

Technical University of Denmark



## Thermoelectric Properties of $\text{Ca}_3\text{Co}_4\text{O}_9$ + synthesis by Auto-combustion

Wu, NingYu; Holgate, Tim; Van Nong, Ngo; Pryds, Nini; Linderoth, Søren

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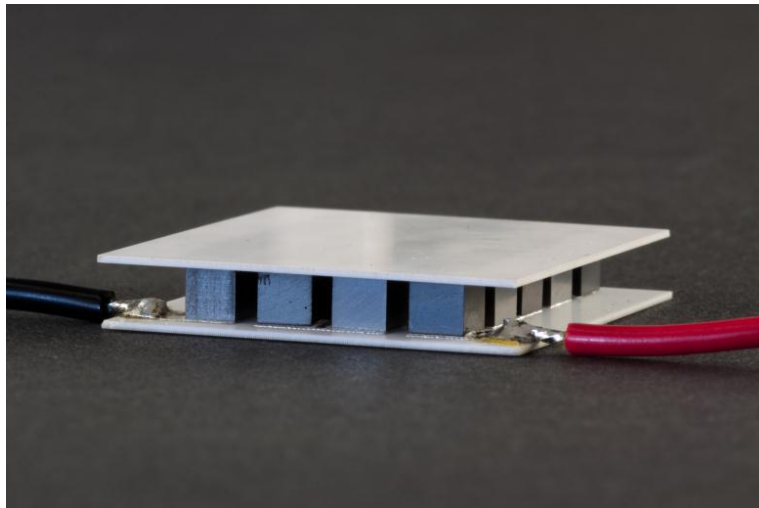
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Materials Science & Technology

## **TEP-CH 2013: SYNTHESIS AND FUNCTION OF THERMOELECTRIC MATERIALS**



### **PROGRAM AND ABSTRACTS**

**Empa, Switzerland  
September 16-19, 2013**

 Swiss Thermoelectric Society



electrosuisse 



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## **WELCOME ADDRESS TO PARTICIPANTS OF THE TEP-CH 2013**

Here we started in 2007 to assemble scientists from universities, scientific institutes as well as industry every second year to promote co-operations on the development of thermoelectric materials and devices. The three previous conferences (in 2007, 2009, and 2011) were very successful. During the last three conferences, we invited about more than 30 international and national distinguished speakers to give high level lectures. So this year, we would like to continue this excellent tradition, and host a wonderful TEP-CH symposium in Switzerland.

We thus thank all our invited speakers for spending their valuable time with us and to provide an introduction to a field of energy harvesting, gaining more and more of importance for real world applications. Particularly we thank our sponsors for supporting our symposium: Swiss Federal Office of Energy (SFOE), V-Zug AG (Zug), Electrosuisse, and Swiss Thermoelectric Society.

In addition we thank our collaborators in helping us for setting up the program and running this symposium!

Anke Weidenkaff (Empa, University of Bern)

Wenjie Xie (Empa)

Angelika Veziridis (Empa)

Sascha Populoh (Empa)

Stéphanie Looser (Empa)

James Eilertsen (Empa)

Gesine Saucke (Empa, University of Bern)

Philipp Thiel (Empa, University of Bern)

## CONFERENCE SCHEDULE

	September 16	September 17	September 18	September 19
08:00-08:20	<b>Registration</b>			<b>Excursions</b>
08:20-08:40				
08:40-09:00				
09:00-09:20		<b>Keynote 2</b>	<b>Keynote 3</b>	
09:20-09:40				
09:40-10:00	<b>Welcome address</b>			
10:00-10:30	<b>Coffee break</b>	<b>Coffee break</b>	<b>Coffee break</b>	
10:30-10:50	<b>Keynote 1</b>	O-6	O-12	
10:50-11:10		O-7	O-13	
11:10-11:30		<b>Invited talk 4</b>	<b>Invited talk 7</b>	
11:30-11:50	O-1			
11:50-12:10	O-2	O-8	O-14	
12:10-12:30		O-9		
12:30-14:00	<b>Lunch break</b>	<b>Lunch break</b>	<b>Lunch break</b>	
14:00-14:20	<b>Invited talk 1</b>	<b>Invited talk 5</b>	<b>Invited talk 8</b>	
14:20-14:40				
14:40-15:00	O-3	O-10	<b>Invited talk 9</b>	
15:00-15:20	<b>Invited talk 2</b>	<b>Invited talk 6</b>	<b>Concluding remarks</b>	
15:20-15:40			<b>Coffee break</b>	
15:40-16:00	O-4	O-11		
16:00-16:30	<b>Coffee break</b>	<b>Coffee break</b>	<b>Visit Empa</b>	
16:30-16:50	<b>Invited talk 3</b>	<b>Poster session</b>		
16:50-17:10				
17:10-17:30	O-5			
18:00-22:00	Free evening	<b>Apéro riche @ ETH Dozentenforum</b>	Free evening	

## DETAILED PROGRAM

**Monday, September 16**

08:00-09:40	Registration Pick up abstract book and badge	
09:40-10:00	Welcome address	Anke Weidenkaff
10:00-10:30	Coffee break	
<b>10:30-11:30</b>	<b>Thermoelectrics and spin caloritronics for solid-state thermal energy conversion</b>	<b>Joseph P. Heremans</b>
11:30-11:50	Spectral functions and resonant impurities – why Tl:PbTe is a good thermoelectric and Ti:PbTe is not	Bartlomiej Wiendlocha
11:50-12:10	Exploring the Properties of Correlated Electrons through the Thermoelectric Effect	Jonathan M. Buhmann
12:10-12:30		
12:30-14:00	Lunch	
14:00-14:40	Theoretical study of Heusler systems with physical properties governed by electronic structure features for thermoelectric applications	Janusz Tobola
14:40-15:00	Phase stability and oxidation studies of $(\text{Ti}_{0.33}\text{Zr}_{0.33}\text{Hf}_{0.33})\text{NiSn}$ half-Heusler compounds	Krzysztof Galazka
15:00-15:40	High performance half-Heusler thermoelectric materials	T.J. Zhu
15:40-16:00	Structure and thermoelectric properties of $\text{EuTi}(\text{O},\text{N})_{3-\delta}$	Leyre Sagarna
16:00-16:30	Coffee break	
16:30-17:10	A comparison between thermoelectric transition metal oxides and sulphides	Antoine Maignan
17:10-17:30	High-Temperature Thermoelectric Converters employing Calcium Manganates	Philipp Thiel

Tuesday, September 17

09:00-10:00	<b>Crystallographic features and thermoelectric properties of inorganic materials</b>	<b>Yuri Grin</b>
10:00-10:30	Coffee break	
10:30-10:50	Thermoelectric Properties of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ synthesis by Auto-combustion	NingYu Wu
10:50-11:10	Development of thermoelectric converters for waste heat recovery based on heavy cation-substituted misfit-layered $\text{Ca}_3\text{Co}_4\text{O}_9$	Gesine Saucke
11:10-11:50	<b>Mg<sub>2</sub>Si-based Ternary and Quaternary Thermoelectric Materials for Power Generation</b>	<b>Theodora Kyratsi</b>
11:50-12:10	Effects of conducting oxide barrier layers on the interface stability of high-chrome iron alloy interconnects and calcium cobaltate	T.C. Holgate
12:10-12:30	Pulsed laser deposition and plasma analysis of $\text{Ca}_3\text{Co}_4\text{O}_9$ thermoelectric compounds	Jikun Chen
12:30-14:00	Lunch	
14:00-14:40	<b>Thermoelectric properties of some transition metal chalcogenides</b>	<b>F. Gascoin</b>
14:40-15:00	Thermodynamics of calcium cobaltate in air	T.C. Holgate
15:00-15:40	<b>Development of High Temperature Thermoelectric Materials via Control of Network Structure</b>	<b>Takao Mori</b>
15:40-16:00	Measurement of the Thermal Conductivity on Nano Scaled Thin Film Thermoelectric Materials	Heinz Renner
16:00-16:30	Coffee break	
16:30-17:30	Poster session	
17:30-18:30	Take tram/train to ETH	
18:30-22:30	Apéro riche @ ETH Dozentenforum	



