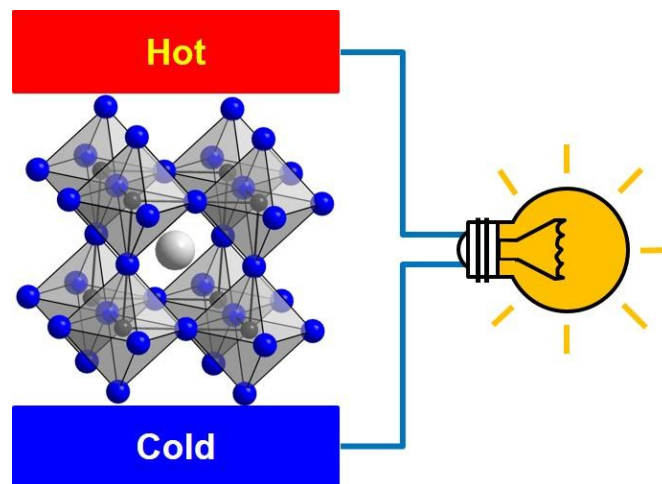


2nd Stuttgart Workshop on Thermoelectrics (SWT 2017)



Program and Abstracts

Stuttgart, Germany
August 8, 2017

Welcome to the 2nd Stuttgart Workshop on Thermoelectrics

Since 2007 we start to assemble scientists from universities, scientific institutes as well as industry to promote cooperation on the development of thermoelectric materials and devices. Five previous workshop and conferences at Switzerland (in 2007, 2009, 2011, and 2013) and Germany (in 2016) were very successful. During the last five conferences, we invited about 50 international and national distinguished speakers to give high level lectures. So this year, we would like to continue this excellent tradition, and host the 2nd **Stuttgart Workshop on Thermoelectrics**. We thank all our invited speakers and participants for spending their valuable time with us and making this workshop valuable.

Wenjie Xie
Juliane Kränzl
Stefan Kilper
Songhak Yoon
Anke Weidenkaff

Detailed Program Agenda

Session I, Chair: Anke Weidenkaff (09:00 – 10:20)

09:00 – 09:05	Opening	Anke Weidenkaff
09:05 – 09:35	Quasicrystals: A Review of the Discovery, History and Thermoelectric Properties of these Amazing Materials	Terry Tritt
09:35 – 09:50	Giant thermopower at high temperatures in SrTiO ₃ /Ca ₃ Co ₄ O ₉ heterostructures	Hanns-Ulrich Habermeier
09:50 – 10:05	Measurement of Physical Properties on Thermoelectric Thin Film Materials	Heinz Renner
10:05 – 10:20	Thermoelectric Properties & Characterizations of SURMOF Thin Films	Engelbert Redel
10:20 – 10:50	Coffee break	

Session II, Chair: Hanns-Ulrich Habermeier (10:50 – 12:05)

10:50 – 11:20	Phase diagrams for development of thermoelectric materials	Juri Grin
11:20 – 11:50	Phonon Engineering for Enhanced Figure of Merit ZT Nanolaminate Thermoelectric Materials	Helmut Baumgart
11:50 – 12:05	High Weighted Mobility Achievement in Tetrahedrite through Sm Substitution	Tianhua Zou
12:05 – 13:30	Lunch break @ MPI canteen	

Session III, Chair: Terry Tritt (13:30 – 15:15)

13:30 – 14:00	TBA	Jan D. König
14:00 – 14:30	Ni-interstitials making strong influence on thermoelectric properties of TiNiSn Half Heuslers	Yinglu Tang
14:30 – 14:45	Material design of thermoelectrically highly efficient Heusler compounds for the XXI century – Upscaling and economic point of view	Benjamin Balke
14:45 – 15:00	Fe-based half-Heusler thermoelectric materials: from FeVSb to FeNbSb	Chenguang Fu
15:00 – 15:15	Structure and Thermoelectric Properties of MgAgSb compound	Pingjun Ying
15:15 – 16:00	Poster session & Coffee break	

Session IV, Chair: Juri Grin (16:00 – 17:30)

16:00 – 16:30	Dynamics of entropy, charge and energy in thermoelectric materials and devices	Armin Feldhoff
16:30 – 17:00	Doping of Conjugated Polymer Films for Flexible Thermoelectrics	Sabine Ludwigs
17:00 – 17:15	Porous Ca ₃ Co ₄ O ₉ with enhanced thermoelectric properties	Michael Bittner
17:15 – 17:30	Band structure modification of the thermoelectric Heusler-phase TiFe ₂ Sn via Mn substitution	Wenjie Xie
18:30	Dinner@ Römerhof restaurant	

Poster:

P-1: Mohammad Yasseri

Studying the miscibility gap in $Mg_2(Si,Sn)$: influence on microstructure and thermoelectric properties

P-2: Xingxing Xiao

Tailoring the structure and thermoelectric properties of $BaTiO_3$ via Eu^{2+} substitution

P-3: N. Farahi

Phase Analysis and Thermoelectric Properties of $TiNiSn$ Based half-Heusler Thermoelectric Materials

P-4: Tianhua Zou

Realizing band structure modification and energy filtering effect in $\beta-Zn_4Sb_3$ based nanocomposites

Invited-1

Quasicrystals: A Review of the Discovery, History and Thermoelectric Properties of these Amazing Materials

Terry M. Tritt*

Dept. of Physics and Astronomy, Clemson University, Clemson, South Carolina, 29634,
USA

