Oral Presentation Program

MONDAY

8:45	**OPENING CEREMONY**		
	OPENING REMARKS		
	PLENARY SESSION (Jihui Yang)		
9:45 **10:30**	**Prof. Dr. Y. GRIN** Max Planck Institute for Chemical Physics of Solids, Dresden, Germany **"Interplay of crystal structure, chemical bonding and thermoelectric behavior"**		
10:30 **11:15**	**Prof. Dr. J-P. FLEURIAL** Jet Propulsion Laboratory - Thermal Energy Conversion Research & Advancement Group, Pasadena, California, United States of America **"A 50 Year-Long Breakthrough in the Making: Radioisotope Thermoelectric Generators with New Materials"**		
11:15 **12:00**	**Prof. Dr. T. MORI** NIMS, Tsukuba, Japan **"Utilization of Magnetism and Other Novel Principles for Thermoelectric Enhancement and Recent Activities in Asia"**		
	Amphitheater Caliste	**Atelier 1**	**Atelier 4 & 5**
	Zintl Phases **Sabah Bux**	**Applications** **Dario Narducci**	**Chalcogenides (S, Se, Te) (Modelization)** **Marco Fornari**
14:00 **14:15**	**INVITED** **Crystal Chemistry of New (and some old) Zintl Phases** Svilen Bobev *University of Delaware (US)*	**Measurement and analysis of thermal conductivity, thermal diffusivity and interfacial thermal resistance of thermoelectric thin films** Takahiro Baba *PicoTherm Corporation (Japan)*	**Electronic structure of $Sn_{1-x}In_xTe$ containing defects from KKR-CPA calculations** Janusz Tobola *AGH University of Science and Technology, Faculty of Physics and Applied Computer Science (Poland)*
14:15 **14:30**		**Wearable Thermoelectric Generators for Powering Health Monitoring Sensors** Daryoosh Vashaee *North Carolina State University (USA)*	**Modeling Dopability in Diamond-like Semiconductors Using Machine Learning for High-throughput Predictions** Samuel Miller *Northwestern University (US)*

14:30 **14:45**	**Zintl ions within framework channels: the complex structure and low-temperature transport properties of Na_4Ge_{13}** Stefan Stefanoski *Benedictine University (US)*	**INVITED** **Development of integrated micro-thermoelectric sensors for IC applications** Guillaume Savelli *Université Grenoble Alpes, CEA-Liten (France)*	**Negative Thermal Expansion of GeTe near the Ferroelectric Phase Transition from First Principles** Djordje Dangic *University College Cork (Ireland)*
14:45 **15:00**	**Experimental Investigation of Thermoelectric Properties of $KSb_{2-x}Sn_x$** Hyungyu Jin *Pohang University of Science and Technology (POSTECH) (South Korea)*		**Engineering thermal conductivity through microstructural lattice softening** Riley Hanus *Department of Materials Science and Engineering, Northwestern University (US)*
15:00 **15:15**	**The $A_{14}MPn_{11}$: good thermoelectric materials with low valley degeneracy.** Geoffroy Hautier *Institute of Condensed Matter and Nanosciences (IMCN), Université Catholique de Louvain (Belgium)*	**New prototype of a thermoelectric heat pump with heat pipes for the air condition of a Nearly Zero Energy Building** Sergio Diaz De Garayo *CENER (Spain)*	**INVITED** **Acoustically mismatched nano-inclusions** Raphael Hermann *Oak Ridge National Laboratory - MSTD (United States)*
15:15 **15:30**	**Thermoelectric properties of a new Zintl phase $NaZn_4As_3$ with ultralow thermal conductivity** Aichi Yamashita *University of Tsukuba (Japan), - WPI-MANA, NIMS - AIST (Japan)*	**Small size thermoelectric power supply for battery backup** Hossein Abedi *CNR-Institute of Condensed Matter Chemistry and Technologies for Energy, Lecco (Italy)*	
15:30 **15:45**	**INVITED** **Thermoelectric Behavior of Silver-Cluster Phosphides: Origin and Optimization** Juergen Nuss *Max Planck Institute for Solid State Research, Stuttgart (Germany)*	**Benefits of integrating vehicular thermoelectric generators with exhaust heat recovery apparatus** Byung-Wook Kim *Corporate R&D Division for Hyundai Motor Company & Kia Motors Corporation (South Korea)*	**Phonon dispersion and scattering considerations for thermoelectrics** Yanzhong Pei *School of Materials Science and Engineering, Tongji University (China)*
15:45 **16:00**		**Heat pipes thermal performance for a reversible thermoelectric cooler-heat pump system** *Aranguren Patricia* *Smart Citites Institute (Spain)*	**Rattling dynamics under a planar coordination in tetrahedrites** Chul-Ho Lee *National Institute of Advanced Industrial Science and Technology (AIST) (Japan)*

16:00 16:30	**COFFEE BREAK**		
	Modules Development and Technology Eckhard Muller	**Modelling Janusz Tobola**	**Chalcogenides (S, Se, Te) Yaniv Gelbstein**
16 :30 16 :45	**Concept of a Thermoelectric Module and Generator for Automotive Applications Based on an Integrated Functional Design** Lars Heber *Institute of Vehicle Concepts, DLR, Stuttgart (Germany)*	**INVITED** **On the Search of Novel Compounds Featuring Thermoelectric Properties. Some Suggestions Based on Theoretical Considerations** Jean-Francois Halet *Institut des Sciences Chimiques de Rennes (France)*	**Improved Thermoelectric Performance in Non-stoichiometric $Cu_{2+\gamma}Mn_{1-\gamma}SnSe_4$ Quaternary Diamond-like Compounds** Qingfeng Song *Shanghai Institute of Ceramics, Chinese Academy of Science, University of Chinese Academy of Sciences (China)*
16:45 17:00	**Demonstrated High-Performance, High-Power Skutterudite Thermoelectric Modules for Space and Terrestrial Applications** Terry Hendricks *NASA Jet Propulsion Laboratory (US)*		**Rhombohedral to Cubic Conversion of GeTe via MnTe alloying Leads to Ultralow Thermal Conductivity, Electronic Band Convergence and High Thermoelectric Performance** Tingting Zhan *Wuhan University of Technology (China)*
17:00 17:15	**Development of High Efficiency Segmented Thermoelectric Couples for Space Applications** Fivos Drymiotis *NASA Jet Propulsion Laboratory (US)*	**Minimum thermal conductivity in the context of diffuson-mediated thermal transport** Matthias Agne *Northwestern University (US)*	**Thermoelectric features of the $Cu_7P(Se_{1-x}S_x)_6$ with high copper ionic mobility** Michal Piasecki *Institute of Physics J.Dlugosz University, Czestochowa (Poland)*

17:15 **17:30**	**Silicides thermoelectric modules: performances and challenges** Krunoslav Romanjek *Université de Grenoble-Alpes (France)*	**Effects of Grain Size and Grain Boundary Nanostructures on Lattice Thermal Conductivity of MgO** Susumu Fujii *Department of Adaptive Machine Systems, Osaka University (Japan)*	**Compatibility investigation between cobalt metallized tellurides-based Thermoelectric legs and an Ag–Cu–In-based brazing alloy** Dana Ben-Ayoun *Department of Materials Engineering, Ben-Gurion University of the Negev, Beer Sheva 84105 (Israel)*
17:30 **17:45**	**Economic profitability of hybrid photovoltaic-thermoelectric solar harvesters** Dario Narducci *Dept. of Materials Science, University of Milano Bicocca (Italy)*	**Investigation of phonon states in a poor thermal crystalline conductor by means of inelastic scattering spectroscopy** Stéphane Pailhès *Institut Lumière Matière (France)*	**Native Defects in SnSe and their Temperature Dependence** Katerina Sraitrova *University of Pardubice, Faculty of Chemical Technology (Czech Republic)*
17:45 **18:00**	**Efficiency of an automated dissipation system applied to Bi_2Te_3 and multi-stage modules** Fabio Puglia *ISC - Balistic (Italy)*	**Three-dimensional finite element simulation of a flexible μ-TEG based on bismuth telluride** Soufiane Eloualid *Institut Jean Lamour (France)*	**Harnessing thermoelectric effects in vertical phase change memory cells** Jyotsna Bahl *Center for Research in Nano Technology and Sciences (CRNTS), IIT Bombay (India)*

TUESDAY

	Amphitheater Caliste Zintl Phases {Mg_3Sb_2} Svilen Bobev	Atelier 1 Chalcogenides (S, Se, Te) Paz Vaqueiro	Atelier 4 & 5 Modules Development and Technology Terry Hendrix
08:30 08:45		**Donor-type doping in BiCuSeO: from high ZT values in p-type materials towards p-to-n type switching** David Berardan *Univ. Paris-Sud (France)*	**µTEGs for Self-Powered Sensor Nodes: Device Optimization and System Integration** Jane Cornett *Analog Devices (US)*
08:45- 09:00	**INVITED** **Phase boundary mapping for the discovery and optimization of thermoelectric materials** Jeff Snyder *Northwestern University (US)*	**Thermoelectric properties of oxysulfide $Bi_{1-x}Pb_xCuOS$ compounds** Jean-Baptiste Labégorre *Laboratoire CRISMAT (France)*	**Human body-heat energy harvesters based on transverse thermoelectric effects** Je-Hyeong Bahk *EECS Dept, University of Cincinnati (US)*
09:00- 09:15		**Data-driven Discovery of Cu-S based Thermoelectric Materials** Ruizhi Zhang *School of Engineering and Material Science, Queen Mary University of London (UK)*	**Characterization of micro thermoelectric coolers with high packing density** Heiko Reith *Leibniz Institute for Solid State and Materials Research - IFW Dresden (Germany)*
09:15- 09:30	**Enhancement of average ZT of n-type $Mg_3(Sb,Bi)_2$ by increasing grain size** Hiromasa Tamaki *Panasonic Corporation (Japan)*	**INVITED** **Interplay between the structural and thermoelectric properties in Cu-S based synthetic minerals** Koichiro Suekuni *Department of Applied Science for Electronics and Materials, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University (Japan)*	**Thermoelectric nanogenerator array: a viable source of power for the autonomy of wireless sensors networks?** Dimitri Tainoff *Institut Néel (France)*
09:30- 09:45	**Probing the Thermal Stability Te-doped $Mg_3Sb_{1.5}Bi_{0.5}$ via Combined Total Scattering and Powder Diffraction** Lasse Rabøl Jørgensen *Center for Materials Crystallography, Department of Chemistry, Aarhus University (Denmark)*		**A High Efficient Thermoelectric Module with Heat Storage utilizing Sensible Heat for IoT Power Supply** Kanae Nakagawa *FUJITSU LABORATORIES LTD. (Japan)*

09:45-10:00	**Observation of Valence band crossing: The Thermoelectric Properties of the $CaZn_2Sb_2$-$CaMg_2Sb_2$ Solid Solution** Max Wood *Northwestern University (US)*	**A structural and thermoelectric study of a Cu-rich sulfide family: the germanite $Cu_{26-x}Fe_{4+x}Ge_4S_{32}$** Laura Paradis-Fortin *Laboratoire CRISMAT - Institut des Sciences Chimiques de Rennes (France)*	**Fabrication and characterization of thermoelectric generators based on silicon nanowire forests** Giovanni Pennelli *Dipartimento di Ingegneria dellÕnformazione, University of Pisa (Italy)*
10:00-10:15	**INVITED** **Chemical bonding in layered thermoelectric materials** Bo Iversen *Center for Materials Crystallography, Department of Chemistry, Aarhus University (Denmark)*	**High-performance thermoelectric bulk colusite by process controlled structural disordering** Cédric Bourgès *Department of Applied Physics, Graduate School of Engineering, Tohoku University (Japan)*	**Development of high durability substrate for thermoelectric module** Koya Arai *Central Research institute, Mitsubichi materials corporation (Japan)*
10:15-10:30		**Effect of composition on thermoelectric properties of as-cast materials: the $Cu_{12-x}Co_xSb_4S_{13-y}Se_y$ case** Antonio Pereira Goncalves *C²TN (Portugal), Institut für Mineralogie (Germany)*	**Experimental evidence for separation of thermally generated bipolar charge carriers within a p-i-n-junction** Franziska Maculewicz *University of Duisburg-Essen, Institute of Technology for Nanostructurs & CENIDE (Germany)*
10:30-11:00	**COFFEE BREAK**		
	Applications **Guillaume Savelli**	**Chalcogenides (S, Se, Te)** **Holger Kleinke**	**Other materials** **Ernst Bauer**
11:00-11:15	**Very long lifetime terrestrial RTG with Americium heat power source** Joël Dufourcq *HotBlock OnBoard (France)*	**Pulsed Hybrid Reactive Magnetron Sputtering as a new technique to obtain high quality selenides** Marisol Martin Gonzalez *Instituto Micro y Nanotecnología IMN-CNM (Spain)*	**Electron-poor Al-Ge narrow gap semiconductors: comparison with thermoelectric Zn-Sb compounds** Mickael Beaudhuin *Institut Charles Gerhardt Montpellier - Institut de Chimie Moléculaire et des Matériaux de Montpellier (France)*

11:15-11:30	**Modeling and Simulation of a Thermoelectric Generator Using Bismuth Telluride for Waste Heat Recovery in Automotive Diesel Engine** Ali Nour Eddine *École Centrale de Nantes (France)*	**Improved electrical transport properties and optimized thermoelectric figure of merit in lithium-doped copper sulfides** Mengjia Guan *Shanghai Institute of Ceramics, Chinese Academy of Science (China)*	**Structural analysis of beta- and gamma-phases of Zn_4Sb_3 thermoelectrics** Kei Hayashi *Department of Applied Physics, Graduate School of Engineering, Tohoku University (Japan)*
11:30-11:45	**RTGs: the enduring and the future** David Woerner *Jet Propulsion Laboratory (United States)*	**Suppressing Intervalley scattering for p-type InTe by nanoprecipitates** Xu Lu *Chongqing University (China)*	**Kondo-like phonon scattering in thermoelectric clathrates** Silke Paschen *Institute of Solid State Physics, Vienna University of Technology (Austria)*
11:45-12:00	**Power Enhancement of Si Membrane-based Thermoelectric Generator by Aluminium Ultrathin Layer Deposition** Ryoto Yanagisawa *IIS, The University of Tokyo (Japan)*	**Unconventional Heat Transport Induced by Phase Transition in $Cu_{2-x}Se$** Dimitri Vasilevskiy *Ecole Polytechnique de Montreal - TEMTE Inc (Canada)*	**Looking for stable thermoelectric materials** Karl Frederik Færch Fischer *Department of Chemistry, Aarhus University (Denmark)*
12:00-12:15	**Holistic Optimization of Thermoelectric Generators for Automotive Applications Reaching a Cost Benefit Ratio of 81 €/g/km** Martin Kober *Deutsches Zentrum für Luft- und Raumfahrt [Stuttgart] (Germany)*	**INVITED** **Intrinsically low thermal conductivity in metal chalcogenides for high performance thermoelectric energy conversion** Kanishka Biswas *Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), (India)*	**Thermoelectric Properties and Search for condition of insulator transition in Al-Ir based quasicrystalline approximants** Yutaka Iwasaki *Department of Advanced Materials Science,The University of Tokyo (Japan)*
12:15-12:30	**A versatile system for Hall effect measurements at high temperature** Murat Gunes *Univ Paris Sud, Univ Paris Saclay (France)*		**Suppression of vacancies boosts thermoelectric performance in type-I clathrate** Xinlin Yan *Institute of Solid State Physics, Vienna University of Technology (Austria)*
12:30-14:00	**LUNCH**		

	Other materials {Heusler} Benjamin Balke	Silicides Bo Iversen	Chalcogenides (S, Se, Te) {Telluride} Jan Konig
14:00-14:15	**INVITED** **Understanding and tuning full-Heusler thermoelectric materials based on Fe_2VAl** Ernst Bauer *Christian Doppler Laboratory for Thermoelectricity, Institute of Solid State Physics, Technische Universitat Wien (Austria)*	**Rapid oxidation in $Mg_2(Si\text{-}Sn)$ alloys; optimization via tin reduction and nanostructuring approach** Christelle Navone *Univ. Grenoble Alpes, CEA-LITEN (France)*	**Thermoelectric Performance of Bi_2Te_3 by Acceptor Type Germanium Doping** Niraj Singh *School of Basic Sciences, Indian Institute of Technology Mandi, (India)*
14:15-14:30		**Exploit Si-kerf from Photovoltaics: A Promising Application on the Thermoelectrics** Theodora Kyratsi *University of Cyprus (Cyprus)*	**Increasing of Z factor for Bi_2Te_3-Sb_2Te_3** Zinovi Dashevsky *SCTB NORD Company (Russia)*
14:30-14:45	**Thermoelectric properties of p- and n-type doped ScNiSb** Donald Morelli *Michigan State University (US)*	**Insight on band structure of p-type $Mg_2Si_{1-x}Sn_x$ with x=0-1 using a single parabolic band** Hasbuna Kamila *German Aerospace Center (DLR) (Germany)*	**INVITED** **Nano-SiC-dispersed Thermoelectric Composites** Jing-Feng Li *State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University (China)*
14:45-15:00	**Facile Synthesis of FeNbSb based Half-Heusler Thermoelectric Materials** Nader Farahi *German Aerospace Center (DLR) (Germany)*	**Contact development for n and p-type $Mg_2(Si,Sn)$** Johannes De Boor *German Aerospace Center (DLR) (Germany)*	
15:00-15:15	**Phonon scattering by antiphase boundaries in Fe_2VAl** Eric Alleno *Institut de Chimie et des Matériaux Paris Est (France)*	**INVITED** **Recent Progress in Silicide-based Thermoelectric Materials** Yuzuru Miyazaki *Department of Applied Physics, Graduate School of Engineering, Tohoku University (Japan)*	**Thermoelectric and transport properties of n-type palladium doped chalcopyrite $Cu_{1-x}Pd_xFeS_2$ compounds** Jiri Navratil *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic (Czech Republic)*

