DS 43: Thermoelectric materials V: Bulk materials (Focused session – Organizers: Meyer, Heiliger)

Time: Friday 13:30–16:00 Location: H 2032

Topical Talk DS 43.1 Fri 13:30 H 2032

Potential Seebeck Microprobe: Considerations on Accuracy and Spatial Resolution — •Pawel Ziolkowski, Gregor Oppitz, Gabriele Karpinski, and Eckhard Müller — German Aerospace Center - Institute of Materials Research, Linder Höhe, D-51147 Köln

Recent developments turned the Potential Seebeck Microprobe (PSM) into a powerful tool for functional materials characterisation. A wide spectrum of applications was demonstrated on a variety of thermoelectric material classes involving bulk and thin film samples. The principle involves a heated probe tip positioned at the surface of a sample coupled to a heat sink. The tip is heating up the sample in a micro-vicinity, forming a locally focused temperature gradient. The thermovoltage of the sample is measured by thermocouples, which are connected to the probe tip and sample respectively and form independent circuits containing the probe-sample contact. By these circuits, thermovoltages and the temperature drop over the gradient region are recorded, yielding the local Seebeck coefficient. Here, we give a summary on the determining factors for accuracy and spatial resolution during Seebeck coefficient measurements. Furthermore a theoretical approach will be presented, which provides the possibility to enhance the spatial resolution by means of a deconvolution algorithm based on the apparatus function, which can be derived from measurements on reference samples containing sharp material property transitions. Based on the idea of this theoretical approach a successor of the PSM was designed for transient operation. First results will be presented, which shall demonstrate the enhanced spatial resolution.

DS 43.2 Fri 14:00 H 2032

Annealed $CoSb_3$ thin films on various substrates — Martin Friedemann, •Marcus Daniel, Gunter Beddies, and Manfred Albrecht — Institute of Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany

Looking for new energy sources, thermoelectric becomes more and more important and especially $CoSb_3$ is a promising alloy for thermoelectric applications. Besides a high figure of merit, the thermal stability of the material has to be assured. Thermal treatment can yield to strain, cracks and formation of different crystal phases. During the annealing process of $CoSb_3$ thin films deposited on thermally oxidized Si substrates, cracks occur at the surface of the films. The reason for the cracks could be the difference of the thermal expansion coefficient of Si and $CoSb_3$. In this study, 40nm thick $CoSb_x$ films have been deposited via MBE at room temperature onto substrates with different expansion coefficient in the range of 0,5 - 12 $\cdot 10^{-6}$ K^{-1}. The samples were post-annealed in ultra-high vacuum for one hour at 500°C. The composition of the films were checked by RBS before and after annealing. The samples show small differences in composition and the Sb content of the annealed samples is slightly lower than that of the initial ones. The phase formation was analysed by XRD, where $CoSb_3$ could be found as major phase. The surface morphology and the roughness of the films was investigated by AFM. For a substrate thermal expansion coefficient between 9 and 11 $\cdot 10^{-6}$ K^{-1} crack formation could be prevented and a minima in roughness was found, resulting also in a minima of electric conductivity.

DS 43.3 Fri 14:15 H 2032

Electronic and Thermoelectric properties of $RuIn_{3-x}A_x$ (A=Sn, Zn) from first principles — •Deepa Kasinathan[1], Maik Wagner[1], Helge Rosner[1], and Klaus Koepernik[2] — [1]Max Planck Institute for Chemical Physics of Solids, Noethnitzer strasse 40, 01187 Dresden, Germany — [2]IFW Dresden, P.O. Box 270116, 01171 Dresden, Germany