## Wednesday, September 18

09:00-10:00	X-ray electron densities as a tool in thermoelectric research	Bo B. Iversen
10:00-10:30	Coffee break	
10:30-10:50	Layered oxychalcogenides with promising high ZT values: the frontier between oxides and intermetallics	C. Barreteau
10:50-11:10	Cu-deficient layered BiCuOSe	Ta-Lei Chou
11:10-11:50	Electron Band Tuning and Preferential Scattering by Interfacial Charged Defects in Few-layered n-type Bi <sub>2</sub> Te <sub>3</sub>	Jian He
11:50-12:10	Electrodeposition of Alloyed p-and n-type Bi <sub>2</sub> Te <sub>3</sub> Nanowires	Maksudul Hasan
12:10-12:30		
12:30-14:00	Lunch	
14:00-14:40	Copper selenides – structural phase transition and thermoelectric properties	Qiang Li
14:40-15:20	Development of new silicide thermoelectric devices	Ryoji Funahashi
15:20-15:40	Concluding remarks	Anke Weidenkaff
15:40-16:00	Coffee break	
16:00-17:10	Visit Empa	

## Thursday, September 19 (optional)

For those who are interested and will have a stopover in Switzerland on Thursday, we offer several excursions near Zurich/Luzern. Please, sign up by email to [James.Eilertsen@empa.ch](mailto:James.Eilertsen@empa.ch).

## LIST OF POSTERS

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## KEYNOTE PRESENTATION ABSTRACTS

### Keynote 1

#### Thermoelectrics and spin caloritronics for solid-state thermal energy conversion

Joseph P. Heremans<sup>1</sup>, Michele D. Nielsen<sup>1</sup>, Hyungyu Jin<sup>1</sup>, Steve Boona<sup>1</sup>, Roberto Myers<sup>1</sup>, Vidvuds Ozolins<sup>2</sup>

1. The Ohio State University, Columbus, Ohio, USA
2. University of California, Los Angeles, California, USA

Solid state thermal energy converters are primarily based on thermoelectric materials. The major goal in thermoelectrics research is to simultaneously enhance the thermopower while maintaining a high electrical conductivity, and minimize the thermal conductivity without affecting the electronic properties. We review here three modern physical principles to achieve these goals.

Starting with the thermal conductivity of thermoelectric materials, we know that heat is conducted mostly by phonons. Historically, impeding their transport has been achieved by alloying TE materials, and in the last decade by nanostructuring them or by adding atoms that locally "rattle" and scatter phonons. To these techniques, we add a new one: engineer solids in which the phonons that carry heat have highly anharmonic properties. This promotes phonon-phonon interactions: indeed, when the bond is anharmonic, the atom displacements due to the passage of one phonon change the local bond strength and perturb the field for a second phonon. We will show how specific types of chemical bonds can be selected and designed to maximize these effects, thereby reducing the lattice thermal conductivity of the material to its minimum possible value, the amorphous limit. We will describe one class of thermoelectric solids as examples, the I-V-VI<sub>2</sub> compounds (I=group I element, alkali or noble metals; V=group V element, Sb or Bi; VI=group VI element, S, Se or Te) in a CaF<sub>2</sub> crystal structure. Here, the anharmonicity arises from the lone pair electrons on the group V element: the atomic displacements that accompany the passage of a phonon distort the orbitals of these electrons (polarizes them) in strongly non-linear ways.

Several years ago, we showed how resonant impurities can lead to an enhancement of the local density of electronic states, which following the theory of Mahan and Sofo leads to an enhancement of the power factor. Our work in this field will be briefly reviewed, with emphasis on the delicate balance that has to be found between the enhancement of the DOS and the loss of mobility.

Finally, the talk will give an introduction to a completely new class of solid-state thermal energy converters based on spin transport. One configuration for such energy converters is based on the recently discovered spin-Seebeck effect. This quantity is expressed in the same units as the conventional thermopower, and we have recently shown that it can be of the same order of magnitude. The main advantage of spin-Seebeck converters is that the problem of optimization is now distributed over two different materials, a ferromagnet in which a flux of magnetization is generated by a thermal gradient, and a normal metal where the flux of magnetization is converted into electrical power. The talk will focus on the basic physics behind the spin-Seebeck effect.

## Keynote 2

### Crystallographic features and thermoelectric properties of inorganic materials

Yuri Grin

Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany

Several groups of compounds from the large family of inorganic materials are recently actively studied in respect to their thermoelectric properties. On the way to found the routes for designing of new thermoelectrics, crystallographic features which reflect structural complexity are considered as one of the factors effecting thermoelectric ability of substances.

In general, structural complexity of materials and thermoelectrics in particular may be discussed taking into account either their basic crystallographic characteristics as point symmetry, number of atoms per unit cell, or considering chemical and positional order/disorder, or even including into considerations thermodynamic phase diagrams and formation conditions of the compounds [1]. Employing crystallographic descriptors, a special family – the so-called complex metallic phases (CMA) – was defined among the intermetallic compounds [2,3].

For the compounds with the characteristic structural features, e.g. clathrates with their cage structures or oxides with crystallographic share planes, structural complexity opens an opportunity to influence more directly the thermal conductivity separating - at least partially – its lattice and electronic parts. So, the lattice thermal conductivity of  $\text{Ba}_8\text{Ni}_{3.5}\text{Ge}_{42.1}\square_{0.4}$  is reduced with respect to the defect-less Ba–Ni–Ge type-I clathrates and to  $\text{Ba}_8\text{Ge}_{43}\square_3$  with ordered vacancies suggesting that the disordered vacancies hinder efficiently the heat transport [4]. An exceptionally low thermal conductivity was observed for the transition-metal oxides [5,6], with values of  $3.0\text{-}4.2 \text{ W K}^{-1} \text{ m}^{-1}$  being lower than the state-of-the-art material for n-type oxides like  $\text{Zn}_{1-x}\text{Al}_x\text{O}$  ( $>5.4 \text{ W K}^{-1} \text{ m}^{-1}$ ).

#### References:

- [1] K. Kreiner, Y. Grin. *Chemie&More* **1** (2011).
- [2] K. Urban, M. Feuerbacher. *J. Non-Cryst. Solids*, **334&335**, 143(2004).
- [3] J. Dshemuchadse, W. Steurer. *MRS Proc.*, **1517**, kk01(2012).
- [4] L. T. K. Nguyen et al. *Dalton Trans.*, **39**, 1071 (2010).
- [5] G. Kieslich et al. Unpublished (2013).
- [6] I. Veremchuk et al. *Inorg. Chem.*, **52**, 4458 (2013).