15:15-15:30	**Industrialized Half-Heusler material and thermoelectric modules therefrom** Daniel Zuckermann Isabellenhütte Heusler GmbH & Co. KGDillenburgGermany		**Effects of defects induced by pressure and temperature on thermoelectric $CuGaTe_2$ chalcopyrite structure materials** Yosuke Fujii *Osaka Prefecture University (Japan)*
15:30-15:45	**High-Entropy Half-Heusler Thermoelectrics with High ZT~1.5** Peter Franz Rogl *Institute of Materials Chemistry, University of Vienna (Austria)*	**INVITED** **$Mg_2Si_{1-x}Sn_x$ solid solutions: phase formation and challenges in their electrical contacting** Vicente Pacheco *Fraunhofer Institute for Manufacturing Technology and Advanced Materials, IFAM (Germany)*	**Transition metals in ternary rocksalt-type tellurides? doping vs. precipitates** Oliver Oeckler *Leipzig University, Faculty of Chemistry and Mineralogy, IMKM (Germany)*
15:45-16:00	**Half-Heuslers, a compound not as stable as one stipulate.** Robin Lefèvre *Interdisciplinary Nanoscience Center (iNANO) (Denmark)*		**Chalcogenide-based nanocomposites for thermoelectric applications** Valentina Giordano *Institut Lumière Matière (France)*
16:00-16:30	**COFFEE**		
	New materials and New Materials Discovery **Jeffrey Snyder**	**Modelling** **Jean-Francois Halet**	**Zintl Phases {Other Phases}** **Jürgen Nuss**
16:30-16:45	**INVITED** **Composite Structures in Thermoelectric Materials** Holger Kleinke *University of Waterloo (Canada)*	**Molecular dynamics simulations to understand phonon transport in nanoporous materials** Laura De Sousa Oliveira *University of Warwick [Coventry] (United Kingdom)*	**Computational Investigation of n-type Doping of Layered Antimonides: Mg_3Sb_2 and KSnSb** Prashun Gorai *Colorado School of Mines, National Renewable Energy Laboratory (US)*
16:45-17:00		**Thermoelectric properties of TiNiSn and ZrNiSn half-Heusler alloys through ab-initio calculation and experiments** Lorenzo Maschio *Università degli Studi di Torino (Italy)*	**New Insight on Tuning Electrical Transport Properties via Chalcogen Doping in n-type Mg_3Sb_2-Based Thermoelectric Materials** Jiawei Zhang *Center for Materials Crystallography, Department of Chemistry, Aarhus University (Denmark)*

17:00-17:15	**High ZT in MnTe via spin physics** Joseph Heremans *The Ohio State University (United States)*	**INVITED** **Defects and their influence on the thermoelectric properties of materials: an ab initio study** Philippe Jund *Institut Charles Gerhardt - Université de Montpellier (France)*	**HRPD and HREM study of p- and n-type semiconductor $Y_xAl_yB_{14}$** Tsuyoshi Kajitani *Institute of Multidisciplinary Research for Advanced Materials (IMRAM) Tohoku University (Japan)*
17:15-17:30	**Dopant Induced Impurity Bands and Carrier Concentration Control for Thermoelectric Enhancement in p-Type $Cr_2Ge_2Te_6$** Guoyu Wang *College of Physics, Chongqing University (China)*		**First principles study on the thermoelectric properties of 122 Zintl phase compounds** Hidetomo Usui *Department of Physics, Osaka University (Japan)*
17:30-17:45	**Large Nernst power factor in polycrystalline topological semimetal NbP** Chenguang Fu *Max Planck Institute for Chemical Physics of Solids (Germany)*	**Quantum transport simulations of thermoelectric power factor in materials with hierarchical nanostructuring** Vassilios Vargiamidis *School of Engineering, University of Warwick (UK)*	**Band engineering of the Mg_3Sb_2-Mg_3Bi_2 alloy composition investigated with transport analysis** Kazuki Imasato *Northwestern University (US)*
17:45-18:00	**Development of high-performance thermoelectric materials guided by large-scale experimental data** Takushi Kodani *National Institute for Materials Science - The University of Tokyo (Japan)*	**Defect-induced simultaneous increase of the conductivity and Seebeck coefficient in p-doped polycrystalline materials and enhanced thermoelectric power factor** Xanthippi Zianni *Dept. of Aircraft Technology, Technological Educational Institution of Sterea Ellada (Greece)*	**High thermoelectric properties of As-based 122-Zintl coupounds $Ba_{1-x}K_xCd_2As_2$** Haruno Kunioka *National Institute of Advanced Industrial Science and Technology (AIST) - Tokyo University of Science (Japan)*
18:00-18:15	**Experimental force multipliers for accelerating thermoelectric material discovery** Eric Toberer *Colorado School of Mines (US)*	**Metamaterials for Harnessing Thermoelectric Flow** Lilia Woods *University of South Florida (US)*	

18:15-18:30	**A Valence Balanced Rule for Discovery of new Dimensions of defective half-Heuslers** Anand Shashwat *Northwestern University (US)*	**Detailed Transient Multiphysics Model for Fast and Accurate Design, Simulation and Optimization of a Thermoelectric Generator (TEG) or Thermal Energy Harvesting Device** Alfred Piggott *Applied Thermoelectric Solutions LLC (US)*	

WEDNESDAY

	Amphitheater Caliste Chalcogenides (S, Se, Te) Emmanuel Guilmeau	Atelier 1 New Materials and New Materials Discovery Eric Toberer	Atelier 4 & 5 Modelling Hsin Wang
08:30-08:45	**Mechanochemistry for Thermoelectrics: Nanobulk Mawsonite $Cu_6Fe_2SnS_8$ Synthesized in an Industrial Mill** Peter Balaz *Institute of Geotechnics (Slovakia)*	**INVITED** **Structure and bonding, and their role in thermal transport of materials for thermoelectrics applications: It's not just about skutterudites and clathrates anymore!** Georges Nolas *University of South Florida (US)*	
08:45-09:00	**Copper rich complex Sulfides for Thermoelectric applications** Pavan Kumar Ventrapati *Laboratoire CRISMAT (France)*		**Direct Current Polarity-Reversal Technique to Measure the Thomson Coefficient to Determine the Absolute Seebeck Coefficient** Yasutaka Amagai *National institute of advanced industrial Technology (Japan)*
09:00-09:15	**Low-temperature structure of tetrahedrite** Paz Vaqueiro *University of Reading (UK)*	**Shock-compression as a novel method of preparation of nanostructured $CoSb_3$ skutterudite** Krzysztof Wojciechowski *AGH University of Science and Technology (Poland)*	**INVITED** **The Effective Mass: Our Stranger Friend** Marco Fornari *Central Michigan University (US)*
09:15-09:30	**Nanoparticle-dispersed $Cu_{12}Sb_4S_{13}$-based thermoelectric composites** Fu-Hua Sun *State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University (China)*	**High-pressure synthesis of tetragonal iron aluminide $FeAl_2$** Kazuki Tobita *The University of Tokyo (Japan)*	

09:30-09:45	**INVITED** **Mineral-Related Sulphides and Selenides for Thermoelectric Energy Harvesting** Anthony V. Powell *University of Reading (UK)*	**Optimization of Thermoelectric Transport Properties on Weak Topological Insulator $Bi_{14}Rh_3I_9$** Ping Wei *State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology (China)*	**A Study on the Reliability of Thermoelectric Couple Networks** Christopher Matthes *NASA Jet Propulsion Laboratory, California Institute of Technology (US)*
09:45-10:00		**Metal Phosphides as Overlooked Thermoelectric Materials** Umut Aydemir *Department of Chemistry, Koc University (Turkey)*	**Phonon transport across a Si/Ge interface: the role of inelastic scattering** Jesse Maassen *Dalhousie University (Canada)*
10:00-10:15	**Thermoelectric Performance of Tetrahedrite Synthesized by a Solution-Phase Method** Daniel Weller *Michigan State University (US)*	**A web application "Starrydata" for collecting and sharing plot data on published papers** Masaya Kumagai *SAKURA Internet Inc. (Japan)*	**The importance of considering parasitic heat losses in modelling TEG performance for high temperature application** Schwurack Roy *Technische Universität Dresden (Germany)*
10:15-10:30	**Structural phase transitions at high temperature of thermoelectric copper-based sulfides studied by in situ techniques** Pierric Lemoine *Institut des Sciences Chimiques de Rennes (France)*	**Phonons across the superionic transition in $CuCrSe_2$ and $AgCrSe_2$** Olivier Delaire *Duke University (US)*	**Theoretical study on thermoelectric properties of metal/semiconductor multilayer with weak electron-phonon coupling** Shin Yabuuchi *Hitachi, Ltd. (Japan)*
10:30-11:00	**COFFEE BREAK**		

	Chalcogenides (S, Se, Te) Anthony Powell	Modules Development and Technology Ryoji Funahashi	Oxides Jiri Hejtmanek
11:00-11:15	**Improving the thermoelectric efficiency of $La_{3-x}Te_4$ via f-orbital chemistry** Sabah Bux *Jet Propulsion Laboratory (US)*	**Reliability Evaluation System for the Thermoelectric Power Generation Module Simulating Thermal Cycle** Joon Heo *BlueSys Co., Ltd. (South Korea)*	**INVITED** **Exploiting Interfaces to Enhance the Performance of Oxide Thermoelectrics** Robert Freer *University of Manchester (UK)*
11:15-11:30	**Phase boundary mapping and phase discovery in a quaternary system: carrier density control in $Cu_2HgGeTe_4$** Brenden Ortiz *Colorado School of Mines (US)*	**A New Model for Characterising Thermoelectric Modules by Impedance Spectroscopy and its Application in Qualification and Assessing In-service Degradation** Hugo Williams *University of Leicester (UK)*	
11:30-11 :45	**INVITED** **Considerations for enhancement of the thermoelectric potential of semiconductors** Yaniv Gelbstein *Ben Gurion University (Israel)*	**Design of Thermal Contacts for High Performances Heusler-Based Thermoelectric Modules** Geoffrey Roy *Université catholique de Louvain, Institute of Mechanics, Materials and Civil Engineering, Materials and process Engineering, IMAP (Belgium)*	**Redox-promoted enhancement of thermoelectric performance in strontium titanate-based materials** Andrei Kovalevsky *CICECO, Aveiro Institute of Materials, Department of Materials and Ceramic Engineering, University of Aveiro (Portugal)*
11:45-12:00		**Effect of electrical contact resistance on the performance of cascade thermoelectric coolers** Volodymyr Semeniuk *Thermion Company (Ukraine)*	**Challenges to enhance the thermoelectric properties of ZnO-based ceramics** Slavko Bernik *Jozef Stefan Institute (Slovenia)*
12:00-12:15	**Promising thermoelectric performance in both rhombohedral and cubic GeTe** Juan Li *Interdisciplinary Materials Research Center School of Materials Science and Engineering, Tongji University (China)*	**Non-linear impedance spectroscopy: beyond the ZT estimation** Etienne Thiebault *Centre de Nanosciences et de Nanotechnologies (France)*	**Thermoelectric properties of doubly substituted $La_{0.95}Sr_{0.05}Co_{1-x}Cr_xO_3$ ($0 \leq x \leq 0.5$) ceramics** Cong Chen *Bundesanstalt für Materialforschung und -prüfung (Germany)*

12:15-12:30	**Anomalous transport phenomena and thermoelectric performance enhancement in the Cu-overstuffed ferromagnetic spinel $Cu_{1+x}Cu_2Te_4$** Jean-Baptiste Vaney *NIMS Tsukuba (Japan)*	**Detachable Contacts for Simultaneous Thermoelectric Characterization** Antoine Micallef *German Aerospace Center (DLR) (Germany)*	**Defect and Schottky Barrier Engineering in Thermoelectric $SrTiO_{3-\delta}$ Ceramics** Soonil Lee *School of Materials Science and Engineering (South Korea)*
12:30-14:00	**LUNCH**		
	Silicides **Vicente Pacheco**	**Other Materials {Skutterudites}** **Eric Alleno**	**Process** **George Nolas**
14:00-14:15	**INVITED** **Silicon and metal silicides nanocomposites as high-performance thermoelectric materials** Ken Kurosaki *Graduate School of Engineering, Osaka University (Japan)*	**Thermoelectric characterization of n-type and p-type skutterudites fabricated in a up-scalable way** Olga Caballero-Calero *Instituto de Micro y Nanotecnología (Spain)*	**Porous thermoelectric materials and their applications** Teruyuki Ikeda *Ibaraki University (Japan)*
14:15-14:30		**Experimental and Computational Phase Boundary Mapping of Co-Sn-Te Phase Space for Skutterudites** Caitlin Crawford *Colorado School of Mines (US)*	**Fabrication of Filled Skutterudites With High Thermoelectric Performance Using Scanning Laser Melting Method** Shengqiang Bai *Shanghai Institute of Ceramics(China)*
14:30-14:45	**Thermoelectric and galvanomagnetic properties of topologically non-trivial (Co-M)Si "new fermion" semimetals (M=Fe, Ni)** Alexander Burkov *Ioffe Institute (Russia)*	**Analysis and Risk Mitigation of Raw Materials Sourcing and the Implications for eMMRTG Skutterudite Couple Performance** Tim Holgate *Teledyne Energy Systems, Inc. (US)*	**Contact layer development on bismuth Telluride thermoelectric materials using novel light sintering technique** Giri Joshi *Nanohmics, Inc. (US)*
14:45-15:00	**Screening silicide thermoelectric materials using ab initio transport calculations** Martin Lovvik *SINTEF (Norway)*	**Synergistically enhancement of thermoelectric properties in partially filled $CoSb_3$ skutterudites through simultaneous doping and nanostructuring** Manjusha Battabyal *International Advanced Research Centre for Powder Metallurgy and New Materials (India)*	**Near-net-shape fabrication of thermoelectric element by flash sintering** Masashi Mikami *National Institute of Advanced Industrial Science and Technology (Japan)*

15:00-15:15	**Demonstration of thermoelectric generation in the metallurgic industry** Marteen Den Heijer, *RGS Development B.V. (Netherlands)*	**Magnesioreduction : a low temperature synthesis route towards $CoSb_3$-based skutterudites with improved thermoelectric properties** Sylvain Le Tonquesse *Institut des Sciences Chimiques de Rennes (France)*	**Laser sintering of thermoelectric compounds** Yoshiaki Kinemuchi *National Institute of Advanced Industrial Science and Technology (Japan)*
15:15-15:30	**A thermal-shock resistant, high performance, SiGe thermoelectric generator for industrial waste heat applications** Axel Schoenecker *RGS Development B.V. (Netherlands)*	**Optimisation Strategies for Double filled $In_xLa_{0.25}Co_4Sb_{12}$ ($0 \leq x \leq 0.5$) skutterudite material** Mohd Faizul Mohd Sabri *University of Malaya (Malaysia)*	**Enhancing transport properties of $Bi_2Te_{3-x}Se_x$ alloys via doping for thermoelectric power generation applications** Omer Meroz *Ben-Gurion University of the Negev (Israel)*
15:30-15:45	**Thermoelectric performance in nanocomposite bulk consisting of $MnSi_{1.7}$ and SiGe** Yosuke Kurosaki *Hitachi, Ltd. (Japan)*	**Enhanced thermoelectric properties of $In_{0.25}Co_4Sb_{12}$ with InSb nanoinclusions** Ramesh Chandra Mallik *Indian Institute of Science (India)*	**Advanced Protective Layers for Improved Chemical Stability in $CoSb_3$, Mg_2Si and Cu_2X Based Thermoelectric Materials** Andrzej Kolezynski *AGH - University of Science and Technology, Faculty of Materials Science & Ceramics (Poland)*
15:45-16:00	**Effect of element substitution on the phase stability of complex $MnSi_x$** Swapnil Ghodke *Toyota Technological Institute (Japan)*	**A new and fast SPD-method to produce high ZT (>1.3) skutterudites** Gerda Rogl *Christian Doppler Laboratory for Thermoelectricity, University of Vienna (Austria)*	**Laser Additive Manufacturing with Bismuth Telluride and Magnesium Silicide** Saniya Leblanc *The George Washington University (US)*
16:00-16:15	**High temperature oxidation of higher manganese silicides and alloys** Antoine De Padoue Shyikira *University of Agder (Norway)*	**Realization of high figure of merit in Ni compensated double filled p-type skutterudites** Tulashi Dahal *Matrix Industries (US)*	**Additive Printing and Photonic Sintering of High-Performance and Flexible Thermoelectric Materials and Devices Using Colloidal Nanocrystals** *Tony Varghese* *Boise State University (United States))*
16:15-16:30	**Mechanical Properties and Failure Analysis of Higher Manganese Silicide** Yu-Chih Tseng *Canmet Materials (Canada)*	**Filling Fraction Fluctuation in $CoSb_3$-based Skutterudites Synthesized by High Pressure** Federico Serrano-Sanchez *Instituto de Cienca de Materiales de Madrid (Spain)*	**On the Study of Electrospinning for Thermoelectric Devices** Ben-Je Lwo *National Defense University (Taiwan)*