Recently, substitution derivatives of the intermetallic compound $RuIn_{3-x}A_x$ (A = Sn, Zn) have been shown to exhibit relatively high Seebeck coefficients. Substitution by Sn results in n-type behavior while p-type is the norm for substitution of In by Zn. We discuss in detail the electronic structure of the parent compound and the substitution derivatives obtained from density functional theory based calculations using the Full Potential Local Orbital code. The substitution effects have been studied using three different approximations: the simple virtual crystal approximation, the ordered supercell approach and the disordered coherent potential approximation. Both Sn and Zn prefer different site symmetry positions in the unit cell. While the parent compound $RuIn_3$ is a semiconductor, the substitution derivatives are not. For small doping concentrations, we observe a rather rigid-band-like behavior due to the parabolic nature of the bands forming the valence band maximum and the conduction band minimum. Transport properties calculated using the semi-classical Boltzmann transport equations based on the constant scattering approximation are consistent with the experiments. *Funding from the DFG via SPP1386 is acknowledged.*

DS 43.4 Fri 14:30 H 2032

Quantum Chemical Investigation of Filled Skutterudites as Thermoelectric Materials — Lukas Hammerschmidt and •Beate Paulus — Institut für Chemie und Biochemie, FU Berlin, Takustr. 3, 14195 Berlin

In the last few years Skutterudites attracted much interest as promising thermoelectric materials [1]. Thermoelectrics directly transform thermal energy into electric energy due to the so called "Seebeck-effect". An enhanced thermoelectric figure of merit ZT is achieved by filling the icosahedral voids of the Skutterudite crystal structure by e.g. lanthanides, actinides, alkaline (earth) metals and other electropositive elements. In our study we apply plane-wave DFT methods implemented in the VASP program package [2] for the In, Ga and Tl doped $CoSb_3$ Skutterudites and study systematically the effects of the doping concentration on density of states (DOS), charges, energies and lattice constants.

[1] B. C. Sales, D. Mandrus, R. K. Williams *Science* 272 (1996) 1325. [2] J. Hafner, *J. Comput. Chem.* 29 (2008) 2044; G. Kresse, J. Hafner, *J. Phys. Condens. Matter* 6 (1994) 8245.

DS 43.5 Fri 14:45 H 2032

Vibronic contribution to thermoelectric properties of Bi_2Te_3 and Bi_2Se_3 from first principles — •Martin Hölzer[1], Nicki F. Hinsche[2], Sergey Ostanin[1,2], and Arthur Ernst[1] — [1]Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle/S. — [2]Martin-Luther-Universität, Institut für Physik, Von-Seckendorff-Platz 1, 06120 Halle/S.

We present *ab initio*-studies of the vibronic properties of Bi_2Te_3 and Bi_2Se_3 in the harmonic approximation. In this work, we used a multi-code-approach, consisting of pseudopotential calculations and a multiple scattering Green function method to investigate the phonon frequencies, electron-phonon-coupling, and the resulting thermoelectric properties for these materials. The influence of spin-orbit interaction, which is very important for the correct description of the electronic properties of these systens, will also be discussed.

DS 43.6 Fri 15:00 H 2032

Transport and thermal properties of single- and polycrystalline $NiZr_{0.5}Hf_{0.5}Sn$ — Siham Ouardi[1,4], Gerhard H. Fecher[1,4], Claudia Felser[1,4], •Christian G.F. Blum[2], Dirk Bombor[2], Christian Hess[2], Bernd Büchner[2], Eiji Ikenaga[3], and Sabine Wurmehl[2] — [1]Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg - Universität, Mainz, Germany — [2]Leibniz Institute for Solid State and Materials Research IFW, 01171 Dresden, Germany — [3]Japan Synchrotron Radiation Research Institute, SPring-8, Hyogo 679-5198, Japan — [4]Max-Planck-Institut für Chemische Physik fester Stoffe, 01187 Dresden, Germany

The thermoelectric properties of a Heusler compound with $NiZr_{0.5}Hf_{0.5}Sn$ composition were studied. A comparison of the properties of a single crystal and a polycrystal was carried out by measurements of the electrical conductivity, Seebeck coefficient, and thermal conductivity. The transport properties are directly compared to the valence band electronic structure measured by photoelectron spectroscopy. The single crystal shows a higher figure of merit (ZT=0.1) at room temperature which originates from the high electrical conductivity that is mediated by "in-gap" states observed by high energy photoemission spectroscopy.