*email: ttritt@clemson.edu

Dan Shechtman first discovered Quasicrystals in 1982, while on sabbatical at Johns Hopkins University and working at the US National Bureau of Standards (now NIST). Shechtman's work and the significant discovery of Quasicrystals in the early 1980's led to him being awarded the 2011 Nobel Prize in Chemistry. Since then, there has been a renewed interest in various aspects of these materials. Quasicrystalline materials exhibit a quasi-periodic structure that appears to exhibit a forbidden 5-fold rotational symmetry. A quasiperiodic structure, as in a Penrose tiling, can fill all space but lacks longrange order. However, there does exist some short-range order. Quasicrystals were really both a crystallographer's dream as well as a nightmare. The discovery of these materials caused much controversy within the crystallographic community and many debates ensued. Eventually, many others starting confirming Shechtman's work and the community eventually recognized his significant discovery and as stated, he was awarded the 2011 Nobel Prize in Chemistry for his work on Quasicrystals. In the news report, Shechtman mentioned two applications of Quasicrystals: one as a hardened non-stick coating for frying pans and the other as potential thermoelectric (TE) materials. From about 1997 until around 2005 my group at Clemson University performed an extensive amount of research on the TE properties of quasicrystalline materials. Recently, I have received many requests for talks on the subject, one being a keynote address at the 2012 International Conference of Thermoelectrics in Denmark. As part of this current talk I will try to walk you through Shechtman's journey: from discovery, to ridicule and then to the Nobel Prize. The aspect that first drew my attention to quasicrystals was their inherently low thermal conductivity ($k \approx 1 \text{ Wm}^{-1}\text{K}^{-1}$) and electrical conductivity, ($\sigma \approx 1000 \text{ S/cm}$), similar to other thermoelectric materials but with an unusual temperature dependence. One of the main challenges was to enhance the thermopower (a) in these materials. In addition, it had been predicted theoretically, that Quasicrystals could possibly exhibit a dimensionless figure of merit, $ZT = \alpha^2 \sigma T / \kappa$, between 1 and 2. This talk will review some background in crystals and crystallography, the history of these

materials and some aspects of thermoelectrics. It will also highlight a fraction of some of the experimental results obtained by my group and others. In the end, I will give an evaluation of my perspective of the potential for Quasicrystals as TE materials and give tribute to an amazing scientist whose discovery forced us to redefine our definition of what a crystal really is.

Oral-1

Giant thermopower at high temperatures in SrTiO₃/Ca₃Co₄O₉ heterostructures

P. Yordanov¹ and H.-U. Habermeier^{2,1}

¹Max-Planck-Institute for Solid State Research, Stuttgart, Germany

²Science Consulting International, Stuttgart, Germany

Transition metal oxides are promising candidates for thermoelectric applications, due to their stability at high temperature and because strong electronic correlations can generate large Seebeck coefficients. Their thermoelectric power factors, however, are limited by the low electrical conductivity. We report transport measurements on Ca₃Co₄O₉ (CCO) films deposited on various perovskite substrates and show that reversible incorporation of oxygen into LaAlO₃ and SrTiO₃ substrates activates a parallel conduction channel for p-type carriers, greatly enhancing the thermoelectric performance of the film-substrate system at temperatures above 450 °C. CCO films with a thickness of 20 nm deposited on SrTiO₃ substrates, e.g. show at 720 °C values for the thermopower exceeding 800 μV/K. Thin-film structures that take advantage of both electronic correlations and the high oxygen mobility of transition metal oxides thus open up new perspectives for thermopower generation at high temperature.

Oral-2

Measurement of Physical Properties on Thermoelectric Thin Film Materials

Heinz Renner¹, Vincent Linseis², Kornelius Nielsch²

1. Linseis Messgeräte GmbH, Vielitzer Str. 43, 95100 Selb, Germany
2. Institute of Applied Physics, University of Hamburg, Hamburg, Germany

h.renner@linseis.de

Due to new research efforts in various fields with a focus on size effects, there is a growing need for measurement setups dedicated to samples with small geometrical dimensions like thin films and nanowires with considerably different physical properties than bulk material. The characterization of these samples is important to learn more about their structure and conduction mechanism but also important for technical applications e.g. in the semiconductor industry or for the development of thermoelectric devices.

We report about new developments to characterize thin thermoelectric films. The chip based system simultaneously measures the electrical and thermal conductivity, the Seebeck Coefficient and the Hall Constant of a thin film sample in the temperature range from liquid nitrogen up to 350 °C. Due to the simultaneous measurement at only one sample, errors caused by different sample compositions, different sample geometries (thickness) and different heat profiles can be avoided. The system consists of two main parts, a structured Si-wafer and a suitable measurement setup [1]. The sample deposition and handling is kept easy and optimized to meet a very broad range of use.

References:

- [1] F. Voelklein et. al., *Phys. Status Solidi A*, 2013, 210, 106–118.

Oral-3

Thermoelectric Properties & Characterizations of SURMOF Thin Films

Engelbert Redel¹ and Helmut Baumgart^{2,3}

1. IFG (Institute for Functional Interfaces), KIT (Karlsruhe Institute of Technology), Hermann-von-Helmholtz Platz 1, Eggenstein-Leopoldshafen, Germany.
2. Dept. Electrical and Computer Engineering, Old Dominion University, Norfolk, VA 23529, USA
3. Applied Research Center, Thomas Jefferson National Accelerator Lab, Newport News, Virginia 23606, USA

Email: engelbert.redel@kit.edu

Organic Thermoelectric Materials and Devices possesses promising application in the field of TE Materials. An overview will be given on Organic and Metal-Organic TE Materials. A new class of thermoelectric materials termed surface-anchored (metal-organic frameworks and coordination network compounds) SURMOFs thin films materials will be introduced. SURMOFs thin films demonstrates promising application potential of organic porous thin films in future thermoelectric and electronic devices working highly efficient in the RT (Room Temperature) region. In our first studies we have characterized the Seebeck coefficient of polycrystalline and highly-ordered SURMOF thin films, see also Fig. 1. [1,2]

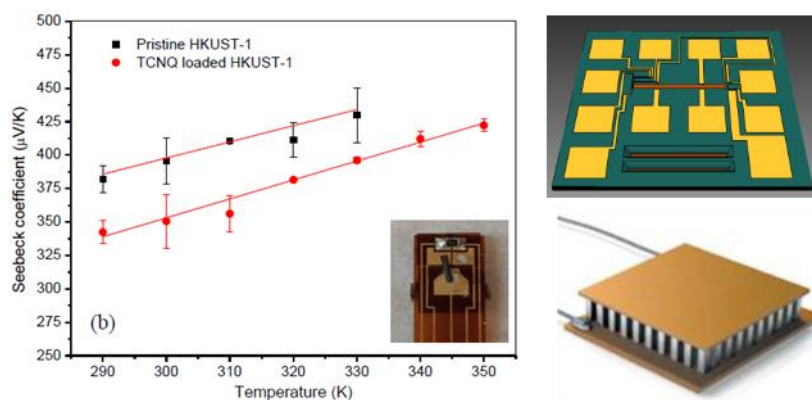


Fig. 1. Schematic Drawing of a thermoelectric characterization (Seebeck measurements) of SURMOFs.