THURSDAY

	Amphitheater Caliste Chalcogenides (S, Se, Te) {SnSe} Wenjie Xie	Atelier 1 Other Materials {Nanowires, Thin Films} Kornelius Nielsch	Atelier 4 & 5 Oxides Soonil Lee
08:30-08:45		**Low-pressure chemical vapor deposition synthesis of metal-chalcogenide materials for thermoelectric micro-generator applications** Stephen Richards *School of Chemistry (UK)*	
08:45-09:00		**Development of a ZT-Measurement system for thin films plus additional Hall constant determination in a temperature range from LN_2 up to 300 °C** Hans-W. Marx, *Linseis Messgeräte GmbH (Germany)*	**Extended Solubility Limit of ZnO on Binary Doping Leading to Anomalously Low Thermal Conductivity** Michitaka Ohtaki *Kyushu University (Japan)*
09:00-09:15	**Thermoelectric performance of spark plasma-textured n-type polycrystalline SnSe** Penpeng Shang *State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University (China)*	**Transport measurements of bismuth nanowire embedded in quartz template by nano-fabrication** Yasuhiro Hasegawa *Saitama University (Japan)*	**Growth and characterization of thin film $CaMnO_3$ and $CaMn_{1-x}Nb_xO_3$ for thermoelectrics** Erik Ekström *Thin Film Physics Division, Linköping University (Sweden)*
09:15-09:30	**Ultra-high average figure of merit in synergistic band engineered $Sn_{1-x}Na_xSe_{0.9}S_{0.1}$ single crystals** Kunling Peng *Chongqing University (China)*	**Scalable, large-area and adaptable thermoelectric nanomaterials with high energy conversion efficiencies** Merce Pacios *Catalonia Institute for Energy Research (IREC) (Spain)*	**Enhanced electronic conduction and phonon scattering in the $Ga_2O_3(ZnO)_m$-$In_2O_3(ZnO)_m$ (m = 9 and 15) solid solution by designing interfaces at the nanoscale level** Diana Talia Alvarez Ruiz *Ben-Gurion University of Negev (Israel)*

09:30-09:45	**Modification of bulk heterojunction and Cl doping for high thermoelectric performance $SnSe_2$/SnSe nano-composites** Yonggao Yan *Wuhan University of Technology (China)*	**High-Performance Thermoelectric Properties of Multiwall Carbon Nanotubes Through Chemical Treatments** André Pereira *Departamento de Fisica e Astronomia da Faculdade de Ciências da Universidade do Porto* (Portugal)	**Transferable nanoporous $Ca_3Co_4O_9$ thin films for flexible thermoelectric applications** Biplab Paul *Thin Film Physics Division, Department of Physics, Chemistry, and Biology (IFM), Linköping University (Sweden)*
09:45-10:00	**Structure and transport properties of nanostructured alloys of the novel thermoelectric material SnSe** Norbert Nemes *Department of Materials Physics, Universidad Complutense de Madrid (Spain)*	**Integrated Silicon/Silicon Germanium Nanowires Thermo-Electric Generators** Alex Morata *Catalonia Institute for Energy Research (IREC) (Spain)*	**Synthesis, sintering and thermoelectric properties of $Sr_{1-x}La_xCoO_3$ cubic perovskite ceramics** Fabian Delorme *Université de Tours (France)*
10:00-10:15	**Reassessment of thermoelectric potential of SnS** Jiri Hejtmanek *Institute of Physics of the Czech Academy of Sciences, Praha (Czech Republic)*	**Simulation, fabrication and measurements of thermoelectric transport properties of crystalline sub-micron silicon beams** Andrej Stranz *IMB-CNM (CSIC) (Spain)*	**Self-assembled oxide 2D nanocomposite with enhanced thermoelectric power factor and reduced thermal conductivity** Armin Feldhoff *Leibniz University Hannover (Germany)*
10:15-10:30	**Effect of resonant dopant In on the thermoelectric properties of $Sn_{1.03}Te$** Shantanu Misra *Institut Jean Lamour (France)*	**Thin film Tin Selenide (SnSe) Thermoelectric Generators Exhibiting Ultra-Low Thermal Conductivity** Matthew Burton *University of Swansea (UK)*	**The Seebeck coefficient in some Ru oxides** Florent Pawula *Laboratoire CRISMAT, Caen (France)*
10:30-11:00	**COFFEE BREAK**		
	Other Materials **Jing Feng Li**	**Modelling** **Philippe Jund**	**Applications** **Olivier Delaire**
11:00-11:15	**Enhancement of Thermoelectric Performances in Topological Crystal Insulator $Pb_{0.7}Sn_{0.3}Se$ via Weak Perturbation of the Topological State and Chemical Potential Tuning by Chlorine Doping**	**INVITED** **Thermopower of thermoelectric materials with resonant levels - beyond the constant scattering time approximation** Bartlomiej Wiendlocha	**Key Issues in Developing Viable PV/TE Hybrid Systems** Gao Min *Cardiff University (UK)*

	Rhyee Jong-Soo *Kyung Hee University (South Korea)*	*Faculty of Physics and Applied Computer Science, AGH University of Science and Technology (Poland)*	
11:15-11:30	Self-compensating defects in $AgSbTe_2$ from first principles studies Szczypka Wojciech *AGH University of Science and Technology (Poland)*		**Harvesting Waste Heat from Cement Kiln by Thermoelectric System** Alireza Rezaniakolaei *Department of Energy Technology, Aalborg University (Denmark)*
11:30-11:45	**INVITED** **Quantum materials for thermoelectricity** Kornelius Nielsch *Leibniz Institute for Solid State and Materials Research - IFW Dresden (Dresden, Germany) (Germany)*	**Anharmonic and highly anisotropic low energy vibrational guest modes in the type IX chiral cubic barium-silicon clathrate** Romain Viennois *Institut Charles Gerhardt Montpellier (France)*	**Zonal thermoelectric passenger cooling: Simulation and Experiment** Guido Francesconi *European Thermodynamics Ltd. (UK)*
11:45-12:00		**Experimental validation of a 3D transient model of a Thermoelectric Generator** Jesus Ernesto Jimenez Aispuro *Laboratoire des Sciences de l'Ingénieur Appliquées à la Mécanique et au Génie Electrique (France)*	**A Study on Forest Soil Thermoelectric Energy Harvesting Method** Ga Latai *School of Technology (China)*
12:00-12:15	**Telluride based Thermoelectrics: from Glasses to Polycrystalline Materials** Bhuvanesh Srinivasan *Institut des Sciences Chimiques de Rennes (France)*	**Angular Anisotropy of Thermoelectric Properties of a Periodic Composite Medium in the Presence of a Magnetic Field** Yakov Strelniker *Department of Physics, Bar-Ilan University (Israel)*	**Comparative analysis of different cooling systems for geothermal thermoelectric generators** Leyre Catalan *Public University of Navarre (Spain)*
12:15-12:30	**Effect of microstructure on the thermoelectric properties of bulk $Ag_{16.7}Sb_{30}Te_{53.3}$ mosaic crystals.** Lamya Abdellaoui *Max-Planck-Institut für Eisenforschung GmbH*	**Modeling and analysis of segmented thermoelectric generator performance with consideration of thermal losses using effective properties** Heonjoong Lee *Virginia Tech (USA)*	**Prototypical thermoelectric generator TEG for waste heat conversion from biogas-fired burner** Rafal Zybala *ITME Institute of Electronic Materials Technology (Poland)*

12:30-14:00	**LUNCH**		
	Other Materials **Takao Mori**	**Applications** **Robin Lefèvre**	**Organic and Hybrid Materials {Hybrids}** **Gao Min**
14:00-14:15	**A Critical Assessment of the Impact of Excess Ni on the Thermoelectric Properties of ZrNiSn** Popuri Srinivasarao *University of Glasgow (UK)*	**New Generation of Micro-Flexible Thermoelectric Devices to be Applied in Electronic Printing** Ana Pires *Universidade do Porto (Portugal)*	**Towards the Fabrication of Flexible and Efficient Organic Thermoelectric Generators by Inkjet Printing Technique** Marco Cassinelli *Italian Institute of Technology (Italy)*
14:15-14:30	**Half-Heusler Thermoelectrics: Stable or Unstable?** Wenjie Xie, *Institute for Material Science, University Stuttgart (Germany)*	**Complete characterization of bulk thermoelectric elements up to 250 °C by means of impedance spectroscopy** Jorge García-Cañadas *Universitat Jaume I (Spain)*	**Enhanced Thermoelectric Properties of PEDOT/Te Quantum Dot Composite Films** Yao Qin *Shanghai Institute of Ceramics (China)*
14:30-14:45	**Efficient waste heat recovery in metal-rich $TiNiCu_ySn$ half-Heusler alloys** Jan-Willem Bos *Heriot-Watt University (UK)*	**Do high efficiency kW pulsed thermoelectric generators exist?** John Stockholm *Marvel Thermoelectrics (France)*	**Energy filtering effect of PEDOT: PSS/Bi_2Te_3 nanowire composites** Wan Sik Kim *GIST (Gwangju Institute of Science and Technology) (South Korea)*
14:45-15:00	**Low Temperature Magnetotransport Anomalies in Fe-Doped (Ti, Hf, Zr)NiSn Alloys** Trevor Bailey *University of Michigan, Department of Physics (US)*	**Maximum Power Point Tracking on a TEG operated under constant heat conditions** Marcos Compadre *School of Engineering, University of Glasgow (UK)*	**Module Design for Organic Thermoelectric Materials** Masakazu Mukaida *Nanomaterial Research Institute, National Institute of Advanced Industrial Science and Technology (AIST) (Japan)*

15:00-15:15	**The decreases of the lattice thermal conductivity of the $FeV_{0.955-x}Hf_{0.045}Ti_xSb$ half-Heusler phases** Kevin Delime-Codrin *Toyota Technological Institute (Japan)*	**A new thermoelectric generator concept for maximizing waste heat recovery under highly variable thermal load** Francisco Brito *Universidade do Minho, Mech. Eng. Dept. (Portugal)*	**Films of carbonaceous nanofillers and polymers as stable n-type materials for thermoelectric devices** Clara M. Gómez *Institute of Material Science (Spain)*
15:15-15:30	**Unique role of refractory Ta alloying in enhancing the figure of merit of NbFeSb thermoelectric materials** Junjie Yu *Zhejiang University (China)*	**Preview Certified Reference Material Data, Measurement Protocols, and Uncertainty Analysis for p-Type Polycrystalline Silicon Germanium at High Temperature** Joshua Martin *National Institute of Standards and Technology (US)*	**Interfacial thermal resistance between Bismuth Telluride and PEDOT: PSS** Koji Miyazaki *Kyushu Institute of Technology (Japan)*
15:30-15:45	**Ultra-fast fabrication of bulk ZrNiSn thermoelectric material through self-propagating high-temperature synthesis combined with in-situ quick pressing** Tiezheng Hu *Wuhan University of Technology (China)*	**Wearable Electrocardiography System Powered by a Flexible Thermoelectric Power Generation Module** Choong Sun Kim *Korea Advanced Institute of Science and Technology (South Korea)*	
15:45-16:15	**COFFEE BREAK**		
	PLENARY SESSION and CLOSING CEREMONY		
16:15-16:55	**Young Investigator Award lecture**		
16:55-17:35	**Outstanding Achievement Award lecture**		
17:35	**CLOSING REMARKS**		

Interplay of crystal structure, chemical bonding and thermoelectric behaviour

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Abstract

Knowledge-based manufacturing of new thermoelectric materials requires insights into the structure-property relationship for solid state compounds, in particular intermetallic phases. Most of the representatives of this family of inorganic substances reveal typically metallic behaviour in electric and thermal transport, i.e. they are in pristine form not suitable as thermoelectrica. There are several structural patterns of intermetallic structures, which - assuming an appropriate electron count - may result in a band structure with (pseudo) gap, e.g. intermetallic clathrates of type I, structure types FeGa3, TiSi2, MgAgAs (half-Heusler phase), etc. The chemistry of these families is still under research. These substances are formed by elements located at and left of the Zintl line in the Periodic Table. The valence electron count per atom is usually less than four. The reduced VEC and the presence of transition and/or rare earth metals in this group of inorganic materials allow only restricted application of the traditional chemical concepts based on two-centre interactions, like the Zintl-Klemm model, for interpretation of composition and crystal structure [1]. Therefore, a general picture of interatomic interactions as well as understanding of chemical composition and crystal chemical features is still under debate. Further progress in this matter require using of the models employing the multi-centre bonding. Use of new quantum chemical tools - bonding indicators in real space - opens the way to qualitative and quantitative interpretation of atomic interactions in thermoelectric materials as combination of covalent polar and non-polar, ionic and multi-centre bonds [2] and may lead to understanding of the electronic counts necessary to stabilize a structural pattern. Introduction of the terms 'inhomogeneity' and 'anisotropy' for atomic interactions contributes to the understanding of chemical and physical behaviours of thermoelectric materials [3]. Furthermore, understanding of chemical bonding allows also a prediction for the new compounds interesting from thermoelectric point of view [4].

Yu. Grin. In: Comprehensive Inorganic Chemistry II, v. 2, Elsevier, 2013. p. 359ff.

F. R. Wagner et al. Dalton Trans. 45, 2016, 3236.

A. Ormeci et al. J. Thermoelectricity, 6, 2015, 16.

D. Bende et al. Angew. Chem. Int. Ed. 56, 2017, 1313.

Keywords: intermetallic, chemical bond, structure, property relationship

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A 50 Year-Long Breakthrough in the Making: Radioisotope Thermoelectric Generators with New Materials

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Abstract

Radioisotope Thermoelectric Generators (RTGs) have proven to be extremely reliable components of space power systems, enabling the scientific exploration of deep space, Mars, and the moon. These systems are based on technological advances completed in the 1960's and 1970's. RTGs have relied on thermoelectric couple technology based on materials identified and developed over 50 years ago, namely PbTe, Te-Ag-Ge-Sb (TAGS) and Si-Ge alloys. NASA constantly seeks the development of more capable and high-performing flight systems in support of future science and exploration missions. The performance of the "state-of-practice" thermoelectric materials have limited RTG system-level efficiencies to less than 6.5% at beginning-of-life with the specific power of the current "off-the-shelf" system being less than 2.8 W/kg.

Research on high temperature thermoelectric materials over the last 30 years has succeeded in identifying several promising candidates, opening up the possibility for potential future RTGs to be much more performant. Continuous advances in high temperature device technologies based on these materials has now enabled NASA to pursue development of two new potential system capabilities, the skutterudite-based enhanced Multi-Mission RTG (eMM-RTG) and the Zintl-based Next-Generation RTG (NG-RTG). Successfully meeting current target dates of 2024 and 2028 respectively for producing flight system Qualification Units, would realize a 50 year-long breakthrough in the making.

Keywords: Radioisotope, Thermoelectric, Generator, Zintl, Chalcogenide, skutterudite

*Speaker

Utilization of Magnetism and Other Novel Principles for Thermoelectric Enhancement and Recent Activities in Asia

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Abstract

We are trying to develop thermoelectric (TE) enhancement principles which can be relatively easily implemented and applicable to a wide range of materials [1].
Dispersion of metallic networks in large Seebeck coefficient, poorly conducting materials can be beneficial [2]. Introducing a moderate volume of nano-micropores with size distribution by simple evaporation of a secondary phase, has led to effective phonon selective scattering, and 100% enhancement to ZT ˜1.6 in rare earth-free ("empty") skutterudites [3]. This should be applicable to other materials.

We have previously proposed to utilize magnetic interactions between carrier and magnetic moments to enhance the power factor [4-6]. Unlike magnon drag, this is not dependent on ordering and can be effective at higher temperatures also. Simple magnetic ion doping for example, has led to TE enhancement for a variety of cases, CuGaTe2 [6], BiCuSeO, Bi2Te3, SnTe, etc., if coupling is effective. Utilizing intrinsic crystal structure features for TE enhancement will also be presented. Carrier control can lead to relatively high ZT for even metallic systems considered to be of low performance, such as thiospinels like CuCr2S4 [7], i.e. no system can be easily disregarded.

We are also developing thermal evaluation methods of microcrystals [8], thin films, and also a TEM in-situ TE total probe. Successful wide-scale application of TE is increasingly critical for our community, and I will present our efforts to utilize high ZT inorganic materials for flexible modules.

I will also give a view on some recent interesting TE activities in Asia.