## Keynote 3

### X-ray electron densities as a tool in thermoelectric research

**Bo Brummerstedt Iversen**

Center for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University,  
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E-mail: bo@chem.au.dk

Knowledge about the atomic structure of a material is a prerequisite for understanding its properties. The crystal structure is the starting point for rationalization and speculation about material behavior, and the standard method to obtain atomic structure information is to analyze X-ray diffraction data using the so-called independent atom model in which the unit cell of the crystal is approximated to consist of a superposition of free spherical atoms. However, X-ray diffraction data contain information about the true electron density distribution in the crystal, which is probably the most information-rich observable available in natural science. For the past three decades electron densities have been determined in numerous crystals based on modeling of accurate structure factors measured by X-ray diffraction [1]. The X-ray electron density method is today well established and it has provided important insight into the nature of chemical bonding and physical properties of systems spanning from small organic molecules to proteins. Inorganic materials such as state of the art thermoelectric materials represent a strong challenge for X-ray electron density determination. In these systems the scattering from the valence electrons is very weak compared with the core electron scattering and inorganic crystals often suffer from strong absorption and extinction effects. However, using third generation synchrotron sources it is now possible to measure accurate X-ray electron densities even for heavy atom high symmetry inorganic materials, and in this talk recent results obtained on various high performance thermoelectric materials will be reported [2, 3]

#### References:

- [1] P. Coppens, *X-ray charge densities and chemical bonding*, International Union of Crystallography; Oxford; New York, **1997**.
- [2] M. Schmøkel, L. Bjerg, J. Overgaard, F. K. Larsen, G. Madsen, K. Sugimoto, M. Takata, B. B. Iversen, *Angew. Chem. Intl. Ed.*, **52**, 1503 (2013).
- [3] S. Kastbjerg, M. Søndergaard, S. Johnsen, N. Lock, M. Christensen, M. Takata, M. A. Spackman, B. B. Iversen, *Adv. Func. Mater.*, **2013**, DOI: 10.1002/adfm.201300722.

### Invite talk 1

#### Theoretical study of Heusler systems with physical properties governed by electronic structure features for thermoelectric applications

Janusz Tobola, Kamil Kutorasinski and Stanislaw Kaprzyk

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

Heusler  $X_2YZ$  and so-called half-Heusler  $XYZ$  phases discovered 110 years ago, still belong to very attracting materials, since they exhibit remarkable variety of physical behaviours (magnetocaloricity, thermoelectricity, heavy fermion behaviours, superconductivity, half-metallic magnetism, shape-memory effect, topological insulators, ...), which appear to be strongly governed by the number of valence electrons. We remind the concept of 'electronic phase diagram' of half-Heusler systems, which was supported by detailed first principles calculations [1]. This simplified model allows to understand critical phenomena such as e.g. semiconductor-metal crossovers accompanied by magnetism onset and/or a change in sign of thermopower [2], appearing in these phases and it may appear to be useful in searching for new thermoelectric materials. A special attention is also paid to influence of chemical disorder (alloying) or defects (vacancy, antisite) on electronic spectra, which strongly modify physical properties of Heusler alloys. Hereafter, recent results of the KKR-CPA multiply scattering methodology combined with the Boltzmann transport theory are discussed [3]. We show that accurate investigation of complex energy Fermi surface properties of half-Heusler systems [4] result in optimization of thermoelectric properties vs. carrier concentration and temperature.

This work was supported by the Polish National Science Center (NCN) under the grant DEC-2011/02/A/ST3/00124.

#### References:

- [1] J. Tobola, J. Pierre, J. Alloys Compd., **296**, 243 (2000).
- [2] J. Tobola, L. Jodin, P. Pecheur, H. Scherrer, G. Venturini, B. Malaman, S. Kaprzyk, Phys. Rev. B, **64**, 155103 (2001).
- [3] K. Kutorasinski, J. Tobola, and S. Kaprzyk, Phys. Rev. B, **87**, 195205 (2013).
- [4] K. Kutorasinski, J. Tobola, and S. Kaprzyk, Phys. Stat. Sol. A, (2013), accepted.

## Invited talk 2

### High performance half-Heusler thermoelectric materials

**T.J. Zhu**, H.H. Xie, C.G. Fu, X.B. Zhao

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MNiSn (M = Ti, Zr, Hf) based half-Heusler alloys have recently been identified as novel high temperature thermoelectric materials for energy harvesting. We apply a combination of levitation melting and spark plasma sintering to prepare a series of  $\text{Hf}_{1-x}\text{Zr}_x\text{NiSn}_{1-y}\text{Sb}_y$  alloys in a time-efficient manner. The maximum ZT value of  $>0.8$  was achieved. To further reduce the lattice thermal conductivity, melt spinning was applied to refine grains. Nanoscale *in situ* precipitates were found embedded in the matrix of submicron grains. The lattice thermal conductivity was decreased due to the enhanced boundary scattering of phonons. The increased carrier concentration and electrical conductivity were observed compared to the coarse-grained counterparts, which is discussed in relation to the existence of nanoscale precipitates, the effect of antisite defects and composition change. Thermoelectric transport features were also investigated. We found that, different from most of high performance thermoelectric materials with dominant acoustic phonon scattering, the promising ZrNiSn based half-Heusler solid solutions exhibit an alloy scattering dominated charge transport. A low deformation potential and a low alloy scattering potential are found for the solid solutions, which is beneficial to maintain a relatively high electron mobility despite of the large effective mass, and can be intrinsic favorable features contributing to the noticeably high power factors for ZrNiSn based alloys. A quantitative description of the different phonon scattering mechanisms suggests that the point defect scattering is an important mechanism that determines the phonon transport process of the solid solutions.

### Invited talk 3

## A comparison between thermoelectric transition metal oxides and sulfides

**Antoine Maignan**\*, Emmanuel Guilmeau, David Berthebaud,  
Oleg Lebedev and Sylvie Hébert

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One unexpected feature of the TE power of transition metal oxides lies in the quasi T-independent  $S(T)$  curve over a large T range. This was first reported in the case of cobaltites, in which the mixed-valency of the  $\text{Co}^{3+}/\text{Co}^{4+}$  low spin cations occupying  $\text{CoO}_6$  octahedras in  $\text{CdI}_2$ -type layers has been involved [1], and a similar behaviour was also found in isostructural rhodates. Consistently with the theory of the strongly correlated electron system [2], well above the temperature of the quasi particles formation, the  $S \sim \text{constant}$  behaviour of these transition metal oxides can be approximated by the generalized Heikes formula by taking into account the spin entropy term [3]. More recently, the case of several sulfides, crystallizing also in structures derived from the  $\text{CdI}_2$ -type, has been the focus of our attention. In particular,  $\text{TiS}_2$ -based materials, in the form of ceramics, prepared by SPS, or single-crystals, obtained by vapour phase transport by using iodine, have been studied. A comparison between these layered oxides and sulfides will be made to enlighten their respective potentialities for thermoelectricity. The case of  $\text{CoS}_2$ , an itinerant ferromagnet, will also be considered [4] to evaluate the impact of spins on the transport properties in 3D sulfides as compared to 3D (simple or quadruple) perovskite ruthenates.

### References:

- [1] For a review: S. Hébert et al, Phys. Status Solidi A, **210**, 69 (2013).
- [2] X. Deng et al, Phys. Rev. Lett. **110**, 086401 (2013).
- [3] *see for instance*: Y.Klein et al, Phys. Rev. B **73**, 052412 (2006).
- [4] S. Hébert et al, J. Appl. Phys (*submitted*).



## Invited talk 4

### **Mg<sub>2</sub>Si-based Ternary and Quaternary Thermoelectric Materials for Power Generation**

**Theodora Kyratsi**

Department of Mechanical and Manufacturing Engineering,  
University of Cyprus, 1678 Nicosia

Mg<sub>2</sub>Si-based materials are very promising candidates due to their high ZT, ample availability of their constituent elements in nature, non-toxicity and low density. Ternary Mg<sub>2</sub>(Si,Sn) series seems to be the most favorable in terms of thermoelectric energy conversion, while the recently developed quaternary Mg<sub>2</sub>(Si,Sn,Ge) exhibited also remarkable properties. Enhancement of the thermoelectric performance of the ternary and quaternary compounds is accomplished by the adjustment of the Si/Sn/Ge ratio, via thermal conductivity reduction, as well as the Bi and Sb doping content, via power factor increase.