Since SURMOFs are highly porous and the size of their pores are highly adjustable,

they can be further functionalized and tailored due to their electrical and thermal conductivity properties. SURMOFs can be therefore regarded as tailorable organic Thermoelectric Material of the future.

An outlook will be given on their further electronic characterization, Hall measurements and thermal conductivity as well as on first *ZT* Chip measurements.

References:

[1] X. Chen et al., *ECS Trans.*, 2016, 75, 119-126.

[2] X. Chen et al., *ECS J. Solid State Sci. Technol*, 2017, 6, 150-153.

Invited-2

Phase diagrams for development of thermoelectric materials

Yuri Grin

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

Phase diagrams of binary and ternary systems play important role in manufacturing of materials in general and thermoelectric ones in particular. A study of basic intrinsic thermoelectric properties can be best realized on single crystals. For the production of large quantities of substances - in particular for commercial applications - the knowledge about the details of the targeted phase diagrams is decisive. In the last decades, lot of efforts was made in studying the phase diagrams of thermoelectric skutterudites- and clathrates-based materials.

For the germanium-containing clathrates, which are most interesting from the thermoelectric point of view, the basic compound – $\text{Ba}_8\text{Ge}_{43}\square_3$ [1] – is found to be stable in the binary phase diagram in a narrow temperature range between 770 °C and 810 °C in a complex phase diagram especially in the germanium-rich part [2]. This substance reveal belongs to the family of the thermoelectric materials with complex crystal structures [3] which reveal often interesting electronic and – especially - phonon transport properties [4].

Adding of the third component M to $\text{Ba}_8\text{Ge}_{43}\square_3$ results in several responses of the crystal structure in different regions of the ternary phase diagram. At the low content of M , the vacancies in the anionic framework are filled. Further increase of the M concentration leads to a complex reorganization of the crystal structure of ternary clathrates toward reduction of the translational symmetry [5].

References:

- [1] U. Aydemir et al., *Dalton Trans.* 2010, 39, 1078-1088.
- [2] W. Carrillo-Cabrera et al., *Z. anorg. allg. Chem.* 2004, 630, 2267-2276.
- [3] S. Bühler-Paschen, C. Godart, Yu. Grin. In: *Complex Metallic Alloys. Fundamentals and Applications.* Wiley-VCH, 2011, 365-384.
- [4] H. Euchner et al., *Phys. Rev. B* 2012, 86, 224303.
- [5] R. Ramlau, Yu. Grin, H. Sawada, *JEOL News* 2016, 5, 2-6.

Invited-3

Phonon Engineering for Enhanced Figure of Merit ZT Nanolaminate Thermoelectric Materials

Helmut Baumgart^{1,2}, Xin Chen^{1,2}, Kai Zhang^{1,2}

1. Department of Electrical and Computer Engineering, Old Dominion University, Norfolk, Virginia 23529, USA
2. Applied Research Center at Jefferson National Accelerator Laboratory, Newport News, Virginia 23606, USA

Email: hbaumgar@odu.edu

Thermoelectric materials and generators contribute to save energy by converting waste heat into electricity based on the Seebeck effect and thus constitute an alternate green renewable energy technology. High efficiency thermoelectric materials have attracted considerable attention because of their application potential in power generation and refrigeration systems. The efficiency of thermoelectric materials is expressed by the figure of merit (ZT), $ZT = S^2\sigma T/(\kappa_l + \kappa_e)$. It is observed that higher thermoelectric efficiency can be obtained by increasing the electron conductivity and reducing the thermal conductivity. In the quest to enhance ZT values, a key strategy involves reduction in thermal conductivity κ , resulting from phonon scattering by numerous interfaces in low dimensional structures. A decrease of thermal conductivity could be achieved by a low dimensional superlattice structure, due to the quantum confinement or phonon scattering. [1]

Recently promising advances have been achieved with phononic crystal (PnC) nanostructures in thermoelectric materials, because the thermal conductivity of PnC samples is lower compared to non-patterned thermoelectric samples due to phonon-boundary scattering. In this study we report on the successful synthesis of PbTe and PbSe thermoelectric layers on patterned porous silicon substrates by a thermal ALD system. PbTe/PbSe nanolaminates grown on porous silicon membranes have higher Seebeck coefficients than the ones grown on regular planar silicon wafers. The higher Seebeck values result from the lower thermal conductivity κ in porous structures, which in turn lead to a higher figure of merit ZT . We demonstrate the feasibility to enhance the figure of merit ZT further by modulating the size and periodicity of the pattern and the thickness of the thermoelectric film in relation to the mean free path (MFP) of the phonons of the thermoelectric material. In our study PbTe and PbSe thin films and nanolaminates were

synthesized by Atomic Layer Deposition (ALD) technology on regular planar silicon wafers and on macro-porous silicon templates. ALD is a surface saturating, self-limiting, absolutely conformal thin film synthesis technique reacting two pulsed precursors that enable film growth of one atomic layer per growth cycle. Lead bis(2,2,6,6-tetramethyl-3,5-heptanedionato) ($\text{Pb}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2$), (trimethylsilyl) telluride ($(\text{Me}_3\text{Si})_2\text{Te}$) and (trimethylsilyl) selenide ($(\text{Me}_3\text{Si})_2\text{Se}$) were employed as the chemical ALD precursors for lead, tellurium and selenium, respectively. The surface morphology observations indicate Volmer–Weber (VW) growth mechanism of PbTe/PbSe nanolaminates during the thermal ALD deposition process rather than classic layer-by-layer growth. The ALD PbTe/PbSe nanolaminates exhibited complete surface coverage on planar bulk silicon wafers and also inside the pores of microporous silicon membranes. For the case of porous Si templates, the Seebeck measurements in both the horizontal and vertical directions revealed significant enhancement in Seebeck coefficients for PbTe/PbSe nanolaminates synthesized inside strictly periodic lithographically defined porous silicon membranes.