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Keywords: thermoelectric enhancement, phonon selective scattering, magnetism, skutterudite, sulfide, measurements, module

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Crystal Chemistry of New (and some old) Zintl Phases

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This talk will highlight some recent discoveries from the Bobev laboratory, dealing with the relationships among the composition, structure, and electronic structure in Zintl phases with d- and f-elements and their properties. I will recount the crystal structures of several new ternary compounds formed between metals and semi-metals with very different electronegativities. The goal of the talk will be to show that despite the apparent complexity in the bonding arrangements, the structures of these compounds can be "broken" down to simpler fragments, which are much easier to describe. This unique aspect of the crystal chemistry allows for the convenient elucidation of the likely geometric and electronic factors that govern the formation of such phases.

Keywords: Anthimonides, bismuthides, Zintl phases

*Speaker

Zintl ions within framework channels: the complex structure and low-temperature transport properties of Na4Ge13

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Single-crystalline Na4Ge13 was synthesized for the first time by employing a high-pressure/high-temperature approach. This complex Zintl compound has a hexagonal crystal structure comprised of a three-dimensional *sp3* Ge framework forming small and large channels along the crystallographic *c*-axis. The most conspicuous aspect of its intriguing crystal structure is the presence of disordered [Ge4]4- Zintl ions surrounded by six-fold Na rings within the larger channels. Na4Ge13 constitutes the first example of an intermetallic system in which an exclusively Ge framework crystallizes in a channel configuration and Zintl ions are confined within these channels. The availability of specimens in the form of agglomerations of single crystals allowed for measurement of the intrinsic low-temperature transport properties of this material for the first time. Seebeck coefficient measurements indicated that Na4Ge13 exhibits semiconductor behavior, and this was corroborated by DFT calculations. Furthermore, it exhibits thermal conductivity that is lower than that of single-crystal Ge, but larger than related clathrate materials. The Na4Ge13 composition is an example of a system with a favorable combination of electronic and thermal properties, which is a necessary condition for an effective thermal-to-electrical energy conversion, according to the phonon-glass electron-crystal concept. The structure-property characteristics of this composition suggest that additional investigation of Zintl phases is warranted in order to explore their potential for efficient thermoelectric conversion applications.

Keywords: Zintl, thermoelectric, single, crystal, DFT, thermal conductivity

*Speaker

Experimental Investigation of Thermoelectric Properties of KSb2-xSnx

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Zintl compounds have attracted much attention as potential high performance thermoelectric materials due to their intrinsic phonon-glass and electron-crystal (PGEC) nature. Recently, a new Zintl compound, KSbSn has been suggested to be a promising n-type thermoelectric material with a favorable combination of high band degeneracy and carrier mobility [1]. Subsequently, a study of first principles calculations has predicted a figure of merit (zT) value of _˜ 2.6 at 800 K if KSbSn can be rendered an n-type semiconductor [2]. Yet, to the best of our knowledge, no experimental results have been reported on this new Zintl compound. Here, we report the thermoelectric properties of n-type KSb2-xSnx ($0 \leq x \leq 1$) compounds. Experimental procedure for sample synthesis and thermoelectric properties measurement is presented. Experimental data for thermoelectric and thermomagetic properties of KSb2-xSnx ($0 \leq x \leq 1$) are presented and discussed in light of band structure evolution with x.
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Keywords: KSbSn, Zintl phases, thermoelectric properties, thermomagnetic properties

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The A14MPn11: good thermoelectric materials with low valley degeneracy.

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A14MPn11 are well known to lead to thermoelectric materials with relatively high zT at high temperature. The Yb14MnSb11 and Yb14MgSb11 have been especially investigated with record zTs around 1 at more than 1000K. Despite these exciting performances, not much about the electronic structure of these A14MPn11 compounds has been reported in the literature. In this talk, we present a DFT-based study of the band structure of these zintl compounds. We study how chemistry influence the shape of the band structure and show that the A14MPn11 actually do not show the high valley degeneracy found in other thermoelectric materials. We use Boltzmann transport theory to compare our results to experimental data and discuss the reason why a low valley degeneracy material can still lead to reasonably high zT.

Keywords: A14MPn11, zintl, bandstructure, valley, degeneracy, dft

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Thermoelectric properties of a new Zintl phase NaZn4As3 with ultralow thermal conductivity

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Zintl phase compounds are one of the most famous groups of thermoelectric (TE) materials with high TE properties originate from good electric conductivity due to their framework of covalent bonding and low thermal conductivity. The intrinsically low thermal conductivity might be attributed to a complicated crystal structure, large unit cell volume and the presence of lone-pair electrons. In 2011, new Zintl phases of $AT4Pn3$ (A: Alkali metal, T: Transition metal, Pn: Pnictide) [1] were reported by Hua He *et al.* Their crystal structures derive from $AT2Pn2$ Zintl compounds (CaAl2Si2-type) with condensing the TPn layers by removing an alkali metal. We focused on their relatively large unit cell volume, which is a common character of intrinsically low kL, and the similarity of their crystal structures to $AT2Pn2$ which shows high ZT values [2, 3].
Here we report the first systematic examination of thermoelectric properties from room temperature to $T = 700$ K including electrical conductivity, Seebeck coefficient and thermal conductivity for NaZn4-xCuxAs3 (space group R-3m) polycrystalline samples. Ultralow lattice thermal conductivity kL with the value of 1.0 W/mK and approximately 0.5 W/mK were observed at room temperature and around 700 K, respectively. The relatively high ZT value of about 0.5 was achieved at around 700 K. Details will be discussed in the conference.

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Keywords: Zintl phase, thermoelectric properties, ultralow thermal conductivity, arsenic compound

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Electronic structure of Sn1-xInxTe containing defects from KKR-CPA calculations

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SnTe belongs to model systems where superconductivity appears in a narrow band semiconductor [1]. The interest for this system has been recently renewed due to discovery of novel behaviors [2,3]. It is also known that electron transport properties of SnTe can be substantially modified upon doping [4]. For that reason, the Korringa-Kohn-Rostoker method with the coherent potential approximation (KKR-CPA) seems to be well-adapted technique for electronic structure calculations [5,6] to account for crystal defects as vacancies, interstitials or doping. Here, we present the KKR-CPA results of density of states (DOS) for SnTe including different types of chemical disorder (vacancies, antisite defects and In as resonant-like impurity) as well as the analysis of their stability in view of total energy calculations. Furthermore, electronic structure of Sn1-xInxTe solid solutions is analysed in the whole composition range (including the presence of vacancies) based on site- and l-decomposed DOSs as well as electronic dispersion curves with complex energy. The obtained results allow to enlighten the character of electrical conductivity as well as to the effect of vacancy in SnTe substituted with In. The KKR-CPA results are discussed in the framework of our recent electrical conductivity and thermopower measurements. [1] P. B. Allen et al., Phys. Rev. 177, 704 (1969).

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Keywords: electronic structure, resonant level, vacancy defects, crystal stability, electron transport

*Speaker

Modeling Dopability in Diamond-like Semiconductors Using Machine Learning for High-throughput Predictions

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High-throughput, low cost, and accurate predictions of thermoelectric properties are beneficial both in driving technology forward and guiding experimental investigation of new materials. Performance metrics such as the material quality factor have been successful in predicting the optimum thermoelectric behavior in a high-throughput fashion by making the assumption that a given material can be optimized to the required carrier concentration. However, in practice, this is often a challenge experimentally, if not a limiting condition, but is a necessary assumption for high-throughput calculations owing to the cost of defect calculations. A computationally efficient way of overcoming this issue is developed using diamond-like semiconductors as a model system. Experimental carrier concentration data on 125 compounds ranging from unary to quaternary was collected from the literature for the learning set. Principal component analysis, clustering, and machine learning are used to elucidate the importance of various features of chemistry, structure, and other properties in determining dopability. Employing cross-validation and other statistical tools to quantify prediction accuracy, the model is used to make predictions of carrier concentration ranges in diamond-like semiconductors, which are then compared to experimental data for well-studied compounds. We also identify opportunities where our predictions indicate that the entire dopability range has not been fully explored experimentally for less well-studied materials, motivating further work. Additionally, the model is compared to defect calculations on choice test case compounds to highlight key features. Finally, the broader implications of high throughput predictions of dopability and application of the methods and findings to other systems is discussed.

Keywords: high, throughput, machine learning, diamond, like semiconductors, carrier concentration, dopability, prediciton

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Negative Thermal Expansion of GeTe near the Ferroelectric Phase Transition from First Principles

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Germanium Telluride (GeTe) is a well-known ferroelectric and thermoelectric material that undergoes a structural phase transition from a rhombohedral to the rocksalt structure at _˜600-700 K. It has been shown recently that increasing the proximity to such phase transition in (Pb,Ge)Te alloys leads to significantly reduced lattice thermal conductivity [1], and potentially enhanced thermoelectric figure of merit. In this work, we analyze the influence of the ferroelectric phase transition on the thermo-mechanical properties of GeTe, such as thermal expansion and elastic constants. We model thermal expansion using density functional theory by minimizing Helmholtz free energy using the elastic and harmonic approximations and Gruneisen theory. Accounting for the temperature dependence of elastic constants, we obtain the temperature variation of the structural parameters of rhombohedral GeTe in very good agreement with experiment [2]. Most importantly, we correctly reproduce a negative volume thermal expansion of GeTe near the phase transition at _˜700 K [2]. Our model shows that the coupling between acoustic and soft transverse optical modes is the dominant mechanism that induces negative thermal expansion. Our results indicate that GeTe will be mechanically stable near the ferroelectric phase transition, and potentially have a very low lattice thermal conductivity and high figure of merit.

Keywords: Germanium Telluride, Thermoelectrics, Negative thermal expansion, Ferroelectric phase transition

*Speaker

Engineering thermal conductivity through microstructural lattice softening

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Experimental work on a PbTe model system is presented which shows that phonon scattering is not the only way in which internal strain fields reduce the lattice thermal conductivity. The speed of sound decreases in PbTe with increased internal strain energy which, in this case, completely accounts for the reduction in lattice thermal conductivity without the addition of microstructural scattering terms. A thermodynamic relation that requires the average phonon frequency to decrease with increasing internal shear strain energy is experimentally validated as the origin for this phenomenon. Thermal transport modeling then shows that lattice softening should be particularly effective at reducing lattice thermal conductivity at high temperatures, where phonon-phonon scattering dominates. This presents new avenues to engineer the lattice thermal conductivity through modifying the phonon dispersion relation with microstructural defects.

Keywords: Phonon, heat conduction, thermodynamics, lattice softening, strain

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Acoustically mismatched nanoinclusions

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Tuning the inhomogeneity of materials presents opportunities for achieving specific functionalities but also renders their characterization challenging. In thermoelectric materials, nanostructuration is an efficient way for achieving low thermal transport. However, this approach opens the question of quantities that control phonon scattering at interfaces notably when nanoinclusions are dispersed in a matrix. The lattice dynamics in thermoelectric AgPbmSbTe2+m (LAST-m with m = 3, 18) and the related Ag0.8Sb1.2Te2.2 and PbTe phases were measured by combining nuclear inelastic scattering and inelastic neutron scattering. The Sb and Te specific densities of phonon states and derived average phonon group velocities reveal the acoustic mismatch between nanoprecipitates and the matrix in LAST-18 that was proposed as the origin of the low thermal conductivity in these alloys. By utilizing the obtained phonon group velocities the scattering at the interface between matrix and nanoinclusions can be estimated. This work thus solves an archetypal problem of characterizing the lattice dynamics in inhomogeneous materials. I specially acknowledge my collaborators on this study, A. Jafari, B. Klobes, P. Fichtl, I. Sergeev, P. Alexeev,A. I. Chumakov, D. Bessas, A. F. May, O. Delaire, M. E. Manley, J. Dadda, E. Müller, as well as access the neutron scattering facilities at the Spallation Neutron Source and synchrotron radiation facilities at the European Synchrotron Radiation Facility.

Keywords: phonons, scattering, LAST

*Speaker

Phonon dispersion and scattering considerations for thermoelectrics

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Manipulation of defects, ranging from atomic scale to nanometer scale, has been leading the advancements in thermoelectrics for many decades through a reduced lattice thermal conductivity. This talk involves 0D vacancy (either intrinsic or extrinsic) and interstitial defects as strategy for effectively scattering phonons[1]. Moreover, the possible clustering of vacancy or interstitial, which forms 1D dislocations, may lead to additional phonon scattering, which opens new possibilities for advancing thermoelectrics[2]. Alternatively focusing on the phonon dispersion and speed of phonon propagation, low sound velocity[3] in complex crystal structures with diffusive species is also desired for a low lattice thermal conductivity[4]. The utilization of above mentioned strategies indeed lead to a great success in improving thermoelectric performance of both new and existing materials.

Keywords: Lattice thermal conductivity, Scattering, Phonon dispersion

*Speaker

Rattling dynamics under a planar coordination in tetrahedrites

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Suppressing lattice thermal conductivity (kL) as low as possible is essential to achieve high thermoelectric performance. One of effective methods is to use the rattling which is large anharmonic vibration of atoms. Typically, rattling atoms locate in oversized atomic cages of caged compounds like clathrates and skutterudites. Recently, we found several new thermoelectric materials that contain rattling atoms without oversized atomic cages. In LaOBiSSe that exhibits low kL, Bi atoms vibrate largely toward out of Bi(S,Se)-plane [1,2]. In tetrahedrites that exhibit extremely low L _˜ 0.5 W/mK with ZT = 1.0 at 673 K, Cu atoms rattle perpendicular to the S3-triangle [3]. In common, rattling atoms have a planar coordination in both compounds. The question is, then, what is the driving force for the occurrence of rattling in a planar coordination? To solve the problem, we investigated crystal structures and phonon dynamics of tetrahedrites. We found that the amplitude of Cu rattling increases with decreasing S3-triangle area. Rattling modes were observed to lie around E = 3 meV by inelastic neutron scattering. The rattling energy decrease with decreasing the S3-triangle area and finally damped demonstrating an enhancement of anharmonicity. The results suggest that chemical pressure is essential for the appearance of rattling under a planar coordination in contrast to caged compounds where free space is essential.

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Keywords: Tetrahedrite, planar rattling, phonon dynamics, crystal structure analysis, inelastic neutron scattering

Improved Thermoelectric Performance in Non-stoichiometric Cu2+δMn1-δSnSe4 Quaternary Diamond-like Compounds

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Novel quaternary Cu2MnSnSe4 diamond-like thermoelectric material was discovered recently based on the pseudocubic structure engineering. In this study, we show that introducing off-stoichiometry in Cu2MnSnSe4 effectively enhances its thermoelectric performance by simultaneously optimizing the carrier concentrations and suppressing the lattice thermal conductivity. A series of non-stoichiometric Cu2+δMn1-δSnSe4 (δ = 0, 0.025, 0.05, 0.075, and 0.1) samples has been prepared by the melting-annealing method. The X-ray analysis and the scanning electron microscopy measurement show that all non-stoichiometric samples are phase pure. The Rietvield refinement demonstrates that substituting part of Mn by Cu well maintains the structure distortion parameter η close to 1, but it induces obvious local distortions inside the anion-centered tetrahedrons. Significantly improved carrier concentrations are observed in these non-stoichiometric Cu2+δMn1-δSnSe4 samples, pushing the power factors to the theoretical maximal value predicted by the single parabolic model. Substituting part of Mn by Cu also reduces the lattice thermal conductivity, which is well interpreted by the Callaway model. Finally, a maximal thermoelectric dimensionless figure-of-merit zT around 0.60 at 800 K has been obtained in Cu2.1Mn0.9SnSe4, which is about 33% higher than that in the Cu2MnSnSe4 matrix compound.

Keywords: thermoelectric, diamond, like, non, stoichiometric, doping, refinement

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Rhombohedral to Cubic Conversion of GeTe via MnTe alloying Leads to Ultralow Thermal Conductivity, Electronic Band Convergence and High Thermoelectric Performance

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In this study, a series of Ge1-xMnxTe (x=0-0.21) compounds were prepared by melting-quenching-annealing process combined with Spark Plasma Sintering (SPS). The effect of alloying MnTe into GeTe on the structure and thermoelectric properties of Ge1-xMnxTe is profound. With increasing content of MnTe, the structure of the Ge1-xMnxTe compounds gradually changes from rhombohedral to cubic, and the known $R3m$ to Fm-$3m$ phase transition temperature of GeTe moves from 700 K closer to room temperature. First-principles density functional theory calculations show that alloying MnTe into GeTe decreases the energy difference between the light and heavy valence bands in both the $R3m$ and the Fm-$3m$ structures, enhancing a multi-band character of the valence band edge that increases the hole carrier effective mass. The effect of this band convergence is a significant enhancement in the carrier effective mass from 1.44 $m0$ (GeTe) to 6.15 $m0$ (Ge0.85Mn0.15Te). In addition, alloying with MnTe decreases the phonon relaxation time by enhancing alloy scattering, and reduces the phonon velocity, and increases Ge vacancies all of which result in an ultralow lattice thermal conductivity of 0.13 Wm-1K-1 at 823 K. Subsequent doping of the Ge0.9Mn0.1Te compositions with Sb lowers the typical very high hole carrier concentration and brings it closer to its optimal value enhancing the power factor, which combined with the ultralow thermal conductivity yield a maximum ZT value of 1.61 at 823 K (for Ge0.86Mn0.10Sb0.04Te). The average ZT value of the compound over the temperature range 400 K-800 K is 1.09, making it the best GeTe-based thermoelectric material.

