretical Study of Thermoelectric Antimonides for Very High Temperature Applications

Vincent Pelletier*[1], Regis Gautier*[2], Jean-Francois Halet[3], David Berthebaud[3], Franck Gascoin[4], Bruno Fontaine[1], and Takao Mori[5]

[1]Institut des Sciences Chimiques de Rennes – Ecole Nationale Supérieure de Chimie de Rennes, Centre National de la Recherche Scientifique – Campus de Beaulieu - Bât. 10 Avenue du Général Leclerc 35042 Rennes Cedex, France

[2]Institut des Sciences Chimiques de Rennes – Ecole Nationale Supérieure de Chimie de Rennes, Centre National de la Recherche Scientifique – Campus de Beaulieu - Bât. 10 Avenue du Général Leclerc 35042 Rennes Cedex, France

[3]Laboratory for Innovative Key Materials and Structures – GREEN/MANA Room 512, 1-1 Namiki, 305-0044 Tsukuba, Japan, Japan

[4]Laboratoire de cristallographie et sciences des matériaux – Centre National de la Recherche Scientifique : UMR6508, Ecole Nationale Supérieure d'Ingénieurs de Caen, Normandie Université, Université de Caen Normandie – 6 Bvd du maréchal Juin 14050 CAEN CEDEX 4, France

[5]National Institute for Materials Science – Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

Abstract

Thermoelectric materials based on the cubic structure Th3P4 are interesting for high temperature applications. Within this family, *n*-type La3Te4-x are good thermoelectrics with ZT above the one at 1000◦C. However, there is little information about their p-type counterparts (anti-Th3P4 antimonides) with however proof of their good performance (ZT slightly below the unity at high temperature); even if a few reports have shown very promising thermoelectric properties and stability at high temperature, for instance a ZT of 0.75 was reported in La0.5Yb3.5Sb3 at 1000◦C [1]
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.

Using these *in silico* tools, we studied R4Sb3 (R = La, Yb,...) binaries. A special attention has been paid to the electronic structure of La4Sb3 and Yb4Sb3 compounds in order to understand the differences in their transport properties.

References

(a) A. Chamoire, F. Gascoin, C. Estournès, T. Caillat, J.-C. Tédenac *Dalton Trans.* (2010)

---

*Speaker

39, 1118; (b) A. Chamoire, R. Viennois, J-C. Tedenac, MM. Koza, F. Gascoin, Antimony based compounds with the anti-Th3P4 structure as potential high temperature thermoelectric materials, *J. Elec. Mater.*, 40, 2011, 1171-1175. (c) G.J. Snyder, E. Toberer Complex thermoelectric materials, Nature Materials volume 7, pages 105– 114 (2008)

Keywords: modeling DFT antimonides high, temperature

Lattice softening driven mid-temperature range thermoelectrics of Ti/Zr/Mn-inserted SnTe

Ahmad Rifqi Muchtar*[1,2], Bhuvanesh Srinivasan†[1,3], Sylvain Le Tonquesse[3], Saurabh Singh[4], Nugroho Soelami[2], Brian Yuliarto[2], David Berthebaud‡[3], and Takao Mori§[1]

[1]WPI-MANA, NIMS – Tsukuba, Japan
[2]Institut Teknologi Bandung – Bandung, Indonesia
[3]CNRS-Saint Gobain-NIMS, IRL 3629, LINK – Tsukuba, Japan
[4]Toyota Technological Institute – Nagoya, Japan

Abstract

Most of the best known SnTe-based materials exhibit attractive thermoelectric figure of merit (zT) only at the high-temperature regime, but their performance at the low-mid temperature ranges is quite uninspiring, and this discordance necessitates a large temperature gradient ($T \geq 550$ K) to effectuate a reasonable efficiency, . Here, the transition elements, Ti and Zr, that were not used in the past are tried as dopants for SnTe and an enhanced device/average zT and/or are reported with a lower T _˜ 400 K and without the requisite for a stupendous peak/maximum zT. This notable performance emanates from – (i) improved weighted mobility by optimally balancing between effective mass, carrier concentration and mobility, (ii) coupling of charge carriers with magnetic entropy, and the paramount factor being the (iii) weakening of the chemical bonds (lattice softening). The thermal damping caused by lattice softening affected the phonon group velocity and the elastic properties, and the resultant increase in the degree of anharmonicity and the high density of internal strain-fields, along with the phonon scattering effects, played an active role in tuning the overall thermoelectric performance. This work also excavates/opens up the discussion of applying the Heikes' equation to qualitatively compare the trend of charge carriers for a given thermoelectric material system.