Reference:

[1] X. Chen et al., *ECS J. Solid State Sci. Technol.* 2016, 5, 503.

Oral-4

High Weighted Mobility Achievement in Tetrahedrite through Sm Substitution

Tianhua Zou¹, Wenjie Xie¹, Zhicheng Zhong², Weiwu Li³, Marc Widenmeyer¹, Yufei Liu⁴, Stefan Kilper¹, Xingxing Xiao¹, Philipp Hansmann², Martin Dressel³, Jian He⁴, Terry M. Tritt⁴, Anke Weidenkaff¹

1. Institut für Materialwissenschaft, Universität Stuttgart, 70569 Stuttgart, Germany
2. Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart, Germany
3. Physikalisches Institut, Universität Stuttgart, 70569 Stuttgart, Germany
4. Department of Physics and Astronomy, Clemson University, Clemson, SC 29634, USA

A high performance thermoelectric material should have a large weighted mobility. However, it is not easy to increase the weighted mobility because of the two factors μ and m^* are coupled and determined by the electronic band structure and scattering mechanism at the same time. In this work, we observed that slight Sm doping increases both carrier mobility and weighted mobility in tetrahedrite $\text{Cu}_{3-x}\text{Sm}_x\text{SbSe}_4$ ($x = 0, 0.005, 0.075, 0.01, 0.015$ and 0.025). In the Sm-doped samples, the relatively lighter valence band will be activated to contribute to the transport as well and the carrier mobility can be increased greatly. At the same time, the decrease of the effective mass is not so obviously. So finally the weighted mobility is enhanced greatly.

Invited-4

Ni-interstitials making strong influence on thermoelectric properties of TiNiSn Half Heuslers

Yinglu Tang¹, Xiaoshuang Li¹, Lukas Martin², Toni Ivas¹, Christian Leinenbach¹, G. Jeffrey Snyder³, Corsin Battaglia¹

1. Empa, Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland
2. Institute for Geochemistry and Petrology, ETH, 8092 Zürich, Switzerland
3. Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, USA

From phase boundary mapping, we find that the TiNiSn phase is stable only in a narrow region of the Ti-Ni-Sn phase diagram. At least four invariant points associated with four three-phase regions with different Ni content are found. We characterized the thermoelectric properties of these invariant points. We demonstrate that Ni excess in TiNiSn results in a narrower Goldsmid gap, which we interpret to be due to the formation of an impurity band from interstitial Ni in the forbidden gap. The excess Ni forms interstitial and scatters both electrons and phonons, with the latter being much stronger and thus compensating the electron mobility decrease and leading to better zT . The temperature dependence of the solubility of TiNiSn is also studied, demonstrating increasing solubility as well as Ni interstitial amount as temperature increases, which could be useful for enhancing zT . A Calphad simulation was performed to model the temperature dependent solubility.

Oral-5

Material design of thermoelectrically highly efficient Heusler compounds for the XXI century – Upscaling and economic point of view

Benjamin Balke

Institute for Materials Science, University of Stuttgart, Stuttgart, Germany

Half-Heusler compounds are one of the most promising candidates for thermoelectric materials for automotive and industrial waste heat recovery applications. In this talk, I will give an overview about our recent investigations in the material design of thermoelectric half-Heusler materials. Since the price for Hafnium was doubled within the last 18 months, our research focusses on the design of half-Heusler compounds without Hafnium. I will present a very recent calculation on ZT per € and efficiency per € for various materials followed by our latest very promising results for n -type half-Heusler compounds without Hafnium resulting in 20 times higher $ZT/€$ values. Additionally and even more important are the investigations about the upscaling possibilities. Any high temperature TE material will only be suitable for the mass market if the material production and the module production is industrial upscalable. Therefore, I will focus on various upscaling approaches, their challenges, how we tackle these challenges and our recent results with the different upscaling approaches. Furthermore, I will present some very recent results on the production of a whole TEG system and how it was tested and build in in an AUDI A6, including some performance data. These results strongly underline the importance of phase separations as a powerful tool for designing highly efficient materials for thermoelectric applications that fulfill the industrial demands for a thermoelectric converter.

All research was conducted within the thermoHEUSLER² project (FKZ: 19U15006F) sponsored by the German Federal Ministry for Economic Affairs and Energy (BMWi). Partners from the German Industry are the Isabellenhütte Heusler GmbH & Co.KG, the Vacuumschmelze GmbH & Co.KG, the Fraunhofer Institute for Physical Measurement Techniques IPM, Faurecia Emissions Control Technologies, Germany GmbH, Siemens AG, and AUDI AG.

Oral-6

Fe-based half-Heusler thermoelectric materials: from FeVSb to FeNbSb

Chenguang Fu*

Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Str. 40, 01187 Dresden, Germany

*This work was done during my PhD in Zhejiang University.