Keywords: GeTe, phase conversion, MnTe alloying, band convergence, thermoelectric performance

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Thermoelectric features of the Cu7P(Se1-xSx)6 with high copper ionic mobility

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Recently have been reported studies of the thermoelectric properties for the chalcogenide compound Cu7PSe6 [1], as a first representative of argyrodite-type ion conducting thermoelectric class. The measured extraordinary low thermal conductivity for Cu7PSe6 below the glass limit were associated with the molten copper sublattice leading to a softening of phonon modes. Thus, considering unusual temperature dependent electrical conductivities of several Cu7P(Se1-xSx)6 (x=0÷1) solid solutions [2] we, for first time, report results of measurements the Seebeck coefficient (SC) and thermal conductivity for such an intriguing group of materials.
The measured thermal conductivity for Cu7PS6 (300-450K) show very low magnitudes < 1W/mK - less than for Cu7PSe6 and SC (thermal hysteresis observed up to structural phase transition at 510 K) varying in range 650 – 750 μV/K, which exceeds more than three times the maximal value (175 μV/K) obtained for Cu7PSe6 [1]. However, simultaneously electrical conductivity significantly decreases when Se is fully replaced by Sulphur. The observed effects indicate how strong are the changes in thermoelectric properties by the successive substitution of Se by S. Therefore we conducted the systematic study for the series Cu7P(Se1-xSx)6 mixed chalcogenides to find optimal composition resulting maximal figure of merit. The DFT band energy structure calculation help us better understood observed phenomenon.

We believe that the investigated argyrodites Cu7P(Se1-xSx)6 may open a new experimental approach to the thermoelectric materials within the phonon-glass electron-crystal picture in thermoelectric copper selenide concept [3].

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Keywords: chalcogenides, argyrodite, thermoelectric copper selenides

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Compatibility investigation between cobalt metallized tellurides-based Thermoelectric legs and an Ag–Cu–In-based brazing alloy

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In thermoelectric (TE) generators, maximizing the direct heat-to-electricity conversion efficiency requires the reduction of any thermal and electrical contact resistances. This requirement is especially challenging in the development of intermediate to high-temperature TE generators. PbTe-based TE materials are known for years to be highly thermoelectrically efficient up to temperatures of around 500∘C; yet, only a few practical TE generators based on these materials are currently commercially available. One reason for that is the insufficient bonding techniques between the TE legs and the hot-side metallic contacts, resulting in high-contact resistances and overall instability in long-term use. This current research is focused on the interaction between cobalt-metallized *n*-type PbI2-doped PbTe TE legs and the eutectic Ag–Cu–In -based brazing alloy, which is free of volatile species. Clear and fine interfaces, without any noticeable formation of adverse intermetallic compounds, were observed following prolonged thermal treatment testing. Furthermore, a reasonable electrical contact resistance was observed upon brazing at 600∘C, highlighting the potential of such contacts while developing practical PbTe-based TE generators for up to 500∘C.

Keywords: lead telluride

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Native Defects in SnSe and their Temperature Dependence

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SnSe has been recently studied as a promising thermoelectric material1. It has been shown that SnSe is very vivid material. Its physical properties depend not only on temperature history of the sample, but also on the current temperature at which the measurement is performed. Most likely, the results depend on measurement kinetics as well. This produces discrepancies in results of individual research groups. This makes even the utilization of theoretical calculations of formation energy of native point defects questionable.
From the literature sources, it is not clear what native defects should be dominant in the structure. Sn vacancies, Se vacancies, Se interstitial defects are mostly discussed. Some of them were even directly observed2,3. Based on other works it follows that no point defects are present, but foreign phase SnSe2 is observed4.

In order to examine presence of native defects in SnSe and their temperature dependence, a series of single crystals was prepared. They were annealed for a long period at desired temperature. Afterwards, they were quenched at room temperature. Prepared samples were characterized by high resolution X-ray diffraction (HR XRD), electrical conductivity, Hall coefficient and Seebeck coefficient. These parameters were measured over a temperature range 93 – 473 K.

HR XRD results suggest presence of Sn or Se vacancies in the structure next to secondary SnSe2. From our results of transport measurements it follows that at temperatures above 300 ∘C the concentration of defects steeply increases while at temperatures below 300 ∘C the compound approaches absolutely stoichiometric structure with very low concentration of defects. This corresponds with low concentration of holes (< 2x1017cm-3). This characteristic is indisputably connected with second order phase transition and stoichiometry variations with temperature.

Keywords: SnSe, native defects, vacancies

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Harnessing thermoelectric effects in vertical phase change memory cells

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Thermoelectric effects have been demonstrated to reduce programming currents in conventional 'mushroom' structure of chalcogenide (Ge2Sb2Te5) based phase change memory (PCM) cells, owing to inherent high current densities and temperatures involved in the operation. After mushroom cells, vertical pillar or nanowire PCM structure is reported to have lesser programming current by limiting the heat loss to surroundings. However, vertical pillar being a symmetric structure, the contribution of thermoelectric effects on programming current reduction is negligible. Thus, to harness the thermoelectric effects in a vertical PCM, keeping energy loss to surroundings minimum, we have proposed a hybrid PCM cell structure, by incorporating material and geometry level asymmetries to enhance Peltier and Thomson effects respectively. An interface layer having high negative Seebeck coefficient and low thermal conductivity is incorporated between the bottom electrode and the active material, which results in an asymmetric heat distribution by enhanced Peltier heating of the active material, along with the thermal boundary resistance at the interface. Geometric asymmetry is introduced by tapering the pillar in accordance with etch induced modifications, which results in an angle dependent Thomson heating within the active region [1]. Using 2D-axisymmetric simulations, we analyse the proposed PCM structure and a programming current reduction up to 60% is observed. Furthermore, we have optimized the cell using an analytical model including thermoelectric effects over geometry and material parameters. Moreover, it is also noted that a smaller amorphous region volume is formed during switching which is always favourable to minimize effective resistance drift.

1. J. Bahl, B. Rajendran and B. Muralidharan, IEEE Trans. Elec. Dev, 62, 12, 4015-4021, (2015)

Keywords: Thermoelectric effects, Phase change memory, Asymmetry, Vertical nanopillar

*Speaker

Thermoelectric Behavior of Silver-Cluster Phosphides: Origin and Optimization

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Within the Zintl phases many attractive thermoelectric materials can be found. However, the phosphides, playing a prominent role in Zintl chemistry, have usually not been considered. One of the reasons is that strong covalent bonds, present in such materials, are expected to cause high thermal conductivity and therefore an insufficient thermoelectric performance. Despite this, phosphides pretend to respectability as thermoelectric material, recently, because they can have excellent electronic properties and in spite of containing lighter elements, they can exhibit remarkably low thermal conductivity for various reasons [1].
The ternary silver-cluster phosphide Ag6Ge10P12 exhibits a complex crystal structure, which is closely related to the high-performance thermoelectric tetrahedrites, shows similar structural details like strong anisotropic behavior, mixed-valent constituted atoms and lone-pair electrons embedded in a covalently bonded framework. These properties are the origin of an anomalously low thermal conductivity $<$ 1 Wm–1K–1. Combining this with enhanced electronic properties, already results in a remarkable thermoelectric performance, with zT $>$ 0.6 [2].

The nature of Ag6Ge10P12 allows the tuning of the thermoelectric properties. Options will be the use of the decomposition behavior to intercalate elemental Ag and Ge into the material, or to replace Ge(IV) by Si(IV) and Ge(II) by Sn(II). DFT calculations show a smaller band gap in the Sn compound, as well as a stiffening of the covalent framework with Si included. Therefore, Ag6Ge10P12 is the prototype of a class of compounds where the electronic as well as phononic properties can be tuned in a controlled way.

J.-H. Pöhls, A. Faghaninia, G. Petretto, U. Aydemir, F. Ricci, G. Li, M. Wood, S. Ohno, G. Hautier, G. J. Snyder, G.-M. Rignanese, A. Jain, M. A. White, J. Mater. Chem. C, **2017**, 5 12441.

J. Nuss, U. Wedig, W. Xie, P. Yordanov, J. Bruin, R. Hübner, A. Weidenkaff, H. Takagi, *Chem. Mater.* 2017, 29, 6956.

Keywords: Phosphides, Zintl Phases, Silver clusters

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On the Search of Novel Compounds Featuring Thermoelectric Properties. Some Suggestions Based on Theoretical Considerations

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The development of thermoelectric (TE) materials, which can generate electricity from waste heat, is contingent on identifying new materials with higher thermoelectric efficiency than available at present. Density functional theory (DFT) methods constitute an alternative way to experiments, which are now sufficiently mature to help in understanding, optimizing and designing new materials with improved thermoelectric properties. Specific examples recently studied such as borides, nitrides or intermetallics will serve as an illustration [1]. [1] (a) B. Srinivasan, R. Gautier, F. Gucci, B. Fontaine, J.-F. Halet, F. Cheviré, C. Boussard-Pledel, M. J. Reece, B. Bureau, *J. Phys. Chem. C* **2018**, *122*, 227; (b) B. Boucher, R. Al Rahal Al Orabi, B. Fontaine, Y. Grin, R. Gautier, J.-F. Halet *Inorg. Chem.* **2017**, *56*, 4229; (c) A. Ullah Khan, R. Al Rahal Al Orabi, A. Pakdel, J.-B. Vaney, B. Fontaine, R. Gautier, J.-F. Halet, S. Mitani, T. Mori *Chem. Mater.* **2017**, *29*, 2988; (d) R. Al Rahal Al Orabi B. Boucher, B. Fontaine, P. Gall, C. Candolfi, B. Lenoir, P. Gougeon, J.-F. Halet, R. Gautier *J. Mater. Chem. C* **2017**, 5, 12097; (e) R. Al Rahal Al Orabi, E. Orisakwe, D. Wee, B. Fontaine, R. Gautier, J.-F. Halet, M. Fornari, *J. Mater. Chem. A* **2015**, *3*, 9945.

Keywords: electronic structure, DFT calculations, transport properties, thermoelectric properties, borides, nitrides, intermetallics

*Speaker

Minimum thermal conductivity in the context of diffuson-mediated thermal transport

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The concept of minimum thermal conductivity, kmin, is important for materials screening and device design, particularly for thermoelectric and thermal barrier technologies. Current models estimate kmin in terms of phonon transport, where phonon velocity (speed of sound) is the operative experimental input. In particular, the Cahill [*Phys. Rev. B* **46**, 6131 (1992)] and Clarke [*Surf. Coat. Technol.* **163**, 67-74 (2003)] models are used extensively. However, recent thermal conductivity experiments on complex materials have been reported that are substantially lower than these models predict.

This study recognizes that atomic vibrations in complex materials at high temperature may be better described by *diffuson* quasi-particles, as defined by Allen and Feldman [*Philos. Mag. B* **79**, 1715-1731 (1999)]. By using the experimentally determined vibrational density of states, we derive the diffuson thermal conductivity, kdiff, and show that it is defined by the average vibrational frequency. Furthermore, the average vibrational frequency is found to be highly correlated with the Debye temperature, allowing kdiff to be estimated from readily accessible speed of sound measurements when the vibrational density of states is unavailable.

Using kdiff as an estimate of kmin gives values that are 37% lower than the Cahill model and 18% lower than the Clarke model, which may reconcile some experimental findings of thermal conductivity below the Cahill model. Additionally, kdiff is proposed to be a good metric for identifying materials with extraordinary physics leading to ultralow thermal conductivity, such as phonon focusing.

Keywords: thermal conductivity, phonon, diffuson, transport, density of states, speed of sound

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Effects of Grain Size and Grain Boundary Nanostructures on Lattice Thermal Conductivity of MgO

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Grain boundaries (GBs) are one of sources of phonon scattering and have been exploited to suppress lattice thermal conductivity (LTC) especially in nanostructured thermoelectric materials. The mechanism is usually explained by the decrease in phonon mean free paths due to finite grain size, assuming that all GBs have the same effect on the suppression on LTC. However, it is generally known that GB properties are not identical to others' and significantly depends on their GB characteristics, e.g. misorientation, GB energy, atomic structures, and so forth. For further suppression of LTC by GBs, it is required to investigate LTC of individual GBs and reveal the factors determining LTC in the vicinity of GBs.
In this study, we obtained more than 80 symmetric tilt GB models which are energetically stable by simulated annealing method, and calculated LTC across GB planes in the presence of a single GB using perturbed molecular dynamics. In addition, we also calculated LTC of a single GB with different GB spacing to precisely investigate size dependency of LTC. MgO was chosen as a model material since their GB structures are geometrically simple so that the relationship between GB atomic structures and LTC is easy to grasp.
LTC of MgO symmetric tilt GBs varied depending on the types of GBs in the range from 9 to 33 W/mK, indicating that local GB atomic arrangements have a significant influence on LTC. By analyzing factors determining LTC of GB models, it wasfound that excess volume of GBs was most correlated with LTC compared to GB energy and number of coordination defects. Spatial dependence of atomic thermal conductivity in the vicinity of GBs showed that the mechanism of lattice thermal conduction is different between low-angle and high-angle symmetric tilt GBs. Further discussion and suggestion to control LTC by GBs will be given in this presentation.

Keywords: lattice thermal conductivity, phonons, grain boundaries, oxide, molecular dynamics

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Investigation of phonon states in a poor thermal crystalline conductor by means of inelastic scattering spectroscopy

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The modeling of thermal transport in dielectrics and semiconductors requires the knowledge of the phonon states in the phase space (**q**,E) and as a function of temperature. Their experimental investigation, and more specifically, that of the anharmonicity which limits their lifetime and is responsible for the thermal resistance, is essential for the theoretical development. However, while phonon energies are experimentally mastered properties, the measurement of phonon lifetime turns out to be difficult even in simple systems. In this talk, we will present the neutrons and X-rays spectroscopy techniques currently used for measuring thermal phonon energies, specifically illustrating their technical limitations, which have prevented until now any measurement of phonons lifetime in most crystals *[1]*. We will focus on the phonon dynamics in clathrates, a family of materials with complex crystal unit cell renowned for their puzzling low (_˜ 1-2 W/mK at 300 K) and almost temperature independent thermal conductivity. Here, we present the first measurement of phonon lifetimes in a clathrate single crystal *[2]*. Surprisingly, we find acoustic phonons with long lifetimes, traveling over distances from a hundred to tens of nanometers as their wave-vectors increase towards the boundary of the BZ. This finding challenges the common belief that low thermal conductivity implies short mean free paths. This apparent contradiction can be reconciled within the simple kinetic theory of thermal transport if only the low energy acoustic phonons are considered.

*Speaker

Keywords: phonon, lifetime, thermal conductivity, clathrate

Three-dimensional finite-element simulation of a flexible μ-TEG based on bismuth telluride

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The new generation of connected objects challenges researchers to find new ways to power these micro-systems and make them fully autonomous. In this context, energy harvesting technologies such as photovoltaics, piezoelectrics or thermoelectrics show great promises as they make possible the conversion of solar radiation, motion or thermal energy into useful electrical energy to charge micro-batteries for example.
Micro-thermoelectric generators (μ-TEG) exhibit several key benefits (no-moving parts, high reliability, no emission of hazardous gas) and take advantage of any temperature difference between their two surfaces. However, their electrical performance critically depends on the architecture of the TEG.
In this communication, the potential of a new flexible μ-TEG design used for thermal energy harvesting is discussed using numerical tools. The thermocouples are made of bismuth telluride thin films. The influence of several boundary conditions (fixed temperature, fixed heat input, electrical contact resistance) on the electrical performance is presented using a finite element analysis with the commercial software Comsol Multiphysics©. As an example, the study shows the possibility to achieve a net output power of 0.3 μW per thermocouple under a temperature difference of 10 K assuming the absence of electrical contact resistance. When this last parameter is taken into account, our results show that above 10-5 Ω.cm2 the electrical performances are drastically reduced. Comparison between simulations and experiments based on a manufactured 120-legs μ-TEG are also presented and discussed.

Keywords: simulation, finite element, flexible, μTEG, bismuth telluride

*Speaker

Concept of a Thermoelectric Module and Generator for Automotive Applications Based on an Integrated Functional Design

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Despite the ongoing electrification of vehicle propulsion systems, combustion engine vehicles will continue to bear the brunt of passenger and goods transport world-wide for the next several years. A major challenge of the automotive industry is the achievement of the required reduction of CO2 emissions for internal combustion engines. Therefore, it is necessary to investigate all potential technologies to improve efficiency. Regardless of whether a conventional or hybrid vehicle concept is used, up to approximately 40 percent of the fuels chemical energy is lost as waste heat in the exhaust system.
As a result, the DLR Institute of Vehicle Concepts, the Institute of Technical Thermodynamics and the Institute of Materials Research focus on utilizing exhaust heat through thermoelectric generators (TEG) in the DLR project Next Generation Car (NGC). Their primary goals are the development of cost-efficient thermoelectric modules (TEM) and TEGs with long-term stability and a maximized energy yield. In addition to overall TEG system design, the development of long-term stable, efficient TEMs for high-temperature applications is a great challenge.
This paper presents the results of internal development activities and demonstrates integrated functional designs of the TEM and TEG. The concept of contacting the TEMs on the surface of the heat exchanger of the TEG will be discussed. The thermodynamic boundary conditions are identified in this connection as well as the thermomechanical interactions. The connection is based on an innovative plasma-sprayed multilayer film. Moreover, the implemented thermodynamic, thermoelectric and thermomechanical models are described. The research results in an integrated functional design, which is primarily focused on high converter efficiency and low manufacturing complexity for the automotive applications.