This presentation reviews our work on Si-rich series that was fabricated by solid-state reaction. The products exhibit compositional inhomogeneities, which extend from nanoscale to macroscale, with Sn-rich and Si-rich phases, as observed with HRTEM (nanoscale), SEM studies and EDX (microscale) and IR Reflectivity mappings (macroscale). The Bi- and Sb doped materials were studied in terms of carrier concentration, Seebeck coefficient, electrical and thermal conductivity. The figure-of-merit was determined at the temperature range of 300-800K and was found to be as high as 1.4.

## Invited talk 5

### Thermoelectric properties of some transition metal chalcogenides

N. Raghavendra, E. Guilmeau, **F. Gascoin**\*

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The search of new, potentially good, thermoelectric materials passes by the exploration of different chemical system. Serendipity and knowledge of crystal chemistry can together lead to the discovery of good candidates or at least to the detection of appealing thermal or electronic transport properties that can sometimes be attributed to the sole crystal structures.

In this presentation, structural features and flexibility of  $\text{CdI}_2$  and pseudo hollandite transition metal chalcogenides will be detailed. Furthermore, based on our recent results, the potentiality of such structures for interesting transport properties will be exemplified. The structure - thermoelectric properties relationship will be also discussed, especially concerning the intrinsic low thermal conductivity associated with complex, disordered crystal structure.

## Invited talk 6

### Development of High Temperature Thermoelectric Materials via Control of Network Structure

Takao Mori<sup>1,2</sup>

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2. University of Tsukuba, Tsukuba, Japan (& Visiting Professor, Hiroshima University, Japan)  
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The direct conversion of waste heat to electricity is a large incentive to find viable thermoelectric (TE) materials and efforts worldwide are intensifying [1]. One need exists for materials which can function at high temperature. We have been developing materials with covalent network structures and good thermal stability, like borides, silicides, etc. Furthermore, particular network structures engender intrinsic low thermal conductivity, an inherent advantage for TE application [2]. I will report several recent notable developments. Boron sulphide,  $B_6S_{1-x}$ , was synthesized and reveals sulphur dumbbell pairs occupying the  $\alpha$ -rhombohedral type boron cluster configuration. Large Seebeck coefficients  $\alpha$  are exhibited at high temperatures with indications this can be a much lower processing temperature replacement to boron carbide, one of the few TE materials previously commercialized. Further doping into the voids and framework of cluster compounds revealed striking effects. For example, through transition metal doping into the voids,  $\alpha$  of  $YB_{22}C_2N$ , the potential n-type counterpart to boron carbide, could be increased by 220% while electrical resistivity was simultaneously reduced by more than 100 times. Carbon substitution into the framework was also shown to be effective. Recently, excellent ( $|\alpha| > 200 \mu V/K$ ) p-type or n-type characteristics could be controlled in  $Y_{-0.6}Al_yB_{14}$  by varying occupancy of the Al site [3]. This is p, n control with same crystal structure (i.e. good matching) and no necessity for doping of foreign elements (i.e. no migration problems). The discovery is surprising, since in metal borides, the metal site occupancies are typically with small homogeneity region. Theoretical investigations reveal the stable configuration of the atomic sites and density of states variation behind the thermoelectric properties.

#### References:

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## Invited talk 7

### Electron Band Tuning and Preferential Scattering by Interfacial Charged Defects in Few-layered $n$ -type $\text{Bi}_2\text{Te}_3$

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The past two decades have witnessed the ball milling-hot pressing, melt spinning-spark plasma sintering, hydrothermal growth-cold pressing, and hot forging processes significantly improving the thermoelectric performance of  $p$ -type  $\text{Bi}_2\text{Te}_3$ . However, these nanostructuring procedures turned out to be *less effective* for  $n$ -type  $\text{Bi}_2\text{Te}_3$  due to the deterioration of the basal plane. We herein present a chemical-exfoliation spark-plasma-sintering (CE-SPS) procedure. This novel CE-SPS procedure leads to a significant decrease in the electrical resistivity despite the presence of numerous grain boundaries, suppresses the detrimental bipolar effect, thus leading to an upshift of the  $ZT$  peak in temperature by  $\sim 100$  K, and also keeps the  $ZT$  to a value above 0.8 over a broad temperature range of  $\sim 150$  K. The results are interpreted in terms of the grain boundary charge buildup, and the resulting charge compensation and preferential grain boundary scattering. The CE-SPS processed  $n$ -type  $\text{Bi}_2\text{Te}_3$  also exhibits a much friendlier compatibility factor for device design and fabrication.

## Invited talk 8

### Copper selenides – structural phase transition and thermoelectric properties\*

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Copper-selenium ( $\text{Cu}_2\text{Se}$ ) compound has been found to have very good thermoelectric properties.[1] In this presentation, a close examination will be given on the relationship between structural and thermoelectric properties of this compound and its derivatives over a wide range of temperature, explored by various probes including neutron scattering and synchrotron-based diffraction. At low temperature (below  $\sim 400\text{K}$ ), stoichiometric  $\text{Cu}_2\text{Se}$  ( $\alpha$ -phase) is an intrinsic semiconductor, and Cu atoms are localized. The non-stoichiometric low-T  $\alpha$ -phase, when cooled down to room temperature, is transformed to a monoclinic structure, and Cu vacancies tend to distribute orderly on one of the  $\{111\}$  planes with a distorted Se fcc sublattice. At high temperature, non-stoichiometric high-T  $\beta$ -phase is a superionic conductor, and Cu ions are kinetically disordered throughout the structure, resulted in very low thermal conductivity and high ZT value at high temperature. Accompany to the phase transition around 400K is a sharp rising of ZT value.[2] Mechanism and implication of these thermoelectric behaviors will be discussed.

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\* In collaboration with Emil Bozin, Milinda Abeykoon, and Xiaoya Shi at Brookhaven National Laboratory, Xun Shi, Wenqing Zhang, and Lidong Chen at Shanghai Institute of Ceramics.

## Invited talk 9

### Development of new silicide thermoelectric devices

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The demand for primary energy in the world was 12,013 million tons of oil per year in 2007. The average total thermal efficiency of the systems utilizing this fuel is as low as 30%, with about 70% of the heat exhausted to the air as waste heat. It is clear that improving the efficiencies of these systems could have a significant impact on energy consumption. Electricity is a convenient form of energy that is easily transported and stored; thus there are a number of advantages to convert the waste heat emitted from our living and industrial activities to electricity. Thermoelectric conversion is attracting attention because it is the strongest candidate to generate electricity from dilute waste heat sources. Temperature of waste heat spreads in widely. Waste heat with temperature in medium region (473-873 K) is high quality energy and the amount of the energy is huge. In order to recover and convert the waste heat to electricity, thermoelectric materials possessing not only good conversion efficiency, but also high oxidation resistance in the medium temperature region even in air are required.

A new silicide material with an-type thermoelectric property in the medium temperature region has been discovered [1]. This silicide possesses a composition of  $Mn_{3-x}Cr_xSi_4Al_2$  ( $0 < x < 0.7$ ) and hexagonal  $CrSi_2$  structure. The absolute values of Seebeck coefficient and electrical resistivity increase by Cr substitution up to 573 K. The dimensionless thermoelectric figure of merit  $ZT$  reaches 0.3 at 573 K for a Cr substituted one with  $x = 0.3$ . Since oxide passive layer is formed around the surface, electrical resistivity measured at 873 K is constant for two days in air, which indicates good oxidation resistance in air of this material. A thermoelectric module consisting of 64 pairs of legs has been fabricated using  $MnSi_{1.7}$  and non Cr substituted  $Mn_3Si_4Al_2$  devices as p- and n-type legs, respectively. Output power reaches 9.4 W, which corresponds to 2.3 kW/m<sup>2</sup> of power density against surface area of the substrate, for a heat source temperature of 873 K in air. Degradation of power of the module is observed at temperatures higher than 873 K of the hot side temperature in air after several hours because of some chemical reaction at the junctions. On the other hand, the generated power is constant even at 973 K for 3 days in vacuum. The n-type  $Mn_3Si_4Al_2$  looks a promising material for the power application in the medium temperature region.