Half-Heusler compounds have attracted considerable attention as promising thermoelectric power generator due to their good electrical properties, mechanical robustness and thermal stability. In this talk, we give an introduction of the newly developed FeRSb ($R = V, Nb$) -based half-Heusler thermoelectric materials. We show a systematical investigation of the differences in band structure and transport properties between FeVSb and FeNbSb, addressing why the TE performance of latter is better. As a typical heavy-band TE material, FeNbSb compound has distinct characteristics, such as large density of state effective mass, high optimal carrier concentration. By rationally selecting heavier Hf dopant, simultaneous optimization of power factor and thermal conductivity can be realized in p-type FeNb_{1-x}Hf_xSb system. As a result, a high zT of ~ 1.5 is obtained at 1200 K, which is one of the highest values among half-Heusler TE materials. Based on the p-type compound and the state-of-the-art *n*-type ZrNiSn-based compound, an 8×8 prototype half-Heusler TE module was assembled through cooperation, which exhibits a high conversion efficiency of 6.2% and a high power density of 2.2 Wcm⁻² at a temperature difference of 655 K. These findings highlight the optimization strategy for heavy-band TE materials and demonstrate a realistic prospect of high-temperature modules based on half-Heusler alloys with low cost, excellent mechanical robustness and thermal stability.

Oral-7

Structure and Thermoelectric Properties of MgAgSb compound

Pingjun Ying¹, Jiong Yang², Wenqing Zhang², Tiejun Zhu*¹, Xinbing Zhao¹

1. State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China.
2. Materials Genome Institute, Shanghai University, 99 Shangda Road, Shanghai, 200444, China.

MgAgSb-based alloy system is a promising thermoelectric (TE) material near room-temperature and is paid increasing attention because of its abundant constituent elements in earth's crust. In the present work, the structure and thermoelectric properties of MgAgSb-based alloy were studied. Firstly, Bulk α -MgAgSb with improved phase purity has been obtained and its carrier concentration has been optimized by In doping. Single parabolic band (SPB) model is applied to analyze the charge carrier transport in α -MgAgSb. A maximum zT of ~ 1.1 was achieved at 525 K for α -MgAgSb_{0.99}In_{0.01} with the optimal carrier concentration of $8\sim 9 \times 10^{19} \text{ cm}^{-3}$. Secondly, we elucidate the coexistence of global and local weak chemical bonds as the origin of the intrinsically low lattice thermal conductivity of non-caged structure Nowotny-Juza compound, α -MgAgSb. The global weak bonds of the compound lead to a low sound velocity. The unique three-centered Mg-Ag-Sb bonds in α -MgAgSb vibrate locally, and induce low frequency optical phonons, resulting in "rattling-like" thermal damping to further reduce the lattice thermal conductivity.

Invited-5

Dynamics of entropy, charge and energy in thermoelectric materials and devices

Armin Feldhoff

Leibniz University Hannover, Institute of Physical Chemistry and Electrochemistry,
Callinstraße 3A, 30167 Hannover, Germany
E-Mail: armin.feldhoff@pci.uni-hannover.de

The beauty and basic principles of thermoelectric energy conversion are hidden to the spectator by viewing it through the glasses of the so-called thermodynamics of irreversible processes, which uses rather abstract kinetic matrix and generalized forces to describe the flux of substance-like quantities electric charge and thermal energy (i.e. heat). However, when entropy is considered as basic substance-like quantity in equal rank to electric charge and energy, an easily interpretable transport equation can be derived, which gives the benefit of a clear view on the energy conversion processes taking place in thermoelectric materials and devices [1, 2]. A direct entropic approach is chosen to describe the fluxes of entropy and electric charge, which appear when a thermoelectric material is placed in gradients of the respective thermodynamic potentials. A thermoelectric material tensor is obtained, which is only composed of the Seebeck coefficient, the isothermal electrical conductivity, and the electrically open-circuited entropy conductivity. The thermoelectric material tensor allows describe the magnitude of flux densities of entropy, electric charge and associated energy (i.e. thermal and electrical), if the thermoelectric material is placed in gradients of the respective thermodynamic potentials (i.e. the absolute temperature and the electrochemical potential). The operational principle of devices, which result from the proper connection of different materials, can be easily understood. The benefit of the direct entropic approach is that it not only provides a new quality to the discussion of thermoelectric materials and devices but also facilitates descriptions of thermoelectric phenomena and the underlying energy transfer process from thermal to electric carrier or vice versa. Theoretical guidance to the material scientist is deduced.

References:

- [1] Feldhoff, *Energy Harvesting and Systems*, 2015, 2, 3-4.
- [2] Feldhoff, *Energy Harvesting and Systems*, 2015, 2, 5-13.

Invited-6

Doping of Conjugated Polymer Films for Flexible Thermoelectrics

Sabine Ludwigs

Chair of Structure & Properties of Polymeric Materials, University of Stuttgart,

Pfaffenwaldring 55, 70569 Stuttgart

Email: sabine.ludwigs@ipoc.uni-stuttgart.de

The talk will give an overview of current research activities in my group on the synthesis of novel semiconducting polymer architectures, film preparation via morphology control and the influence of doping on film properties. I will introduce electrochemical and chemical doping strategies for applications in thermoelectric devices.

One of the recent highlights includes in-situ doping and crosslinking of a redox conjugated polymer system based on polythiophene and triphenylamine units as pending redox moieties. These films provide very high stabilities with high conductivities as evidenced by four-point-probe measurements. Reversible charging with high degrees of doping is furthermore achieved by reduction of an n-type semiconducting polymer with naphthalenebisimide units in the main chain.