Keywords: Thermoelectric Generator, Thermoelectric Module, Integrated Functional Design, Converter Efficiency

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Demonstrated High-Performance, High-Power Skutterudite Thermoelectric Modules for Space and Terrestrial Applications

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Thermoelectric technology has key benefits and strengths in many terrestrial and spacecraft applications, such as potential modularity, high reliability, and solid state performance. The Jet Propulsion Laboratory (JPL) has developed high-efficiency, high-power-flux thermoelectric (TE) modules using skutterudite materials and micro-scale design techniques in high-specific-power thermoelectric generators (TEG) critical for terrestrial energy recovery applications. New compact skutterudite-based TE modules with small cross-sectional footprints have demonstrated high power levels up to 20 We and module-level power fluxes greater than 3.75 We/cm2. The modules have demonstrated high powers levels and high efficiency ($>$ 9%) at working temperature differentials associated with a hot side temperature range of Th = 440∘C to 530°C and cold side temperatures of Tc = 20∘C. Both JPL and U.S. Army Research Laboratory performed module testing to confirm the experimental performance and validate performance predictions. Detailed ANSYSTM models predicting module-level I-V curves, internal resistance, interface heat fluxes, and power output were developed to guide the design process, predict the module performance, and correlate with recent test data. The detailed models were used to investigate and characterize internal module resistances, including interfacial electrical and thermal contact resistances that were uncertain prior to module testing. This work will discuss the design process, module modeling, testing, and test data/analytic prediction correlations associated with this module development. This paper will examine potential use of this thermoelectric technology supporting future NASA deep-space science and exploration missions; and transitioning to some Earth-based industrial processing and aircraft applications.

Keywords: High Power Density, Skutterudite, Thermoelectric Modules, Space Power, Terrestrial Power

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Development of High Efficiency Segmented Thermoelectric Couples for Space Applications

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Radioisotope Thermoelectric Generators (RTG) have been used by NASA to reliably power spacecraft for deep space exploration for over 40 years. Current state of the practice systems are limited to device-level efficiencies of 7.5% or less and system level specific powers of 2.8 to 5.1 W/Kg. NASA's Radioisotope Power Systems Thermoelectric Technology Development Program (TTDP) is pursuing development of more efficient thermoelectric technologies that could increase performance by a factor of 2 to 4x over these state of the practice systems. NASA's TTDP is developing high-efficiency segmented couples/modules with the following design goals: a) system conversion efficiency $\geq$ 11% ($\geq$ 60% improvement over MMRTG at BOL) and b) $\geq$ 6-8.5 We/kg specific power (2-3 x improvement over MMRTG), for a temperature gradient DT = 800 K (TH=1273 K and TC = 473 K). We will be discussing the state of development of the aforementioned couples and the tools that we use to guide this development.

*Speaker

Keywords: JPL, Next Generation RTG, modules, couples, high, efficiency

Silicides thermoelectric modules : performances and challenges

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Thermoelectric modules are powerful devices to harvest waste heat to electrical power. Industrial end-users needs are mainly restricted to low (0-250∘C) and medium (250-500∘C) temperature ranges. For low temperature, available devices on the market are based on Bismuth Telluride alloys. For medium temperature, modules based on silicide, skutterudite or Half-Heusler materials are under development but there are facing challenges concerning cost, mass production capability and robustness.
The French project RELIATEG is dedicated to the development of robust silicides modules covering low and medium temperature ranges. The materials used are High Manganese Silicide for n-type and Tin-Magnesium Silicide for p-type. X-ray diffraction analysis demonstrated the obtaining of the forecasted phase for both materials after by Spark Plasma Sintering. ZT values are in line with the state-of-art*: ZTmax=1.2(0.5) for n(p)-type at 500∘C. Thermoelectric modules with free-electrodes design were processed. Tomography pictures shows that modules are mechanically safe (no cracks). The performances are in line with the state-of-art*: maximal electrical power output of 958mWcm-2 (hot: 450∘C ; cold: 50∘C). These performances are reproducible: standard deviation of 43 mWcm-2 measured on 20 modules. Comsol Multiphysics simulations show a good agreement between expected and measured performances (80% reached).

For the low temperature range, the modules show a good robustness: performance maintained after 500 hours at constant ΔT (hot: 250∘C; cold: 50∘C) or after 1000 cycles with variable ΔT (hot: 150↔250∘C; cold: 50∘C). To reach a good robustness at 500∘C, there are still challenges to face off: oxidation/diffusion and thermomechanical issues. Technological solutions are under investigation.
* : G. Skomedal et al., Energy Conversion and Management, Vol. 40, pp. 13-21, 2016

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Keywords: thermoelectric modules, silicides, low temperature, medium temperature, performance, reliability

Economic profitability of hybrid photovoltaic-thermoelectric solar harvesters

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Over the last few years, a growing interest has surfaced about the possibility of enhancing solar harvester efficiency by coupling photovoltaic (PV) cells with thermoelectric generators (TEGs). To be effective solutions, hybrid photovoltaic-thermoelectric (HTEPV) solar harvesters must not only increase solar conversion efficiency but should also be economically competitive approaches to solar conversion. Today, the market of solar converters is dominated by silicon-based PV cells and modules, which set the reference cost-of-ownership and the power and energy costs that any alternate technology must defeat. Analyses of the economic sustainability of TEGs compared to other thermal engines have quite a long tradition. Instead, much less is available on the profitability of HTEPV generators. We propose an approach to a preliminary estimate of power costs that proceeds by splitting HTEPV generator costs as fixed costs and the costs of the PV cell, of the TEG stage, and of the eventual selective solar absorber. A hybridization figure of merit h is defined and used to assess the economic sustainability of hybridization. It is found that for non-concentrated modules, heat exchanger costs dominate h. Hybridization is convenient only over small areas, i.e. for very limited power outputs. In concentrated modules, instead, hybridization does not require the addition of heat exchangers, which are already part of the PV module. As a result, profitability extends to module areas of several squared meters already at modest concentrations. Favorable hybridization figures of merit are obtained for any module area when concentration further increases, with filling factors farther extending hybridization profitability.

Keywords: Hybrid solar converters, solar harvesting, economic sustainability

*Speaker

EFFICIENCY OF AN AUTOMATED DISSIPATION SYSTEM APPLIED TO Bi2Te3 AND MULTI STAGE MODULES

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The study described herein aims to analyze a thermal coolant dissipation system of thermal flows deriving from a non-fossil-based combustion capable of self-regulating through the applied sensors and to field actuators and applied to a thermoelectric device for the industry and for the automotive sector. This system has been designed to keep the efficiency of the modules as constant as possible, despite the variability of the thermal conditions around the system. The optimization is made in terms of electrical power and therefore also includes the management of the MPPT applied to the series of modules. The focus of the work is the comparative analysis of the management of BiTe and Multi Stage modules installed in the system and operating in different sectors of the exchanger. The study process starts from Comsol simulations for internal fluid dynamics and heat exchange. The modules were then best characterized by experimentally tracing the voltage-current-power curves. The first prototype was constructed from the theoretical study by programming the automation system in response to the estimated process curves and measurements were made on a working prototype. The system was also evaluated in conditions of rapid variability of the dissipated heat flux thus creating a sort of pulsed model.

Keywords: Multi Stage Modules, FEM analisys, MPPT, Heat Exchanger

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Measurement and analysis of thermal conductivity, thermal diffusivity and interfacial thermal resistance of thermoelectric thin films

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In order to determine thermoelectric figure of merit, thermal conductivity must be measured reliably. The laser flash method is the standard, reliable and the most popular method to measure thermal diffusivity and thermal conductivity of dense bulk materials including thermoelectric materials. There is growing needs to measure these thermophysical properties of nanostructured thermoelectric materials which are often available only as thin films instead of bulk shape. Since conventional laser flash method cannot measure thin films, pulsed light heating thermoreflectance method has been developed to replace the laser flash method. Whereas front heating - front detection (FF) configuration is popularly used for time domain thermoreflectance method, rear heating - front detection (RF) configuration is an analogy to the laser flash method which can determine thermal diffusivity with small uncertainty. We have developed versatile coverage of thermoreflectance in order to measure thermophysical properties of variety of ranging from several nanometers to several micrometers thick with the options of pulse laser from picosecond pulse duration to nanosecond pulse duration under RF configuration and FF configurations. When multi-layered thin films are measured, not only thermal diffusivity and thermal effusivity of each layer but also interfacial resistance between layers can be determined with small uncertainty based on heat diffusion equation.

Keywords: thin films, thermal conductivity, thermal diffusivity, thermal effusivity, interfacial thermal resistance, pulsed light heating thermoreflectance method, picosecond thermoreflectance method, electrical delay technique, repetitive pulse heating, TDTR

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Wearable Thermoelectric Generators for Powering Health Monitoring Sensors

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Abstract

As we continue to move to an era where health monitoring becomes part of our everyday life, there will be more needs to keep up the technologies that can support such needs. One of the main problems for the operation of wearables today is their dependency on battery power, which would need frequent recharging and can cause interruptions in their operation. Thermoelectric generators (TEG) convert the body heat directly into electricity and can provide energy for low power sensors. A TEG is a device in which electrons are driven by thermal energy and create an electrical current. TEGs can last years without losing efficiency, and are eco-friendlier than batteries; therefore, they can play a key role in future body powered healthcare and recreational electronic devices. ASSIST, or Advanced Systems of Integrated Sensors and Technologies, at North Carolina State University, is entitled to developing battery-less wearable electronics for health and environmental monitoring by employing nanotechnology enabled energy harvesters and sensors. After a brief introduction of the ongoing efforts in ASSIST, the prospect of TEGs for powering wearable technologies will be discussed. Recent advances in nanocomposite thermoelectric materials for body heat harvesting and device optimization strategies for wearable applications will be discussed in detail. Such devices can be implemented into the healthcare systems and become available for public use.

Keywords: Wearable thermoelectric generators

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Development of integrated micro-thermoelectric sensors for IC applications

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The continuous increase of applications in portable systems, such as mobile phones or laptops, inducing by a continuous increase of microelectronic chips number and power density in modern circuits and systems, leads to a critical level of thermal management. Indeed, too high temperatures can damage strongly the chips or even destroy them.
CEA is developing integrated thermal sensors based on Seebeck effect, enabling the accurate measurement of thermal flow at low scales.

These micro-ThermoElectric Sensors (μTES) feature very high sensitivities (several tens of mV/K) with fast response times (lower than the second range), are completely power-free (no power consumption compared to conventional systems) and can supply predictive information, allowing critical chips to be protected from thermal damage.

μTES have been manufactured by using conventional CMOS technologies from microelectronic industry, ensuring these components to be fully compatible and integrable in this environment.

The thin film thermoelectric materials used in μTES are based on silicon and deposited by Chemical Vapor Deposition (CVD). Polycrystalline silicon, silicon-germanium alloys and nanostructured alloys (quantum dots superlattices integrating silicide nanoparticles into doped SiGe matrix) are investigated.
Moreover, several technologies of thermal sensors have been developed to propose solutions adapted to various microelectronic environments: in-IC, stand-alone and on-interposer (H2020 STREAMS project) configurations have been processed and will be presented.

Keywords: sensors, thermal flow, thin film, microelectronic

*Speaker

New prototype of a thermoelectric heat pump with heat pipes for the air condition of a Nearly Zero Energy Building

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This paper presents a new prototype of an air-to-air thermoelectric heat pump, designed for the air conditioning of a Nearly Zero Energy Building (nZEB). The European Performance of Buildings Directive requires that Member States shall ensure that by 31 December 2020 all new buildings are nZEBs, which will reduce considerably the energy demand for air conditioning (as a reference, Passivhaus standard limits the heating/cooling demand at 15 kWh/(m^2yr), 10 W/m2 in terms of power demand). In this context, it is possible to maintain the comfort inside the building by heating/cooling the ventilation airstream.
A combination of a mechanical ventilation heat recovery system with a thermoelectric air to air heat pump (THP) demonstrated to be effective at maintaining the comfort conditions in a flat of 85 m2 in previous studies [1,2]. However, this THP prototype showed a limited COP. A new design based on heat pipes as heat exchangers reduces considerably the thermal resistance between the thermoelectric modules (TEC) and the airstreams, leading to an improved COP of 1-1,4 for cooling, at least two times the previous performance.

A mathematical model developed in Engineering Equation Solver predicts the performance of the TEC and the heat transfer through the heat pipes. The model is further integrated in a dynamic simulation of an nZEB with TrnSYS to analyse the energy performance and the comfort conditions in 5 European climates.

A. Martínez, S. Díaz de Garayo, D. Astrain. Air-to-air thermoelectric heat pump for heating, ventilation and air-conditioning in passive houses. Proceedings of the 37th ICT; 2017 Jul 31 – Aug 4; Pasadena (CA), USA.

S. Díaz de Garayo, A. Martínez, D. Astrain. Air-to-air thermoelectric heat pump for heating, ventilation and air-conditioning in passive houses. Proceedings of the 15th ECT; 2017 Sep 25 – 27; Padova, Italy.

Keywords: nZEB, passivhaus, heat recovery, thermoelectric heat pump

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Small size thermoelectric power supply for battery backup

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In the past years, a lot of works have been reported on thermoelectric generators (TEGs) as power supplies and as alternative technology. In this work, a TEG based on a catalytic combustor fed with propane/air mixture has been developed having as target output and dimensions the one proper of AA batteries. Catalytic combustion is particularly appealing for thermoelectric conversion due to its high power density coupled to the relatively low burning temperature.
The electrical output and size of the largely used AA batteries, together with catalytic TEG benefits such as reliability in continuous operating conditions, fast source recharging and adaptability are strategic features opening interesting opportunities for thermoelectric technology applications.

The system has been electrically characterized in different ranges of fuel flow rates at constant power and constant temperature conditions. All the Power contributions have been identified through the balance of power in/out at the maximum power production condition. TEG efficiencies and thermal resistances have been calculated thanks to high quality temperature and power characterization. Besides, using FT-IR analysis for exhaust gas composition the chemical efficiency has been determined. Finally, a discussion on output and thermal circuit suitability of the TEG has been presented.

The TEG system has been achieved an output up to 4.5 W (4.5 V at 1 A) by a fuel consumption of 4 g/hr, an output allowing to use such a device as a battery side technology.

Keywords: Thermoelectric generator, Catalytic combustor, Thermoelectric device, Battery backup

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Benefits of integrating vehicular thermoelectric generators with exhaust heat recovery apparatus

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It is more beneficial to incorporate thermoelectric generators (TEGs) with other apparatus than utilizing TEG alone for vehicles. When applying TEGs onto exhaust gas pipe with additional circulating coolant on the other side, the dimension and performance would be restricted due to interference with neighbors, electric power consumption, and weight increase, resulting in low cost benefit. In this study, we combined vehicular TEGs into existing exhaust heat recovery apparatus, expecting to overcome the restrictions and to enhance the cost benefit. Two different prototypes were fabricated to alternately operate for generating thermoelectric power and recovering exhaust heat, being evaluated in each mode at the same driving conditions. Performance of those prototypes was analyzed to compare thermoelectric power generation, exchanged heat, pressure drop, etc, so that one can consider own pros and cons according to application purpose.

Keywords: Thermoelectric generator, exhaust heat

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Heat pipes thermal performance for a reversible thermoelectric cooler-heat pump system

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The Energy Performance of Buildings Directive requires all new buildings to be nearly zero-energy buildings (nZEB) by the end of 2020 while all new public buildings must be nZEB by 2018. The integration of a thermoelectric cooler-heat pump system within the mechanical ventilation of these buildings could achieve the comfort temperature of the building at any season, as it could supply heating power to the entering air flow or it could absorb heating power, cooling down the enclosure. Consequently, by switching the supplied voltage of the thermoelectric modules, the same system could cool down or heat up the air flow that enters the building. As these systems have to be integrated within the architecture of the buildings, their size and weight are restricted. Thus, heat pipes are proposed to be used on both sides of the modules in order to have high efficiency heat transfer with a compact system.
The heat pipes would have to work in both directions, with the evaporator at the end in contact with the thermoelectric modules and consequently the condenser at the finned end, and the other way around, the evaporator at the finned end and the condenser at the end in contact with the modules. This situation occurs because the same system would have to heat up the entering air flow in winter and cool down the same air flow in summer. Thus, it is very important to evaluate the thermal performance of theses dissipation systems working both in summer and winter. To that purpose, an experimental methodology is presented. It would evaluate the thermal resistance of the heat pipes working in both seasons and as a function of the calorific power to evacuate and the air mass flow.
Moreover, the obtained data would be used to develop a computational model able to simulate the behavior of the system at any season, a really powerful optimization tool.