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O-1

### **Spectral functions and resonant impurities – why Tl:PbTe is a good thermoelectric and Ti:PbTe is not.**

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This work presents results of detailed study on the "Fermi surface" and thermopower of Tl and Ti doped PbTe within the KKR-CPA method and Kubo-Greenwood formalism [1]. Thallium atom is known to be a resonant impurity in PbTe, which results in enhancement of thermopower and very good thermoelectric properties [2]. On the other hand, titanium is a resonant impurity as well, however no enhancement in thermopower in Ti:PbTe against other impurities was observed. In this work, Bloch spectral functions (BSF), which replace dispersion relations in disordered system, are calculated for Tl and Ti doped PbTe, and BSF intensity maps over the Brillouin zone ("Fermi surface" cross-sections) are presented. It is directly shown that Tl does not create impurity band near the Fermi level in PbTe, but the existence of resonant level strongly affects the host band structure, leading to disappearance of well-defined energy bands. In contrast, Titanium tends to form almost flat impurity band, which is not favorable for thermoelectric performance of the system. The differences between those two systems help to understand the mechanism of thermopower enhancement by the resonant level and gives clues how to select the resonant impurities in order to improve the thermoelectric properties of the material.

To further support our conclusions, transport properties of Tl:PbTe are studied. As the well-defined energy bands do not longer exist in this system, application of Boltzmann transport theory to this case is impossible. Thus, we apply the Kubo-Greenwood formula to calculate the energy-dependent electrical conductivity, with no adjustable parameters. Using the full Fermi integrals and conductivity, thermopower is calculated and compared with experimental results, confirming the enhancement in thermopower by the resonant state.

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## Exploring the Properties of Correlated Electrons through the Thermoelectric Effect

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The thermoelectric effect of correlated electron systems shows a much richer structure than expected from a simple description of the charge transport of ordinary metals. A quantitative theoretical understanding of the unconventional features of the Seebeck coefficient in model systems of correlated electrons opens the possibility to use low-temperature thermopower experiments as a diagnostic tool to probe features of the fermionic many-body system.

In our presentation we demonstrate that the widely used Mott's formula breaks down in the presence of anisotropy in the quasiparticle distribution function, caused either by anisotropic scattering rates or strongly angular dependent quasiparticle velocities. Moreover, we show how the measurement of the Seebeck coefficient can be used in order to map out critical regions in the phase diagram of correlated electron systems such as a band-filling driven Lifshitz transition. Within our numerical simulation of correlated electron systems, we have also shown that in temperature induced sign changes of the thermopower appear naturally in the presence of anisotropy.

Our method is based on a semiclassical description of the charge and heat transport in a two-dimensional metal on a square lattice. We solve the linearized Boltzmann equation with particular consideration of the angular and radial degrees of freedom in the collision integral. This approach represents a substantial sophistication compared to a single-relaxation-time approximation and ensures that important consequences of the anisotropy are not eliminated from the theoretical description.

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### Phase stability and oxidation studies of $(\text{Ti}_{0.33}\text{Zr}_{0.33}\text{Hf}_{0.33})\text{NiSn}$ half-Heusler compounds

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The ternary TiNiSn-based half-Heusler (HH) compounds are promising, environmentally friendly thermoelectric materials. However, besides high energy conversion efficiency the fundamental requirement for thermoelectric material is its stability under operating conditions. Additionally, it is important to study the oxidation behavior of the material in case of using it in a converter without a protective atmosphere and sealing. In this work  $(\text{Ti}_{0.33}\text{Zr}_{0.33}\text{Hf}_{0.33})\text{NiSn}$  half-Heusler compounds were synthesized and exposed to air at elevated temperatures. They were found to be a two-phase system composed of Ti- and (Zr,Hf)-rich phases with half-Heusler structure. The influence of operating conditions on the sample was studied in- and ex-situ by microscopy and thermal analysis. Exposure to air resulted in surface oxidation starting at 545 K. During the heat treatment the Ti-rich phase decomposed while the (Zr,Hf)-rich phase was stable in the examined temperature range. In-situ Atomic Force Microscopy and Scanning Kelvin Probe Force Microscopy experiments confirmed that interfaces, especially grain boundaries, are most prone to phase decomposition.

### Structure and thermoelectric properties of $\text{EuTi}(\text{O,N})_{3-\delta}$

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Transition metal oxides with strong electron correlations show interesting properties and a wide range of applications. The thermoelectric properties of  $\text{EuTiO}_3$  were studied and a high Seebeck coefficient ( $S$ ) was found ( $-1053 \mu\text{V/K}$  at 300 K). The electrical conductivity was enhanced by partial Nb substitution at the Ti site, leading to a thermoelectric figure of merit of  $\text{EuTi}_{0.98}\text{Nb}_{0.02}\text{O}_{3-\delta}$  of  $ZT = 0.4$  at  $T = 1040 \text{ K}$  [1]. Although anion (i.e. oxygen) substitutions are less commonly used than cation substitutions due to the more complex synthesis methods [2], they can lead to very interesting electronic and optical properties [3]. In this work, partial N substitution in  $\text{EuTiO}_3$  was investigated. The crystal structure, thermoelectric properties, morphology and electronic structure were analyzed and compared with pristine  $\text{EuTiO}_3$ . The space group of  $\text{EuTi}(\text{O,N})_{3-\delta}$  was orthorhombic  $Pnma$  due to the tilt and rotation of the anion octahedra, compared to cubic  $Pm\bar{3}m$  of  $\text{EuTiO}_3$ . The thermoelectric properties of oxynitride pellets were investigated in the temperature range of  $300 \text{ K} < T < 950 \text{ K}$ .  $S$  of the oxynitride was lowered compared with the oxide and the electrical resistivities ( $\rho$ ) was about one order of magnitude increased. The calculation of the activation energies ( $E_A$ ) indicated a higher band gap for  $\text{EuTi}(\text{O,N})_{3-\delta}$  than for pristine  $\text{EuTiO}_3$  ( $\sim 1.3 \text{ eV}$  compared to  $0.98 \text{ eV}$ ). A morphological characterization by electron microscopy illustrated intrinsic nanopores within the particles and weak grain-interconnections indicating poor intergrain electron transport. *Ab initio* calculations of the electronic density of states (DOS) of pristine  $\text{EuTiO}_3$  and  $\text{EuTi}(\text{O,N})_{3-\delta}$  confirmed a larger band gap of the latter. The crystal deformation of the oxynitride caused the shift of the intense  $4f$  peak of  $\text{EuTiO}_3$  to lower energies, which explained the decrease of the measured  $S$  [4].

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## High-Temperature Thermoelectric Converters employing Calcium Manganates

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Oxide-based materials are well suited for high-temperature thermoelectric modules due to their resistance to thermal degradation, low-costs, and ease of substitution. P-type oxides with high dimensionless figure-of-merits (ZTs) have been developed; however, the search for high ZT n-type materials is still ongoing. Consequently, the n-type, tungsten-substituted  $\text{CaMn}_{1-x}\text{W}_x\text{O}_{3-\delta}$ ;  $x = 0.00-0.05$  is investigated. The impact of tungsten substitution on the crystal structure, thermal stability, phase transition, electronic and thermal transport properties is evaluated. Additional negative charge carriers, due to tungsten substitution and dynamic oxygen deficiencies, dominate the transport properties – particularly in the temperature region around  $T=1000$  K, where “self-doping” due to oxygen deficiencies plays a key role in enhancing the ZT. The best ZT of 0.25 is found for  $x = 0.04$  at 1225 K.