Oral-8

Porous $\text{Ca}_3\text{Co}_4\text{O}_9$ with enhanced thermoelectric properties

M. Bittner^{1,*}, L. Helmich¹, F. Nietschke², B. Geppert¹, O. Oeckler², A. Feldhoff¹

1. Institute of Physical Chemistry and Electrochemistry, Leibniz University Hannover, Callinstraße 3A, D-30167 Hannover, Germany

2. Institute for Mineralogy, Crystallography and Materials Science, Leipzig University, Scharnhorststraße 20, D-04275 Leipzig, Germany

*E-Mail: michael.bittner@pci.uni-hannover.de

Porous $\text{Ca}_3\text{Co}_4\text{O}_9$ thermoelectric oxide ceramics for high-temperature application [1-3] were obtained by sol-gel synthesis and subsequent conventional sintering. Growth mechanism of misfit-layered $\text{Ca}_3\text{Co}_4\text{O}_9$ phase, from sol-gel synthesis educts and upcoming intermediates, was characterized by in-situ X-ray diffraction, scanning electron microscopy and transmission electron microscopy investigations. The $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramic exhibits a relative density of 67.7%. Thermoelectric properties were measured in pressing direction and perpendicular to it in the range from 373 K to 1073 K. At 1073 K a power factor of $2.46 \text{ W cm}^{-1}\text{K}^{-2}$, a very low heat conductivity of $0.63 \text{ W m}^{-1}\text{K}^{-1}$ and entropy conductivity of $0.61 \text{ mW m}^{-1}\text{K}^{-2}$ were achieved. The maintained figure of merit ZT of 0.4 from sol-gel synthesized $\text{Ca}_3\text{Co}_4\text{O}_9$ is the highest obtained from conventional, non-doped $\text{Ca}_3\text{Co}_4\text{O}_9$. The high porosity and consequently reduced thermal conductivity, see Fig. 1, leads to a high ZT value.

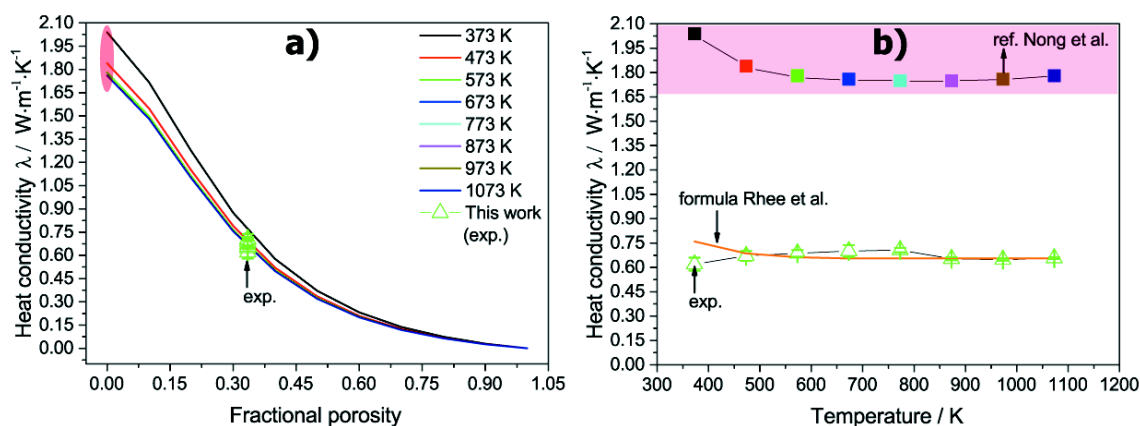


Figure 1: Heat conductivity: (a) as a function of the fractional porosity of a ceramic $\text{Ca}_3\text{Co}_4\text{O}_9$ sample. (b) as a function of temperature for a dense (red rectangle), taken from [4] and a porous (green, triangle) $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramic sample and calculated values (orange), according to [5]. Figure taken from [1].

References:

- [1] M. Bittner et al, *J. Eur. Ceram. Soc.*, [doi:10.1016/j.jeurceramsoc.2017.04.059](https://doi.org/10.1016/j.jeurceramsoc.2017.04.059)
- [2] M. Bittner et al., *Energy Harvesting and Systems*, 2016, 3, 213-222.
- [3] A. Feldhoff er al., *Energy Harvesting and Systems*, 2014, 1, 69-78.
- [4] N.V. Nong et al., *Adv. Mater.*, 2011, 23, 2484–2490.
- [5] S. K. Rhee, *Mater. Sci. Eng.*, 1975, 20, 89–93.

Oral-9

Band structure modification of the thermoelectric Heusler-phase TiFe_2Sn via Mn substitution

Tianhua Zou¹, Tiantian Jia^{2,3}, Wenjie Xie¹, Yongsheng Zhang^{2,3}, Marc Widenmeyer¹, Xingxing Xiao¹, Anke Weidenkaff¹

1. Institute for Materials Science, University of Stuttgart, 70569 Stuttgart, Germany.
2. Key laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, 230031 Hefei, P.R. China.
3. University of Science and Technology of China, 230026 Hefei, P.R. China

Doping (or substitution)-induced modification of the electronic structure to increase the electronic density of states (eDOS) near the Fermi level is considered as an effective strategy to enhance the Seebeck coefficient, and may consequently boost thermoelectric performance. Through density-functional theory calculations of Mn-substituted $\text{TiFe}_{2-x}\text{Mn}_x\text{Sn}$ compounds, we demonstrate that the *d*-states of the substituted Mn atoms induce a strong resonant level near the Fermi energy. Our experimental results are in good agreement with the calculations. They show that Mn substitution results in a large increase of the Seebeck coefficient, arising from an enhanced eDOS in Heusler compounds. The results prove that a proper substitution position and element selection can increase the eDOS, leading to a higher Seebeck coefficient and thermoelectric performance of ecofriendly materials.

Poster-1

Studying the miscibility gap in $Mg_2(Si,Sn)$: influence on microstructure and thermoelectric properties

M. Yasseri^{1,2}, A. Sankhla¹, H. Kamila¹, N. Farahi¹, J. de Boor¹, E. Müller^{1,2}

1. German Aerospace Center (DLR), Institute of Materials Research, Germany
2. JLU Giessen, Institute of Inorganic and Analytical Chemistry, Giessen, Germany

In recent years, n-type $Mg_2Si_xSn_{1-x}$ has attracted much attention, giving high zT_{max} values of ~ 1.1 - 1.4 for Sb-doped $Mg_2Si_{0.4}Sn_{0.6}$ solid solutions due to a convergence of the two lowest lying conduction bands [1]. The theoretical predictions for the optimum Si:Sn ratio vary from around 40:60 to 30:70. According to previous studies it is claimed that there is a miscibility gap for the $Mg_2Si_xSn_{1-x}$ system, where it is not possible to obtain a single solid solution. However, there is a contradiction in the exact values of the miscibility range boundaries reported, where the miscibility range varies from $0.4 < x < 0.6$ to $0.03 < x < 0.9$ [2-4]. A miscibility gap gives a chance for in-situ nanostructuring and hence for further reduction of the thermal conductivity; hence its understanding is important for a possible further optimization.