DS 43.7 Fri 15:15 H 2032

TiNiSn and $Zr_{0.5}Hf_{0.5}NiSn$ superlattices for thermoelectrics — •Tino Jaeger[1], Michael Schwall[2], Xeniya Kozina[2], Ben-

jamin Balke[2], Sascha Populoh[3], Anke Weidenkaff[3], Claudia Felser[2], and Gerhard Jakob[1] — [1]Institut für Physik, Universität Mainz, 55099 Mainz — [2]Institut für Analytische und Anorganische Chemie, Universität Mainz, 55099 Mainz — [3]EMPA, Ueberlandstrasse 129, 8600 Duebendorf, Switzerland

In order to increase the attractiveness of thermoelectric devices, their efficiency must be increased. Beside others, the properties of the thermoelectric material can be improved. That can be achieved by either increasing Seebeck coefficient or conductivity or by a depressed thermal conductivity along the thermal gradient. For thin films, superlattices or multilayers can be used to lower the cross plane thermal conductivity. As a bottom up approach, artificially layered films with a periodicity of about 5-6 nm are assumed to generate the most phonon scattering at the interfaces. If electrical properties remain unchanged or less effected, the thermoelectric efficiency is enhanced. Semiconducting Half-Heuslers are well studied thermoelectric bulk materials. Among others, TiNiSn and $Zr_{0.5}Hf_{0.5}NiSn$ are potential candidates. Essentially, their similar lattice constants enable epitaxial layers on top of each other. Furthermore, varied atomic masses of Ti, Zr and Hf generate the aspired alternating mass distribution. By rotating the substrate in between simultaneously burning cathodes, significant film thicknesses can be achieved by sputter deposition.

DS 43.8 Fri 15:30 H 2032

Investigations on the $Ti_xZr_yHf_zNiSn$ system. — •Michael Schwall and Benjamin Balke — Institute of Inorganic Chemistry and Analytical Chemistry, Johannes Gutenberg - University, Mainz

Half-Heusler compounds exhibit very promising thermoelectric properties for high temperature applications, combined with several additional advantages such as environmental friendliness, low production-costs and future availability of raw materials. The high thermoelectric potential can be mainly attributed to the high Seebeck coefficient and the low electrical resistivity values found recently in several half-Heusler alloys. The main obstacle is still their relatively high thermal conductivity. The best reported n-type materials are consisting of $Ti_xZr_yHf_zNiSn$ with different x ,y ,z (x+y+z=1). In this study, we investigated the reasons for this outstanding thermoelectric properties. The effect of the microstructure on the transport properties will be described in details. The authors gratefully acknowledge the financial support by the "thermoHeusler" Project (Project No. 0327876D) of the German Federal Ministry of Economics and Technology (BMWi).

DS 43.9 Fri 15:45 H 2032

Heusler compounds with $C1_b$ structure as promising p-type thermoelectric materials. — •Elisabeth Rausch, Michael Schwall, and Benjamin Balke — Institute of Inorganic Chemistry and Analytical Chemistry, Johannes Gutenberg - University, Mainz

This work reports on the experimental investigations of XCoSb (X= Ti, Zr or Hf) based Heusler compounds discussed as potential p-type thermoelectic materials. A lot of n-type materials are known and exhibt high ZT values (ZT_{max}=1.5), but there are only a few p-type materials which can achieve ZT values above 0.5. We tried to improve the thermoelectric properties by nano structring the materials. The samples were mechanical alloyed by means of a high energy ball mill. The thermoelectric properties could be enhanced due to the nano structuring of the material. We will present structural and physical properties of the synthized coumpounds including a complete high temperature thermoelectric characterisation. The authors gratefully acknowledge the financial support by the "thermoHeusler" Project (Project No. 0327876D) of the German Federal Ministry of Economics and Technology (BMWi).