Keywords: SnTe thermoelectric, lattice softening, Ti, Zr, Mn doped SnTe, weighted mobility, Heikes equation

---

*Speaker

†Corresponding author: s.bhuvanesh5@gmail.com

‡Corresponding author: David.BERTHEBAUD@cnrs.fr

§Corresponding author: MORI.Takao@nims.go.jp

Superior Characteristics of Graphenized Porous Silicon Nanomaterial for Thermoelectric Applications

Sibel Nar*†1, Mohammad Reza Aziziyan‡2, Arnaud Stolz§3, Nicolas Dumuis¶4, Denis Machon‖2, Abderraouf Boucherif**5, and Nadjib Semmar††4

[1] Laboratoire Nanotechnologies Nanosystèmes (LN2)- CNRS UMI-3463 – Université de Sherbrooke, 3000 Boulevard Université, Sherbrooke, J1K OA5, Québec, Canada

[2] Laboratoire Nanotechnologies Nanosystèmes (LN2)- CNRS UMI-3463 – Université de Sherbrooke, 3000 Boulevard Université, Sherbrooke, J1K OA5, Québec, Canada

[3] Groupe de recherches sur l´nergétique des milieux ionisés – Université d'Orléans : UMR7344, Centre National de la Recherche Scientifique : UMR7344 – 14 Rue dÍssoudun - BP 6744 45067 ORLEANS CEDEX 2, France

[4] Groupe de recherches sur l´nergétique des milieux ionisés – Université d'Orléans : UMR7344, Centre National de la Recherche Scientifique : UMR7344 – 14 Rue dÍssoudun - BP 6744 45067 ORLEANS CEDEX 2, France

[5] Laboratoire Nanotechnologies Nanosystèmes (LN2)- CNRS UMI-3463 – Université de Sherbrooke, 3000 Boulevard Université, Sherbrooke, J1K OA5, Québec, Canada

Abstract

Thermoelectric materials enable transforming thermal energy into electrical energy and vice versa, making them an attractive alternative to make inexpensive and clean form of energy. The figure of merit (ZT) characterizing the thermoelectric (TE) performance of such materials essentially depends on Seebeck coefficient as well as thermal and electrical conductivities. Therefore, optimization of these factors is of great importance to the enhancement of conversion capacity for the thermoelectric materials. In this regard nanostructuration of materials has been one of the most effective strategies for optimizing ZT.

Silicon (Si) is a semiconductor material that has been used for several years in microelectronic industry, owing to its outstanding properties. When porosified, surface of porous Si allows a significant decrease of thermal conductivity, which is highly desired for maximizing the ZT in the thermoelectric applications. However, the nanostructure of porous Si reduces the electrical conductivity. This issue could be alleviated by integrating nano-graphene into porous structure of Si, as illustrated by *Thiyagarajan et al* [1]. Indeed, the possibility of coating porous surface of Si with graphene, using a "thermal carbonization" approach, was demonstrated by *Boucherif et al* [2], which will ensure a viable electrical conduction. The potential of such a novel nanomaterial in thermoelectricity, however, has not been investigated.

---

[*] Speaker

[†] Corresponding author: sibel.nar@usherbrooke.ca

[‡] Corresponding author: mohammad.reza.aziziyan@usherbrooke.ca

[§] Corresponding author: arnaud.stolz@univ-orleans.fr

[¶] Corresponding author: nicolas.dumuis@univ-orleans.fr

[‖] Corresponding author: denis.machon@univ-lyon1.fr

[**] Corresponding author: abderraouf.boucherif@usherbrooke.ca

[††] Corresponding author: nadjib.semmar@univ-orleans.fr

This requires a thorough examination of electrical, thermal, and thermoelectric properties of nano-graphene coated porous silicon.

In this work, we report the improvement of a custom-made thermoelectric device that enabled the simultaneous measurements of the Seebeck coefficient and the electrical conductivity on the graphenized mesoporous materials.

P. Thiyagarajan et al., **2014**, " Thermoelectric properties of nanoporous three-dimensional graphene networks ", *Applied Physics Letters*, vol. 105, no 3, p. 033905.

A. Boucherif et al, **2017**, Graphene-Mesoporous Si Nanocomposite as a Compliant Substrate for heteroepitaxy, *Small,* vol. 13, no 18, p. 1603269.

Keywords: porous silicon, graphenized porous silicon, thermoelectric, porosification, graphene