In order to determine the efficacy of the electron-doped calcium manganates, thermoelectric oxide modules (TOMs) were manufactured, then their maximum power output, conversion efficiency, and stability in oxidizing atmosphere was evaluated. The modules attained power densities of  $240 \text{ W/cm}^2$  and were found to be thermally stable up to 1100 K.

**Thermoelectric Properties of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  synthesis by Auto-combustion**

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A rapid method for the synthesis of  $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$  powder is introduced. The procedure is a modification of the conventional citric-nitrate sol-gel method where an auto-combustion process is initiated by a controlled thermal oxidation-reduction reaction. The resulting powders inherit the advantages of a wet chemical synthesis, such as morphological and compositional homogeneity, and fine, well-defined particle sizes coming from the controlled nature of the auto-combustion. Optimized spark plasma sintering (SPS) processing conditions were determined and used to fabricate dense samples. The microstructure and thermoelectric transport properties were determined both parallel ( $\parallel$ ) and perpendicular ( $\perp$ ) to the SPS pressure axis in order to investigate any possible anisotropy variations in the transport properties. At 800 °C, power factors of  $506 \mu\text{W}/\text{m}\cdot\text{K}^2$  ( $\perp$ ) and  $147 \mu\text{W}/\text{m}\cdot\text{K}^2$  ( $\parallel$ ), thermal conductivities values of  $2.53 \text{ W}/\text{m}\cdot\text{K}$  ( $\perp$ ) and  $1.25 \text{ W}/\text{m}\cdot\text{K}$  ( $\parallel$ ), and resulting figures-of-merit,  $ZT$ , of 0.21 ( $\perp$ ) and 0.13 ( $\parallel$ ) were observed.

**Development of thermoelectric converters for waste heat recovery based on heavy cation-substituted misfit-layered  $\text{Ca}_3\text{Co}_4\text{O}_9$**

**Gesine Saucke**<sup>1</sup> Philipp Thiel<sup>1</sup> Kailash Mogare<sup>2</sup> Leyre Sagarna<sup>1</sup> Nina Vogel-Schäuble<sup>1</sup> Lassi Karvonen<sup>1</sup> Sascha Populoh<sup>1</sup> Anke Weidenkaff<sup>1,2</sup>

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The misfit-layered  $\text{Ca}_3\text{Co}_4\text{O}_{9-\delta}$  is one of the most promising p-type materials for high temperature thermoelectric applications, due to its high Seebeck coefficient, good electrical conductivity along the  $\text{CoO}_2$  layers and low thermal conductivity because of the misfit-layered structure. To further improve the figure of merit ( $ZT$ ) heavy cation-substitution was investigated.

Polycrystalline misfit-layered cobalt oxides were synthesized using a solid-state reaction route. The thermoelectric properties were modified by cationic substitution with heavy elements like Ru and In. For both substitutions a decrease of the thermal conductivity was observed, which led to an increase of  $ZT$  in the case of Ru substitution. Due to uniaxial pressing of the pellets a preferred orientation of the crystallites was observed by X-ray diffraction and scanning electron microscopy giving rise to anisotropic thermoelectric properties.

For the fabrication of a layered cobalt-oxide (p-type)/perovskite manganese oxide (n-type) module, the compatibility approach was considered via an adjusted ratio of the leg cross-sections. The resulting efficiencies of the modules were determined using a thermoelectric-module test rig and compared with theory.

**Effects of conducting oxide barrier layers on the interface stability  
of high-chrome iron alloy interconnects and calcium cobaltate**

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Practical implementation of oxide thermoelectrics on an industrial or commercial scale for waste heat energy conversion requires the development of chemically stable interfaces between metal interconnects and oxide thermoelements that exhibit low electrical contact resistances. A commercially available high-chrome iron alloy (i.e., Crofer 22, SS430) serving as the interconnect metal was spray coated with lanthanum nickel oxide or cobalt-manganese oxide spinels and then interfaced with a p-type thermoelectric material—calcium cobaltate—using spark plasma sintering. The interfaces have been characterized in terms of their thermal and electronic transport properties and chemical stability.

## Pulsed laser deposition and plasma analysis of $\text{Ca}_3\text{Co}_4\text{O}_9$ thermoelectric compounds

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$\text{Ca}_3\text{Co}_4\text{O}_9$  is a typical p-type thermoelectric oxide material and its thin film deposition has been most commonly achieved through a pulsed laser deposition (PLD) process. Nevertheless, during the PLD process, the film structure of  $\text{Ca}_3\text{Co}_4\text{O}_9$  has been reported to be rather sensitive to the PLD conditions. Hence, a deep understanding of the physical as well as chemical properties of the laser induced plasma plume is required. In this work, we establish the correlation of background pressure, plasma properties during the PLD process of  $\text{Ca}_3\text{Co}_4\text{O}_9$  compounds using combinational approaches of mass spectrometry as well as plasma imaging technique.

### Thermodynamics of calcium cobaltate in air

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Calcium cobaltate ( $\text{Ca}_3\text{Co}_4\text{O}_9$ ) has received much attention as one of the best oxide candidates for high-temperature thermoelectric power generation. However, as with most oxides, the transport properties are highly sensitive to the oxygen partial pressure. The isobaric heat capacity, thermal expansion, and thermogravimetric measurements, as well as the electrical resistivity, have all been measured in air up to 800°C. All measurements corroborate a first-order transition in the vicinity of 300°C, which is nearly 200°C higher than previously reported. Additionally, the system becomes dynamic above 600°C with oxygen flowing in and out of the system upon heat cycling.



## Measurement of the Thermal Conductivity on Nano Scaled Thin Film Thermoelectric Materials

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Reliable thermophysical data are necessary to develop efficient thermoelectric materials. Nano scaled thermoelectric materials are in the current focus to increase the Figure of Merit. The thermal conductivity of bulk materials can be measured with the standardized Laser Flash Method. However this technique can only be used for samples with a minimum thickness in the mm range. A Transient Thermoreflectance Method is introduced which enables the measurement of the thermal conductivity on nanometer scaled thin films with high accuracy. On various application examples it can be proved that the thermal conductivity is strongly dependent on the thickness of the material. The thermal conductivity decreases with decreasing sample thickness. The thermal conductivity of the bulk material is much higher by one or two orders of magnitude.

## Layered oxychalcogenides with promising high ZT values: the frontier between oxides and intermetallics

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Recently, our team has shown that layered oxychalcogenide materials [1], with parent compound BiCuSeO, exhibit promising thermoelectric properties and high figure of merit with  $ZT \approx 1$  around 600°C. These p-type materials crystallize in a two dimensional structure analogue to the well-known 1111 iron-pnictides superconductors' one, with alternating intermetallic  $[\text{Cu}_2\text{Se}_2]^{2-}$  covalent layers and oxide  $[\text{Bi}_2\text{O}_2]^{2+}$  insulating layers. They are moderate band gap semiconductors and they can be hole doped by substituting  $\text{A}^{2+}$  in the trivalent cation site to optimize the charge carrier concentration. Their promising ZT values mainly originate from their very low lattice thermal conductivity values, of the order of  $0.3 \text{ W.m}^{-1}.\text{K}^{-1}$  at high temperature. However, their thermoelectric power factor,  $\sigma S^2$ , keeps moderate due to their low holes mobility, despite the increase of carriers concentration induced by doping. The most interesting characteristic of the layered oxychalcogenides is that they can constitute a bridge between oxides and intermetallics by combining the main advantages of distinct classes of materials, with the moderate electrical resistivity and good thermopower of chalcogenide semiconductors, the low thermal conductivity of layered compounds, and a thermal stability under air which is strongly enhanced as compared to intermetallic materials due to the oxide layer. I will present the thermoelectric properties of the family and discuss how these properties can be linked to the crystal structure and the electronic band structure, and the route we have followed to increase their ZT from 0.75 in 2010 to 1.4 in 2013.