Keywords: heat pipe, passive house, thermoelectric cooling, thermoelectric heat pump

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Phase boundary mapping for the discovery and optimization of thermoelectric materials

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For the discovery of new thermoelectric materials, we typically think we only need to make the sample pure, often determined by X-ray diffraction, and measure its thermoelectric properties. Many new thermoelectric semiconductors are thought of as "line compounds" where all samples of the same nominal composition will have the same properties.
However for a compounds semiconductor, such as Mg3Sb2 there are at least two different thermodynamic states: Mg3Sb2 with *Mg*-excess or Mg3Sb2 with *Sb*-excess have distinctly different properties: one possibly being *n*-type and the other could be *p*-type. This is because thermodynamics requires the *Mg*-excess state to be in equilibrium with Mg and therefore the chemical potential of Mg is that of Mg metal while the *Sb*-excess has a Mg chemical potential vastly different, by 0.86eV, determined by equilibrium with elemental Sb. Because the defect formation energy depends on the chemical potentials of elements involved in defect creation, such a large change in chemical potential has a major impact in the concentration of intrinsic defects such as vacancies. In the case of *Sb*-excess Mg3Sb2 the Mg-vacancy formation energy, which produces holes, is less than zero at the conduction band edge making it an electron "killer defect." Any attempt to make n-type *Sb*-excess Mg3Sb2 will result in the formation of Mg-vacancies that produce counteracting holes. The discovery of high performance *n*-type Mg3Sb2, only recently, highlights the importance of examining all the distinct thermodynamic states by identifying the phase boundaries (Mg-excess as well as Sb-excess in this case) we call *phase boundary mapping*.
In CoSb3 skutterudites the confusion about solubility of filler elements can be explained by understanding phase diagram. In complex ternary compounds such as Ca9Zn4+xSb9 the defect chemistry is so complex the principle of phase boundary mapping has made the optimization of these high performance thermoelectric materials much more straightforward. This understanding of the existence of multiple inherently distinctly different thermodynamic states of the same nominal compound will vastly multiply the number of new complex semiconductors to be discovered for high zT thermoelectrics or other applications.

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Keywords: magnesium antimony, skutterudites

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Enhancement of average ZT of n-type Mg3(Sb,Bi)2 by increasing grain size

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Zintl compound n-type Mg3(Sb,Bi)2 was recently found to exhibit excellent thermoelectric figure of merit ZT_˜1.5 at 700K. We investigated the effect of grain size of sintered samples to improve the thermoelectric performance in the whole temperature range. By increasing the average grain size from 1.0 micrometer to 7.8 micrometer, the hall mobility below 500K was significantly improved, possibly due to suppression of grain boundary scattering. Consequently, the sample with larger grains exhibited enhanced average ZT. The calculated efficiency of power generation reaches 14.5% (at temperature difference of 420K), which is quite high for a polycrystalline pristine material. We also confirmed good thermal stability of Mg3.2Sb1.5Bi0.49Te0.01 against an oxidizing atmosphere at 673K. High performance and high stability in its polycrystalline form are advantageous for practical applications of waste heat recovery.

Keywords: Zintl phase, Mg3Sb2, grain size

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Probing the Thermal Stability Te-doped Mg3Sb1.5Bi0.5 via Combined Total Scattering and Powder Diffraction

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The thermal stability of thermoelectric materials has been highlighted as a critical bottleneck in their commercialization. The aim of the work encompassed in this project is to investigate the effect of extensive thermal cycling on the n-type Te-doped Mg3Sb2-based compound (ZT of 1.65 at 725 K) synthesized by a combination of ball milling and arc-melting. Suspicious temperature dependency of the Seebeck coefficient and electrical restitivity motivates the search for thermally induced structural events in the investigated temperature interval (300-725 K). Through combined *in-situ* PXRD and PDF, it is possible to examine the impact of heat on the short and long-range order of the atomic structure simultaneously. The PDF technique differs from PXRD by considering the full coherently scattered pattern from the sample instead of just the Bragg peaks. Because of this, signal from amorphous components and deviations from the average structure are included in the data and thus adds further information to the conventional crystallographic approach. Using a combination of DSC, STEM-EDS, PXRD and PDF, the thermal events in the n-type Te-doped Mg3Sb2-based compound were successfully described. The responsible mechanism could not be explained from X-ray diffraction experiments alone, but statistically significant correlations between parameters extracted from the PDF model successfully explains the observed behavior. This study seeks to emphasize the applicability of Pair Distribution Function in high temperature stability analysis of thermoelectric materials.

Keywords: Thermal stability, PDF, Total scattering, synchrotron, PXRD, DSC

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Observation of Valence band crossing: The Thermoelectric Properties of the CaZn2Sb2-CaMg2Sb2 Solid Solution

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Zintl phase compounds have long been of interest to the thermoelectric community, as they often are low band gap semiconductors and have complex crystal structures. These complex crystal structures lead to low lattice thermal conduct ivies and therefore overall enhanced efficiency. The layered 1-2-2 Zintl type structure is ubiquitous across different elemental systems, permitting for easily made substitutions and solid solutions. This allows for the fine-tuning of a material's electronic properties and possibly even band structure such that a maximum efficiency can be realized1. Herein we investigate the thermoelectric properties of the CaZn2Sb2-CaMg2Sb2 solid solution. We show through an effective mass analysis that as the composition is varied, transport in our materials is switching from one set of bands to another.

Keywords: Layered Zintl Compounds, Band Engineering

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Chemical bonding in layered thermoelectric materials

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Layered (2D) materials exhibit a variety of extraordinary properties, and recent focus has included topological insulators, electrode materials, monolayers, hetero structures – and thermoelectrics. The physical properties such as band gap or thermal and electrical conductivity are related to the detailed structural characteristics as well as the specific chemical bonding both within the covalent layers and across the van der Waal gap.
Using advanced crystallographic analysis including charge density modelling as well as *ab initio* theoretical calculations we have studied the crystal structures and chemical bonding of a range of important layered materials including Cu2Se [1], Mg3Sb2 [2], SnS2 [3] and TiS2 [4].

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Keywords: heusler, clathrates, zinc antimonide, magnesium silicide, thermal stability

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Computational Investigation of n-type Doping of Layered Antimonides: Mg3Sb2 and KSnSb

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Computational predictions suggest that n-type layered antimonides such as Mg3Sb2 and KSnSb are promising thermoelectric materials. The recent realization of high zT of 1.5 in n-type Mg3Sb2 has renewed interest in this class of materials. Growth with excess Mg, combined with extrinsic doping with Se or Te, was the key to realizing the high thermoelectric performance of n-type Mg3Sb2. The dopability of a material (n-type, p-type, or both) is determined by its intrinsic defect chemistry. In this work, we use state-of-the-art first-principles defect calculations to investigate the intrinsic defect chemistry of Mg3Sb2 and KSnSb. Our findings reveal diverse defect behaviors, which highlight the complexity of doping even in seemingly simple binary and ternary compounds. Specifically, we find that the growth conditions play a key role in defining the dopability of these layered antimonides. For Mg3Sb2, we also assess 12 different possible extrinsic n-type dopants. We find that Se and Te are effective anion-site n-type dopants, in agreement with previous experimental works. Interestingly, we have now identified a new cation-site n-type dopant for Mg3Sb2. Nb and Zn are ineffective n-type dopants primarily due to the high formation energy of the desired dopant-related defects; these findings warrant reconsideration of experimental studies that have reported n-type doping with transition metals.

Keywords: Zintl, Mg3Sb2, KSnSb, defects, first, principles calculation, doping

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New Insight on Tuning Electrical Transport Properties via Chalcogen Doping in n-type Mg3Sb2-Based Thermoelectric Materials

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N-type Te-doped and Se-doped Mg3Sb1.5Bi0.5 were discovered with excellent thermoelectric performance.[1,2] The high thermoelectric performance mainly originates from the strongly enhanced power factors due to a nontrivial conduction band minimum with six conducting carrier pockets.[1,2] Although n-type Mg3Sb1.5Bi0.5 is very promising, the effective n-type dopants are mainly limited to Te or Se. This might be attributed to the lack of chemical insight of n-type doping. Here we first synthesized and characterized S-doped Mg3Sb1.5Bi0.5 with a maximum zT of _˜1.0 at 725 K.[3] By comparing the effects of different chalcogen dopants Q (Q = S, Se, and Te) on the electrical transport, we explore the underlying chemical nature based on the electronegativity.[3] Experimentally, it is found that the chalcogen dopants Q become more efficient with decreasing electronegativity difference between Q and Mg, which is mainly due to the increasing carrier concentration and mobility. Using density functional theory calculations, we show that the improving carrier concentration originates from the increasing doping limit induced by the stabilizing extrinsic defect. Moreover, the increasing electron mobility with decreasing electronegativity difference between Q and Mg is attributed to the smaller effective mass resulting from the enhancing chemical bond covalency, which is supported by the decreasing theoretical density of states. According to the above trends, a simple guiding principle based on the electronegativity is proposed to shed new light on n-type doping in Zintl antimonides.

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Keywords: Mg3Sb2, electronegativity, bond covalency, doping limit, extrinsic defect, thermoelectric

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HRPD and HREM study of p- and n-type semiconductor YxAlyB14

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Maruyama and Mori [1,2] found previously that the title material with x≈0.56 and y=0.41-0.63 changes from the p-type to n-type semiconductor by the increase of Al content. High resolution powder neutron diffraction (HRPD) and high resolution electron microscopy (HREM) study was performed to determine where and how Al ions were located in the modified MgB14 type unit cell. HRPD data was obtained for either the p- and n-type powder samples using a HRPD machine in J-Parc. Since strong absorption effect was expected by the B10 isotope in the natural boron, B11 isotope enriched samples were prepared for the HRPD works. Unfortunately, some amount of B10 was still present in the samples. Neutron energy dependent absorption correction was needed for this case. Improved JANA2006 code was newly obtained for Rietveld structure analysis. The electron diffraction patterns in the hol-type Laue zone show two types of structural modulations for the p- and n-type samples, respectively. (2/3 0 0)-type satellites were observed in the p-type sample. Circular diffuse intensities were observed in the n-type sample. The former pattern corresponds to the ordered grains, which were observed in the HREM images. The latter corresponds to the short-range ordering.

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Keywords: boride, HRPD, HREM, structure, Rietveld analysis, modulation, satellites, diffuse scattering

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First principles study on the thermoelectric properties of 122 Zintl phase compounds

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Good thermoelectric materials are required to have large power factor and low thermal conductivity at the same time. However, it is difficult to obtain large power factor because the Seebeck coefficient and the electric conductivity are usually in a trade-off relation. From the band structure point of view, the conductivity increases while the Seebeck coefficient remains unaffected for a fixed Fermi level when the degeneracy of the bands increases [1].
Recently, 122 Zintl phase compounds have been found to have large dimensionless figure of merit ($ZT > 1$) [2,3]. Theoretical investigations have shown that the degeneracy of the bands at the band edge strongly affects the power factor and the dimensionless figure of merit in these materials [2,3]. These previous studies have mainly concentrated on the thermoelectric properties of Sb-based materials, but there can also be As- and P-based materials which exhibit high thermoelectric performance.

Given this background, we investigate the thermoelectric properties of various Sb-, As-, and P-based 1-2-2 Zintl phase compounds by means of first principles calculations. We calculate the power factor divided by the relaxation time, where it is found that that of As- and P- based systems is larger than that of Sb-based ones, e.g. Mg2Sb3, due to the large degeneracy at the band edge. We will discuss the relation between the shape of the band structure, the band degeneracy, and the thermoelectric properties in detail.
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Keywords: First principles calculations, Zintl phase compunds, 122 system

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Band engineering of the Mg3Sb2-Mg3Bi2 alloy composition investigated with transport analysis

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The recent success in improving n-type Mg3Sb2 based compounds with excellent thermoelectric properties have led to a great interest in the potential of n-type Zintl compounds. The strategy of alloying in the Mg3Sb2-Mg3Bi2 thermoelectric compound has originally been understood mostly as the thermal conductivity reducer by employing alloy scattering. However, Mg3Bi2-alloying may also be expected to significantly change the electronic transport properties and band structure. To fully understand the optimum alloy composition for thermoelectrics, it is essential to model both the p- and n-type compounds as a function of the Mg3Sb2 vs. Mg3Bi2 composition. We establish a model for the optimum alloy composition and find that the electronic property enhancement accounts for about 50 % of the benefits from alloying. We discuss how the Mg3Bi2-alloying impacts on the band structure in terms of the band gap, mass, and convergence, which are the critical factors that should be considered for band engineering in this material. By quantifying both electronic and thermal influences of Mg3Bi2 alloying, we reveal the optimum Mg3Bi2 content for thermoelectrics to be in the range of 20–30%, which is consistent with the most commonly reported composition Mg3Sb1.5Bi0.5.

Keywords: Mg3Sb2, Band Engineering, Alloying, Transport Analysis

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High thermoelectric properties of As-based 122-Zintl compounds Ba1-xKxCd2As2

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122-Zintl phase is well known as a high performance thermoelectric material. For the past decade, Sb-based 122-Zintl compounds have been intensively explored and found that the dimensionless figure-of-merit (ZT) exceeds the value of 1. Especially, Mg3Sb2 exhibits ZT = 1.65 at T = 725 K [1-2]. In contrast to the intense studies on Sb-based compounds, there are only few studies on As-based Zintl compounds. Lighter atomic mass of As than Sb discourages exploring As-based compounds because the lattice thermal conductivity (kL) usually becomes higher with lighter atoms. Recently we have found that Ba1-xKxZn2As2 exhibits low kL of 0.8 W/mK and high ZT of 0.67 at 900 K [3]. This discovery demonstrates that the As-based 122-Zintl compounds also have a potential for a high performance thermoelectric material. We, thus, further explored As-based 122-Zintl compounds in this study.
First, we conducted the first principle calculation and revealed that substituting Cd for Zn can improve the power factor. Being based of the calculation, we decided to examine thermoelectric properties of Ba1-xKxCd2As2. Polycrystalline samples of Ba1-xKxCd2As2 was synthesized by the solid reaction method. The high dense sample was obtained by hot-press.

The power factor of Ba1-xKxCd2As2 reached to 1.3 mW/mK2 at T = 773 K. kL was 0.5 W/mK at T = 773 K. Consequently, ZT reached to 0.81 at 773 K, which is the highest ZT value at As-based 122-Zintl compounds.

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Keywords: Zintl phase, Arsenic compound

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Donor-type doping in BiCuSeO: from high ZT values in p-type materials towards p-to-n type switching

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Since 2010, layered oxychalcogenide materials, with general formula RCuChO, (with R a trivalent cation and Ch a chalcogen element), have emerged as promising p-type thermoelectric materials. They are moderate (Bi) to large (rare-earth) band gap semiconductors and they can be easily hole doped by substituting A2+ in the trivalent cation site or by Cu vacancies to optimize the charge carrier concentration. Due to moderate carriers mobility, their promising ZT values mainly originate from their very low lattice thermal conductivity values, of the order of 0.3 W.m-1.K-1 at high temperature. By combining carriers concentration optimization and band structure engineering or microstructure optimization, a large figure of merit can be reproducibly obtained, with ZT values that reaches ZT ≈ 1.3-1.5 around 650∘C, which makes these materials among the best lead-free or tellurium-free polycrystalline p-type thermoelectric materials in this temperature range. However, till very recently, their actual potential for applications was limited by the absence of n-type counterparts, the low energy of formation of acceptor Cu-vacancies in these materials making n-type a distant dream.
In this talk, I will summarize our very recent results, which show that using a new donor-type dopant on the copper site, combined to a double-substitution on bismuth and copper sites, the transport properties of BiCuSeO can be:

- *switched from p-type to n-type*

- *optimized in p-type compounds to reproducibly reach ZT=1.5* in non-textured non microstructurally-optimized materials
and I will discuss the perspectives these results open for the future.

Keywords: oxychalcogenides, BiCuSeO

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Thermoelectric properties of oxysulfide Bi1-xPbxCuOS compounds

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Since 2010,(1) numerous studies focused on the thermoelectric properties of the layered oxychalcogenide BiCuOSe. Thanks to its intrinsically low lattice thermal conductivity and the increase of the power factor through cationic substitutions and texturation, a high ZT of 1.4 at 923 K was achieved.(2) Despite its lower cost and toxicity, the sulfur counterpart (BiCuOS) remains poorly documented, owing to its high electrical resistivity. In our study, Bi1-xPbxCuOS samples ($0 \leq x \leq 0.05$) have been synthesized with a short process ($<$ 5 hours) by means of mechanical alloying followed by reactive spark plasma sintering. Thanks to the Pb for Bi substitution, the charge carriers concentration increases by more than two orders of magnitude for x = 0.05. As a result, the electrical resistivity decreases, leading to a power factor 5 times higher (0.2 mW m-1 K-2 at 700 K) than the value reached in the pristine compound. The power factor being enhanced with a minimal impact on the thermal conductivity, the ZT reaches 0.2 at 700 K for x = 0.05. The experimental results are supported with Density Functional Theory (DFT) calculations of the band structure and vibrational properties.