In this work, high energy ball milling was used as a non-equilibrium synthesis route and the effect of sintering/ annealing on the microstructure was studied to investigate thermodynamic stable phases and, hereby, the range of the miscibility gap. Three groups of n-type Sb- doped $Mg_2Si_xSn_{1-x}$ samples with compositions of $x = 0.3$ and $x = 0.4$ (supposedly outside the miscibility gap) and $x = 0.5$ within the miscibility range were synthesized. After ball milling, the samples were sintered at different temperatures and holding times. The phase evolution of the three compositions was investigated using XRD and SEM/EDAX. EDAX results revealed that there is a fluctuation in the silicon content of the doped $Mg_2Si_{0.3}Sn_{0.7}$ solid solution over its matrix after sintering at $750\text{ }^\circ\text{C}$ for 5 min, which could likely be resolved by increasing the sintering/ annealing time. The samples with the $Mg_2Si_{0.5}Sn_{0.5}$ and $Mg_2Si_{0.4}Sn_{0.6}$ compositions (sintered at $700\text{ }^\circ\text{C}$ for 20 min) contain Si-rich secondary phases in a micro range size with an area percentage of $\sim 11\%$ and $\sim 1\%$, respectively, implying the existence of multiphase materials. Upon increasing the sintering time up to 60 min for $Mg_2Si_{0.5}Sn_{0.5}$, the percentage of Si-rich phases reduced to an area percentage of $\sim 2\%$ possibly through an interdiffusion within the matrix. Furthermore, a single solid solution of $Mg_2Si_{0.5}Sn_{0.5}$ was obtained at $750\text{ }^\circ\text{C}$ after 20 min of sintering. These results indicate that there is no miscibility gap for the

Mg₂Si_xSn_{1-x} composition at temperatures higher than 750 °C. The lattice thermal conductivity of the single phase Mg₂Si_{0.3}Sn_{0.7} and Mg₂Si_{0.5}Sn_{0.5} samples was obtained as 1.8±0.1 Wm⁻¹K⁻¹ at RT, while that of the multiphase Mg₂Si_{0.5}Sn_{0.5} was 1.9±0.1 Wm⁻¹K⁻¹. The higher thermal conductivity of the latter might be due to the existence of the secondary phases together with the lower Sn content. A maximum figure of merit (zT_{\max}) of 1.2±0.2 (at 800 K) was achieved for Sb-doped Mg₂Si_{0.5}Sn_{0.5} and zT_{\max} of the Sb-doped Mg₂Si_{0.4}Sn_{0.6} and Mg₂Si_{0.3}Sn_{0.7} composition was ~1.4±0.2 (at 800 K), comparable with the best results reported in literature [1]. The single phase Mg₂Si_{0.5}Sn_{0.5} sample had a density of 11% lower than that of Mg₂Si_{0.3}Sn_{0.7} along with a competitive zT_{\max} (1.2±0.2). These traits corresponding to Mg₂Si_{0.5}Sn_{0.5} might be more attractive for space or any application where light weight material is desired.

References:

- [1] W. Liu et al., *Phys. Rev. Lett.*, 2012, 108, 166601.
- [2] A.U. Khan et al., *Acta Materialia.*, 2014, 77, 43-53.
- [3] I.-H. Jung et al., *CALPHAD*. 2007, 31, 192–200.
- [4] R. Vennois et al., *Intermetallics*, 2012, 31, 145-151.

Poster-2

Tailoring the structure and thermoelectric properties of BaTiO₃ via Eu²⁺ substitution

Xingxing Xiao¹, Marc Widenmeyer¹, Wenjie Xie¹, Tianhua Zou¹, Songhak Yoon¹, Marco Scavini^{2, 3}, Stefano Checchi², Zhicheng Zhong⁴, Philipp Hansmann⁴, Stefan Kilper¹, Andrei Kovalevsky⁵, Anke Weidenkaff¹

1. University of Stuttgart, Institute for Materials Science, Heisenbergstr. 3, 70569 Stuttgart, Germany
2. University of Milan, Chemistry Department, Via C. Golgi 19, I-20133 Milano, Italy
3. CNR-ISTM, Ist. Sci. & Tecnol. Mol., I-20133 Milan, Italy
4. Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany
5. CICECO - Aveiro Institute of Materials, University of Aveiro, Department of Materials and Ceramic Engineering, 3810-193 Aveiro, Portugal

A series of Ba_{1-x}Eu_xTiO_{3-δ} (0.1 ≤ x ≤ 0.9) phases with ~ 40 nm particle size were synthesized via a Pechini method followed by annealing and sintering under reducing atmosphere. The effects of Eu²⁺ substitution on the BaTiO₃ crystal structure and thermoelectric transport properties were systematically investigated. According to synchrotron X-ray diffraction data only cubic perovskite structures were observed. On the local scale below about 20 Å (equal to ~ 5 unit cells) deviations from the cubic structure model (Pm3̄m) were detected by evaluation of the pair distribution function (PDF). These deviations cannot be explained by a simple symmetry breaking model like in EuTiO_{3-δ}. The best fit was achieved in space group Amm2 allowing for a movement of Ti and Ba/Eu along <110> of the parent unit cell as observed for BaTiO₃. Density functional calculations delivered an insight into the electronic structure of Ba_{1-x}Eu_xTiO_{3-δ}. From the obtained density of states a significant reduction of the band gap by the presence of filled Eu²⁺ 4f states at the top of the valence band was observed. The physical property measurements revealed that barium europium titanates exhibit n-type semiconducting behavior and that at high temperature the electrical conductivity is strongly depended on the Eu²⁺ content, shown in Fig.1. Activation energies calculated from the electrical conductivity and Seebeck coefficient data indicate that at high temperature (800 K < T < 1123 K) the conduction mechanism of Ba_{1-x}Eu_xTiO_{3-δ} (0.1 ≤ x ≤ 0.9) is a polaron hopping when 0 < x ≤ 0.6 and is a thermally activated process when