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**Cu-deficient layered BiCuOSe**

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Recently extraordinary thermoelectric performance was discovered for the layered oxyselenide BiCuOSe. The compound adopts a ZrCuSiAs-type (symmetry group  $P4/nmm$ ) structure, consisting of fluorite-type  $[\text{Cu}_2\text{Se}_2]$  and anti-fluorite-type  $[\text{Bi}_2\text{O}_2]$  sub-blocks stacking alternatively along  $c$  axis. The soft oxyselenide network provides the compound with low thermal conductivity. Meanwhile, the electronic transport properties of this  $p$ -type semiconducting compound can be effectively improved either by hole doping in the  $[\text{Bi}_2\text{O}_2]$  block or by introducing Cu vacancies in the  $[\text{Cu}_2\text{Se}_2]$  block. We have synthesized a series of Cu-deficient  $\text{BiCu}_\delta\text{OSe}$  ( $0.925 \leq \delta \leq 1.0$ , nominally) phases and characterized them for their thermal stabilities, local structures and low-temperature thermoelectric properties. The decent thermopower and electrical conductivity values together result in a peak in the power factor, which grows and shifts to lower temperatures with increasing concentration of Cu vacancies. On the other hand, the dramatic modification of the  $\text{CuSe}_4$  tetrahedron in the Cu-deficient phases could be the origin of the hysteresis behaviour seen in the resistivity *versus* temperature curves.

## Electrodeposition of Alloyed p-and n-type $\text{Bi}_2\text{Te}_3$ Nanowires

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Solid-state cooling and power generation based on thermoelectric Seebeck and Peltier effects have potential applications in waste-heat recovery, air conditioning and refrigeration. The idea of increasing ZT value using the same material but in a lower dimensional structures was introduced by Hicks and Dresselhaus in 1993<sup>1</sup>. During the past decade several groups<sup>2-4</sup> have reported enhancement in the ZT values ( $>1$ ) with low dimensional structures mainly due to the reduced phonon thermal conductivity. However, quantum confinement of electronic carriers to improve thermoelectric performance has yet to be realized. Bismuth and antimony telluride based materials are considered to be the best for thermoelectric applications in the temperature range of 200 to 400 K.  $\text{Bi}_2\text{Te}_3$  alloys exhibit the highest ZT near room temperature, and are the leading candidates for low temperature thermoelectric applications. Furthermore, it is expected that forming nanowires of  $\text{Bi}_2\text{Te}_3$  to realize a 1D geometry will increase the ZT value due to quantum size effects<sup>5,6</sup>. Realizing these materials for practical application is challenging since the current state-of-the-art materials and fabrication processes are difficult to scale up to practically useful device dimensions and costs are significant.  $\text{Bi}_2\text{Te}_3$  thin films have been prepared by various techniques, such as pulsed laser deposition (PLD), metal-organic chemical vapour deposition (MOCVD), and molecular beam epitaxy (MBE). Recently, electrodeposition has attracted wide attention in the fabrication of  $\text{Bi}_2\text{Te}_3$ -based thermoelectric devices because of its low cost, simple equipment, easy control and high productivity.

In this paper, we report the pulsed electrodeposition of  $\text{Bi}_2\text{Te}_3$  nanowires from a single aqueous electrolyte using track-etched polycarbonate membranes as templates. The deposition of the nanowires was controlled by tuning the applied potential waveforms and pulse times. Distinctive reduction potentials were observed corresponding to the formation of p- and n-type  $\text{Bi}_2\text{Te}_3$  nanowires. We demonstrate the influence of the pulse parameters on the stoichiometry, crystallographic orientation, grain size and boundary, and thermal and electrical conductivity of both p- and n-type the  $\text{Bi}_2\text{Te}_3$  nanowires.

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**P-1**

**Effects of particle size on thermoelectric properties of  $\text{CuCrO}_2$**

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$\text{CuCrO}_2$  has attracted attention as a promising thermoelectric material because its electrical conductivity can be greatly increased by doping. Here we study the effect of crystallite size on the thermal conductivity, another important factor for thermoelectric properties. We have synthesized polycrystalline  $\text{CuCrO}_2$  by three routes (solid state reaction, sol-gel method and hydrothermal synthesis) and characterized the crystallite size by X-ray diffraction and scanning electron microscopy. The smallest crystallites have a quasi-hexagonal shape of dimensions  $\sim 20\text{nm}$ . The thermal conductivity as well as the electrical resistivity and Seebeck coefficient of the particles have been measured and will be discussed as a function of particle size.

## Enhancing the figure of merit of GeTe based thermoelectric materials

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Bulk thermoelectric materials are of interest for the generation of electricity from waste heat. However, for widespread commercial use, materials with better thermoelectric performance are required. The alloys  $(\text{GeTe})_x(\text{AgSbTe}_2)_{1-x}$  (commonly known as TAGS) are among the best known high-temperature thermoelectrics, largely due to their low thermal conductivity. This is thought to be due to a dense network of twin domain boundaries formed by a phase transition from cubic to rhombohedral on cooling. Here we report on the structural properties of TAGS as a function of temperature and how this depends on processing conditions and thermal cycling. Furthermore, the effect of doping TAGS with magnetic rare-earth and transition metals will be discussed with respect to the electrical conductivity and Seebeck coefficient.

## Thermoelectric properties of doped PbSe

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Bulk thermoelectric materials are of interest in the field of energy conversion technology due to their potential in the conversion of waste heat to electrical power [1]. Lead chalcogenide compounds show high performance at room temperature and above, especially in the range 600-850 K. As narrow gap semiconducting compounds, they exhibit outstanding electrical transport properties, and they also exhibit low thermal conductivities at high temperature, which is unusual for materials with simple structures (PbSe adopts the rock-salt structure) [2]. Doping with 4f electrons can introduce resonant states just below the Fermi level and shows promise for enhancing the thermopower and hence the thermoelectric figure of merit. Here we investigate the influence of Ce-doping on the thermoelectric properties of PbSe. We have synthesized  $\text{Pb}_{1-x}\text{Ce}_x\text{Se}$  ( $x=0.00, 0.01, 0.03$  and  $0.05$ ) alloys and examined the structural, magnetic and thermoelectric properties.

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**Investigation of the thermal conductivities across metal-insulator transition  
in polycrystalline VO<sub>2</sub>**

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Previous reports about the thermal conductivities of VO<sub>2</sub> showed various temperature dependences across metal-insulator transition (MIT) temperature. In this work, polycrystalline VO<sub>2</sub> samples were fabricated by spark plasma sintering of VO<sub>2</sub> powder. Temperature dependences of their thermal conductivities were investigated using laser flash technique, and the thermal conductivity showed a significant decrease trend from metal-phase to insulator phase. Electrical transport properties were investigated to confirm both carrier and lattice contribution to the thermal conductivity. It is found that the lattice thermal conductivity decreased significantly across MIT point, which may be caused by soft phonon mode in metal phase of VO<sub>2</sub>.



## Thin-Films of the Zinc-Antimony System

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One way to enhance  $zT$  is to lower the dimensions of the thermoelectric (TE) material, and this approach is utilized in TE thin-films. Sun *et al.* has previously shown that it is possible to make  $Zn_4Sb_3$ , ZnSb and mixed thin-films, by a co-sputtering technique with a Zn and a  $Zn_4Sb_3$  target. The different phases are created by varying the substrate temperature and followed by an annealing step. [1] The zinc-antimony system proved to be even more complex with the discovery of two unknown phases during the study. For reproducibility of high quality TE thin-films, good control of the quality of the targets is important. A fast and reliable way of making  $Zn_4Sb_3$ , using a Spark Plasma Sintering system has been developed by Iversen *et al.* [2] In the present work this method has been utilized for producing ZnSb as a pure target for use in magnetron assisted sputtering.

A series of 1 inch targets of starting material Zn:Sb = 1:1 have been produced, where ramping time, maximum temperature and sintering/reaction time were varied. The targets were investigated with X-Ray diffraction (XRD) and Potential Seebeck Microprobe (PSM) to identify the products. The homogeneity of the targets is very dependent on the maximum temperature and the sintering/reaction time. The effect of Zn-migration, similar to the migration seen in  $Zn_4Sb_3$  made by SPS, is observed for some of the targets. [3]

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**P-6**

**Resonant scattering induced thermopower in one dimensional disordered systems**

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We present a simple model in order to investigate the thermopower of one dimensional disordered systems in presence of resonant scattering. Our idealized model consists of arbitrarily placed identical impurities which give rise to perfect transmission in the vicinity of resonance energies whereas strongly suppressed transmission is found elsewhere due to localization of the charge carrier. As a consequence of the transmission peaks, the Seebeck coefficient  $S$  (as a function of temperature) shows a peak whose characteristics can entirely be expressed in terms of parameters of the underlying model. The computation of the  $ZT$ -value and further properties render our outcome.

## Development of robust and long-term stable heat flux sensors

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The ETH spin-off company greenTEG AG has launched its first product, a highly sensitive low-cost heat flux sensor based on thermoelectric effects [1]. In the framework of a CTI project, the Micro- and Nanosystems group of ETH Zurich has further developed the underlying technology leading to the robust and long-term stable gSKIN heat flux sensor [2,3].

The main applications of these sensors are found in the fields of heat flux sensing in building technology and radiation measurement in solar and laser power applications. Main improvements were made in the quality of the thermoelectric material and the device packaging. All employed processes are compatible with requirements for mass production.

The material and device stability was tested by thermal ageing and automotive-based thermal cycling (TC) as well as highly accelerated stress test (HAST) procedures. The device sensitivity was shown to drift less than 5% over 48h at 200°C, which corresponds to an extrapolated lifetime of more than 10 years at 80°C. Further development towards long-term high temperature stability and even higher sensitivity are ongoing.

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## Chemical Composition of the $\text{Sr}_x\text{CoO}_z \cdot r\text{H}_2\text{O}$ Misfit-Layered Cobalt Oxide Determined Using TGA-MS

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Layered cobalt oxides - described with the general formula,  $[\text{M}_m\text{A}_r\text{O}_{m+r-\delta}]_q\text{CoO}_2$  ( $\text{M} = \text{Co}, \text{Bi}, \text{Pb}, \text{Tl}, \text{etc.}; \text{A} = \text{Ca}, \text{Sr}, \text{Ba}, \text{etc.}; m = 0, 1, 2; q \geq 0.5; r \geq 0; \delta \geq 0$ ) - possess a layered crystal structure consisting of two types of layer blocks: hexagonal  $[\text{CoO}_2]$  block and rock-salt-structured  $[\text{M}_m\text{A}_r\text{O}_{m+r-\delta}]$  block stacked incoherently to each other forming a composite crystal. The high structural anisotropy and weak inter-block interaction results into an easy modifiability of the physical and chemical properties of these compounds making them interesting objects for the research exploring new oxide materials.

In this work we have focused on ( $r = 2, m = 0$ )-type phases of the layered cobalt-oxide family. First reported in year 2006, only two compounds have been discovered so far with  $[\text{Sr}_2\text{O}_2]_q\text{CoO}_2$  and  $[\text{Ca}_2\text{O}_2]_q\text{CoO}_2$  fundamental stoichiometries. Synthesis of the ( $r = 2, m = 0$ )-type phases is a sintering procedure taking place under elevated pressures of  $\text{O}_2$  (g) and is known to be facilitated by the presence of  $\text{H}_2\text{O}$  (g). [1]

To understand the stabilizing role of  $\text{H}_2\text{O}$  in the ( $r = 2, m = 0$ )-type phases,  $\text{Sr}_x\text{CoO}_2$  and  $[\text{Sr}_2\text{O}_2]_q\text{CoO}_2$  containing sample-mixtures with a general sample stoichiometry of  $\text{Sr}_x\text{CoO}_z \cdot r\text{H}_2\text{O}$  were synthesized and analyzed for their elemental compositions using TGA-MS. The TGA measurements were performed for each sample in both inert and reductive atmospheres. While the sample decomposition under the inert atmosphere leads into a formation of mixture of  $\text{SrCoO}_{2.5+\delta}$  (s) (orthorhombic perovskite compound) with  $\text{CoO}$  (s), the decomposition under the reductive atmosphere results into a residual mixture of  $\text{SrO}$  (s) and  $\text{Co}$  (s). Under the inert atmosphere, the  $\text{H}_2\text{O}$  extraction steps were also possible to resolve from the  $\text{O}_2$ -generating thermal reduction steps with the help of the MS detection of the TGA exhaust gas flow. Additionally, X-ray diffraction (XRD) was used for a qualitative confirmation of the sample compositions and the TGA residuals. Combining the data of the two different TGA runs under different atmospheres enabled an explicit determination the sample composition.

TGA-MS measurements revealed for the first time, that the phase commonly known as  $[\text{Sr}_2\text{O}_2]_q\text{CoO}_2$  contains large amounts of  $\text{H}^+$  bound either as  $\text{H}_2\text{O}$  or  $\text{OH}^-$  species. The almost 1:1 relation of the Sr and  $\text{H}^+$  in the  $[\text{Sr}_2\text{O}_2]$  block implies that the given block might rather have hydroxide than oxide nature.

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## Development of a thermoelectric heat exchanger (T-Hex) for application in a car

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Hybrid-electric vehicles (HEV), combining the excellent efficiency of electrical power trains with easy refueling and long fueling cycle of liquid/gaseous combustion engines, will play an important role in the mobility of the next twenty years. As around 60% of the primary energy burned in a combustion engine is lost as dissipated waste heat, thermoelectric converters capable of using such waste heat enthalpy as energy sources are a very promising concept enabling even higher fuel savings in an HEV. The project was part of the CCEM project “Customized Hybrid Powertrains” (Cohyb) handled by a consortium of five partners.

The goal is to recuperate ~100W from the exhaust gas with an actual system weight of 10kg. This would lead to a calculated fuel reduction in a hybrid car of up to 5%. The experiments were carried out in the internal combustion engines laboratory at Empa on a test bench equipped with a single cylinder engine with a displacement of 0.25 liters, manufactured by the Swiss company Swissauto Wenko AG (Burgdorf).

In order to extract sufficient energy from the exhaust gas, the thermoelectric heat exchanger (T-Hex) was positioned directly behind the catalytic converter. In a first trial commercially available modules using BiTe-based thermoelectric leg material were mounted on the T-Hex. Performance, energy balance as well as the influence of the T-Hex on the engine was fully characterized. However, with its upper temperature limit of 300°C this material limits the applicable exhaust-gas temperature and therefore the output engine power. During later tests, high-temperature-stable and environmentally benign modules based on half-Heusler compounds and complex metal oxides were developed and characterized.