$0.6 < x < 1$. Besides, the thermal conductivity increases with increasing Eu^{2+} concentration. Due to a remarkable improvement of the power factor, $\text{Ba}_{1-x}\text{Eu}_x\text{TiO}_{3-\delta}$ showed a ZT value of 0.24 at 1123 K. [1]

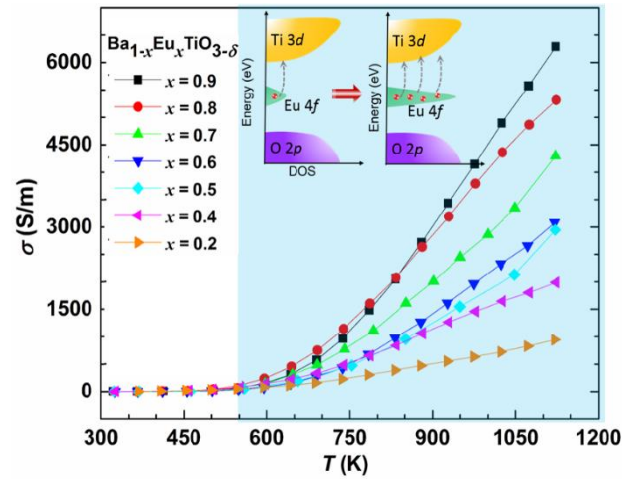


Figure 2: Temperature dependence of the electrical conductivity of sintered $\text{Ba}_{1-x}\text{Eu}_x\text{TiO}_{3-\delta}$ bulk samples.

References:

[1] Xingxing Xiao et al., *Phys. Chem. Chem. Phys.* 2017,19, 13469-13480.

Poster-3

Phase Analysis and Thermoelectric Properties of TiNiSn Based half-Heusler Thermoelectric Materials

N. Farahi^{1,*}, C. Stiewe¹, P. Ziolkowski¹ and E. Müller^{1,2}

1. Institute of Materials Research, German Aerospace Center, 51147 Cologne, Germany
2. Institute of Inorganic and Analytical Chemistry, Justus Liebig University Giessen, D- 35392 Giessen, Germany

*Nader.Farahi@dlr.de

Half-Heusler materials are ternary systems of the composition XYZ, in contrast to the full Heusler materials of composition XY₂Z. X belongs to the transition metals (group 3 to 8), Y and Z are metals of group 9 to 13 and 14 to 16, respectively. Half-Heusler materials offer a wide range of compositions which allows for partial substitution, which can be used for fine tuning of thermoelectric properties and specifically reducing the thermal conductivity through optimized phonon scattering.

Interesting candidates for n-type thermoelectric (TE) materials are TiNiSn and compounds derived from that by partial substitution of these elements. A major challenge in the synthesis of TiNiSn system is its incongruent melting and decomposition into TiNi₂Sn (full Heusler), Ti₂Sn and Sn at 1453 K. In contrast, known TE half-Heuslers materials like ZrNiSn and HfNiSn melt congruently. Another obstacle for material preparation is the high reactivity of the melt, especially interaction of refractory crucible materials with melted NiTi shape-memory alloy, which leads to the contamination of the TE material. Thus melting the material in graphite, alumina or zirconia is not practical. One suitable synthesis route could be the arc melting of the pure elements due to high melting point of Ti and Ni. Because of the very different melting temperatures and vapour pressures of the individual melts, arc melting may lead to evaporation and thus loss of some constituents, resulting in a change in stoichiometry of the material. Furthermore homogenization of the melt turns out to be an important issue. Therefore several times re-melting of the droplet and subsequent annealing have been studied. An excess of Ni could result in the formation of a nano- or micro structure full-Heusler (FH) phase in the half-Heusler (HH) matrix, leading to a reduced thermal conductivity [1, 2].

In this study, sample series of TiNi_{1.1}Sn-based materials have been synthesised with partial substitution of Ti by Zr, Sn by Si and combined substitution. Results of the phase and microstructure analyses, functional homogeneity and thermoelectric properties will

be presented and discussed.

References:

- [1] A. Bhardwaj, et al., *Phys. Chem. Chem. Phys.*, 2015, 17, 30090-30101.
- [2] S. Chen, et al. *Mater. today* 2013, 16, 387-395.

Poster-4

Realizing band structure modification and energy filtering effect in β -Zn₄Sb₃ based nanocomposites

Tianhua Zou^{*}, Wenjie Xie, Xingxing Xiao, Marc Widenmeyer, Anke Weidenkaff
Institute for Materials Science, University of Stuttgart, 70569 Stuttgart, Germany

β -Zn₄Sb₃ is one of the most promising thermoelectrics on account of its low glasslike thermal conductivity and good electrical properties at moderate temperature. We found that La-substitution in β -(Zn_{1-x}La_x)₄Sb₃ enhances electrical conductivity and power factor (PF) as well as it substantially reduces the thermal conductivity. These synergistic effects of La-substitution are discussed in terms of the substitution-induced resonant distortion in electronic density of states as well as stronger phonon scattering. Further in β -Zn₄Sb₃ based composites incorporated with nanophase Cu₃SbSe₄, we concurrently realize ~30% increase in PF through an energy filtering effect (EFE) and twofold reduction in lattice thermal conductivity. Finally, we achieve ~40% increase of PF by simultaneous resonant distortion via Pb-substituting and EFE via introduction of interface potentials, and a twofold reduction of the lattice thermal conductivity due to interface scattering in Cu₃SbSe₄/ β -(Zn_{1-x}Pb_x)₄Sb₃ nanocomposites.