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Keywords: oxysulfide, mechanical alloying, DFT

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Data-driven Discovery of Cu-S based Thermoelectric Materials

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Copper-containing sulfides are potentially low cost and environmentally friendly TE materials. In recent years, they are of great interest due to the world's demands for green energy generation. With guidance from data-driven models, we prepared several new thermoelectric sulfides using mechanical alloying and spark plasma sintering. Meanwhile, the underpinning physics for their good thermoelectric performance was also investigated. A Cu-S tetrahedral network was used as a crystal structural descriptor to screen 2000+ compounds from the Inorganic Crystal Structure Database (ICSD). Two minerals, Cu6Fe2SnS8 (mawsonite, zT=0.75@673K) and Cu16Fe4.3Zn1.7Sn4S24 (stannoidite, zT=0.47@673K) were successfully identified as thermoelectric materials for the first time. These materials were also prepared using an industrial scale ball mill to demonstrate the possibility of scale up. Inspired by the recent discovery of high entropy oxides, multi-component sulfides Cu4SnMgGeZnS7 and Cu3SnMgInZnS7 with five types of cation were designed, and were then successfully fabricated as dense ceramics. XRD confirmed that they were single phase and EDX showed that the cations were homogenously distributed. The zT value of Cu4SnMgGeZnS7 achieved 0.58 @ 773K, and the other Cu3SnMgInZnS7 is a semiconductor for which no suitable dopant has yet been found.

Keywords: Sulfide, Mineral, High entropy, High throughput

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Interplay between the structural and thermoelectric properties in Cu-S based synthetic minerals

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Copper-based chalcogenides have attracted increasing attention as thermoelectric materials. Examples are synthetic minerals of tetrahedrites and colusites, for which the combination of large Seebeck coefficient and low thermal conductivity less than 0.5 W K-1 m-1 leads to a high dimensionless figure of merit ZT = 0.5–1.0 at 673 K.
For the tetrahedrite Cu12Sb4S13, the suppressed lattice thermal conductivity has been attributed to the out of plane rattling of Cu atoms at a trigonal planer site. Our investigations of the crystal structures and phonon dynamics of the tetrahedrites Cu12(Sb, As)4S13 and Cu10Zn2(Sb,As)4S13 have revealed that the rattling of Cu atom originates from the chemical pressure inherent in the sulfur triangle. Furthermore, this rattling vibration shakes neighboring metalloid atoms via assistance from the lone pairs of the metalloids, resulting in the low thermal conductivity.

For the colusites, the mechanism of the low thermal conductivity is still controversial. We have studied the relationship between crystal structures and thermoelectric properties of Nb-colusites synthesized with the nominal compositions of Cu26–xNb2Sn6+xS32 (–0.3 $\leq x \leq$ 1.2). Highly densified samples were obtained by hot-press sintering. Different structures with ordered and disordered cation arrangements, respectively, have been found for the end compositions of x = –0.3 and 1.2. When the sintering temperature increased to 973 K, the thermal conductivity was much reduced irrespective of x, indicating that the sulfur-deficiency effectively lowers the lattice thermal conductivity.
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Keywords: tetrahedrite, colusite, crystal structure, thermal conductivity, rattling

*Speaker

A structural and thermoelectric study of a Cu-rich sulfide family: the germanite Cu26-xFe4+xGe4S32

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The increase in research on thermoelectric (TE) materials has been partly due to the need to find sustainable sources of energy. To this day, TE generation systems are the most viable method of waste heat exploitation. In this context, Cu-containing sulfides with complex crystal structures have enticed much attention after the discovery of high ZT values in mineral derivative materials such as tetrahedrite Cu12Sb4S13[1-3], colusite Cu26V2Sn6S32[4-6], and bornite Cu5FeS4[7-9]. Motivated by those pioneering studies, we are focusing on the germanite Cu26-xFe4+xGe4S32 (ZT= 0.17 at 575K for x= 3.6) family and the study of its crystal structure and TE properties. We herein discuss (i) the crystallographic structure from both powder XRD and neutron diffraction, Mössbauer spectroscopy and TEM results, and (ii) the thermoelectric properties of copper deficient germanite Cu26-xFe4+xGe4S32 samples synthesized from two different techniques (ball-milling and sealed tube).

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Keywords: Copper, rich, Germanite, chalcogenide, crystallography, substitution, ball, milling, neutron diffraction, XRD

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High-performance thermoelectric bulk colusite by process controlled structural disordering

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Recently, copper-containing sulfides have been attracting much attention because the main components comply the actual requirement of low cost, earth abundant, and less toxic. The colusite is a promising thermoelectric (TE) material characterized by a low thermal conductivity induced by complex cubic structure ($P\text{-}43n$, a ¯˜ 10.7 Å) and electronic band structure leading to obtain intermediate power factor (PF). We have previously demonstrated that colusite can be synthesized by ball milling of elemental stoichiometric mixtures followed by Spark Plasma Sintering. This synthetic methodology offers many advantages over high temperature solid-state reactions as it is faster, safer and readily scalable. Through this presentation, we will present new results recently published about the significant process effect in the colusite structure. By combining experiments with band structure and phonons calculations, we elucidate the underlying mechanism at the origin of intrinsically low thermal conductivity in colusite samples. We have exhibited that the Hot Pressing induced a copper-rich stoichiometry, by larger sulfur loss, and created local point defect. We have demonstrated that this random point defect which can took the form a stripe or random local point and coming from the pure tin column substitution by copper. We have shown, at the same time, the presence of order and disorder areas by the random contrast and the intensity of atomic columns using HAADF-STEM analysis. Both defects, contributed to a significant decreasing of the thermal conductivity. The measurements are rationalized with the aid of total energy and band structure calculations as well as the calculation of harmonic vibrational properties. As a result, the ZT value of bulk colusites rises to near unity at 675K, making this material one of the best p-type TE materials in this temperature

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region.

Keywords: Sulphide, colusite, mechanical alloying, sintering

Effect of composition on thermoelectric properties of as-cast materials: the Cu12-xCoxSb4S13-ySey case

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Tetrahedrites are world spread minerals that show high potential for thermoelectric applications. They have the Cu10M2Sb4S13 (M=Cu, Mn, Fe, Co, Ni, Zn) general formula, crystallizing in a body centered cubic symmetry, with 58 atoms in the unit cell. The main constituents of tetrahedrites are the non-expensive, non-toxic and earth-abundant Cu and S elements, which make them particularly interesting for practical uses. They intrinsically present very low thermal conductivities and, after proper power factor tuning through doping, can have figures of merit as high as zT=1. The partial substitution of Cu for Co and S for Se are changes of composition that have been reported to produce materials with good thermoelectric properties. However, these sulfosalt minerals are reported to not melt congruently, being usually prepared by melting followed by long-term annealing. Therefore, albeit some rapid preparation methods, as mechanical alloying, solvothermal synthesis and glass crystallization, have been reported, their economical and rapid production is still a challenge. The ideal situation would be to prepare them directly from the liquid phase (from the melt). In this presentation we report the preparation of Cu12-xCoxSb4S13-ySey ($0 \leq x \leq 2$, $0 \leq y \leq 1$) materials and their crystallographic, microstructural and thermoelectric characterization. These studies have shown that almost pure tetrahedrite materials can be prepared directly from the melt. Moreover, x=0.5 Co substitutions lead to high power factor values, while higher substitutions strongly increase the electrical resistivity and decrease the power factor, which points to an optimized small value. Additionally, the increase of Se content up to y=1 leads to an increase of the power factor, pointing to the possibility of the production of good as-cast thermoelectric tetrahedrites.

Keywords: Tetrahedrites, as, cast materials, thermoelectric materials, power factor

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Pulsed Hybrid Reactive Magnetron Sputtering as a new technique to obtain high quality selenides

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In this work, a high zT value at room temperature is obtained for n-type Ag2Se and p-type Cu2Se films when grown by pulsed hybrid reactive magnetron sputtering (PHRMS). PHRMS is a novel technique developed in our lab that allows to grow film of selenides with different compositions in a few minutes with great quality.

As an example, the zT value reported for room temperature Ag2Se films is the results from the combination of the high power factors, similar to the best values reported for bulk Ag2Se (2440 ± 192 μW m–1 K–2), along with a reduced thermoelectric conductivity as low as 0.64 ± 0.1 W m–1 K–1. The maximum power factor for these films is of 4655 ± 407 μW m–1 K–2 at 103 ∘C. This material shows promise to work for room temperature applications. Obtaining high zT or, in other words, high power factor and low thermal conductivity values close to room temperature for thin films is of high importance to develop a new generation of wearable devices based on thermoelectric heat recovery.

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Keywords: selenides, Ag2Se, Cu2Se, sputtering

*Speaker

Improved electrical transport properties and optimized thermoelectric figure of merit in lithium-doped copper sulfides

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Copper sulfide Cu2S is a p-type semiconducting compound that has attracted great attentions in the thermoelectric (TE) community most recently. Considering the intrinsic ultralow lattice thermal conductivity, the enhancement of TE performance in Cu2S should be achieved through improving its electrical transport properties. To achieve this goal, lithium element was doped into Cu2S in this study. A series of Cu2-xLixS samples with different Li contents (x = 0, 0.005, 0.01, 0.05, and 0.1) was synthesized by the melting-annealing method. When x $\leq$ 0.05, the Cu2-xLixS samples are stable and pure phases, having the same monoclinic structure with the pristine Cu2S at room temperature. The electrical conductivities in the Cu2-xLixS samples are greatly improved with increasing the Li-doping content due to the enhanced carrier concentrations. Meanwhile, doping Li into Cu2S increases the ionic activation energy and lessens the influence of mobile Cu ions on the heat-carrying phonons. Thus, the thermal conductivities of the Li-doped Cu2S samples are increased. A maximal zT of 0.84 at 900 K is obtained in Cu1.99Li0.01S, about 133% improvement as compared with the Cu2S matrix.

Keywords: Thermoelectric, Copper sulfide, Doping, Superionic conductor

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Suppressing Intervalley scattering for p-type InTe by nanoprecipitates

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High thermoelectric performance requires multiple valley transport character for electronic carriers. However, strong intervalley scattering may occur at elevated temperature, which causes dramatic typically exponential drop in carrier mobility and degrades electrical transport performance. In this study, thermoelectric properties of hot-pressed InTe polycrystalline samples are investigated by adding extra amount of Sb. The results show that the carrier concentration of InTeSbx samples is not altered but the carrier mobility at high temperature is well maintained as compared to the pure InTe sample.The temperature dependence of carrier mobility is recovered from an exponential drop for pure sample to the trend similar to acoustic phonon dominant case. We ascribe such phenomenon to the InSb nanoprecipitates, which possess high mobility. Meanwhile, these nanopreciptates show no influence on thermal transport and finally a zT of 0.7 at 673 K is achieved. Our finding provides a new route to suppress intervalley scattering for thermoelectric materials with multiple valley transport character by creating nanoprecipitates with high mobility.

Keywords: intervalley scattering, mobility, nanoprecipitates, InTe

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Unconventional Heat Transport Induced by Phase Transition in Cu2-xSe

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Unconventional Heat Transport Induced by Phase Transition in Cu2-xSe.

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Research in copper selenide thermoelectric (TE) alloys has raised the possibility of a significant enhancement of the TE figure of merit ZT when the Seebeck coefficient is affected by a concurrent phase transformation. This ZT increase has also been related to a radical reduction of the thermal conductivity evaluated by transient laser flash thermal diffusivity measurements. In contrast, steady state Harman based measurements do not support a significant ZT increase, only a modest one, because the thermal conductivity instead of decreasing goes through a sharp maximum as it approaches the critical temperature of 407 K. The nature of this sharp increase of heat transfer has not been related to electronic or phononic mechanisms. Near the critical temperature, when the alloy is exposed to a steady state temperature gradient, an additional heat transfer takes place, induced by the ongoing gradual phase transition. We show that the a to b and b to a phase transformation can lead to heat flow in the direction of the temperature gradient above and beyond conventional heat conduction. This unconventional heat transfer disappears when the temperature rises above the critical temperature where only a stable b-phase remains. We propose a model of such heat transport which leads to the sharp maximum of the related thermal conductivity. Results of numerical simulation are compared to the experimentally observed parameter.

Keywords: thermal conductivity, phase transition, chalcogenides

*Speaker

Intrinsically low thermal conductivity in metal chalcogenides for high performance thermoelectric energy conversion

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One of the fundamental challenge in developing high-performance thermoelectric materials has been to achieve low lattice thermal conductivity (L). The exploration of new materials with intrinsically low L along with a microscopic understanding of the underlying correlations among bonding, lattice dynamics and phonon transport is fundamentally important towards designing promising thermoelectric materials. InTe [i.e. In+In3+Te2], a mixed valent compound, exhibit an ultralow L, which manifests an intrinsic bonding asymmetry with coexistent covalent and ionic substructures.[1] The phonon dispersion of InTe exhibits, in addition to low-energy flat branches, weak instabilities associated with the rattling vibrations of In+ atoms along the columnar ionic substructure. These weakly unstable phonons originate from the $5s2$ lone pairs of adjacent In+ atoms and are strongly anharmonic, which scatter the heat-carrying acoustic phonons through phonon-phonon interactions. Similarly, a Zintl compound, TlInTe2, also exhibit ultralow L due to low energy ratting modes of weakly bound Tl.[2] Soft phonon modes and optical-acoustic phonon coupling cause an ultralow lattice thermal conductivity in the room-temperature hexagonal phase of AgCuTe, while the dynamic disorder of Ag/Cu cations leads to reduced phonon frequencies and mean free paths in the high-temperature rocksalt phase. A high thermoelectric figure of merit (zT) of 1.6 is achieved in the p-type AgCuTe at ~670 K.[3]

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Keywords: Intrinsic low thermal conductivity, lone pair, rattling, metal tellurides and soft phonons

*Speaker

Thermoelectric Performance of Bi2Te3 by Acceptor Type Germanium Doping

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Research in thermoelectric (TE) materials and devices requires optimization of three interdependent physical parameters. Stoichiometric Bi2Te3 is expected to be a p-type semiconductor, but hole-dominated charge transport is seldom realized in practice because of dominant electron donor Te vacancies and TeBi anti site defects.1, 2 We will present our work on the effect of Ge incorporation on structural and thermoelectric properties of Bi2Te3. With Ge doping, the carrier density increases by one order suggesting formation of acceptor states, consequently enhancing the electrical conductivity by _˜5 times and the power factor by _˜7.5 times. Thus, the estimated thermoelectric figure of merit reaches _˜0.95 for Ge doped samples at room temperature. Additionally, we will discuss the applicability of prepared Ge doped Bi2Te3 materials for segmented thermoelectric devices.3

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Keywords: Bi2Te3, Chalcogenides, Ge doping, Compatibility factor

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Increasing of Z factor for Bi2Te3-Sb2Te3

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The detailed experimental study of classic chalcogenides Bi2Te3-Sb2Te3 resulted in discovery of new opportunities for their efficiency increasing. Proposed solution allows to achieve at 25 % higher efficiency of thermoelectric generator working in temperature range 70C - 350C

Keywords: chalcogenides of bismuth and antimony, efficiency, generator materials

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Nano-SiC-dispersed Thermoelectric Composites

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A good thermoelectric material requires a combination of high electrical conductivity, large Seebeck coefficient and low thermal conductivity, but it is difficult to optimize these three interrelated parameters. Nevertheless, approaches to decouple their interaction can be found by designing nanocomposites which lead to additional ZT enhancement beyond band structure engineering of semiconductors. A series of our studies revealed that SiC nanoparticles dispersed in the p-type (Bi,Sb)2Te3 matrix can increase ZT due to simultaneously increased Seebeck coefficient and electrical conductivity. On the other hand, for n-type Bi2(Se,Te)3, the SiC nanodispersions lead to ZT enhancement, but limited to the temperatures below 450 K, and with a decrease in carrier concentration due to its significant influence on charged point defects. The SiC dispersions in the PbTe-based LAST alloys also can increase ZT, but the main contribution is the reduction of thermal conductivity resulting from the mismatched interfaces. A more recent study found a new effect of SiC nanodispersions in PbSe, which greatly increase the carrier concentration in spite of the chemical inertness of SiC in the PbSe matrix. A mechanically doping mechanism instead of conventional chemical doping effect should be responsible for the significant change in carrier concentration caused by dispersing chemically inert nanoparticles like SiC or even diamond in PbSe. Therefore, the dominating mechanisms for ZT enhancement in thermoelectric nanocomposites are quite complicated, which are different depending on the features of the thermoelectric matrix. The related discussions will be the main contents of this talk.

Keywords: Nanocomposite, Bismuth Telluride, Lead Telluride, Lead Selenide, SiC

*Speaker

Effects of defects induced by pressure and temperature on thermoelectric CuGaTe2 chalcopyrite structure materials

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Thermoelectric materials with chalcopyrite structure have been gathered much attraction since they have potential thermoelectric properties. In particular, Te-based chalcopyrite structure materials show high thermoelectric performance: ZT = 1.4 at 950 K for CuGaTe2 and ZT = 1.18 at 850 K for CuInTe2. Many attempts to enhance their thermoelectric properties were performed through various approaches such as band structure engineering to form a pseudo-cubic structure, tuning carrier concentration by elemental substitution, and reducing thermal conductivity by increased phonon scattering. Defect engineering of state-of-the-art thermoelectric materials have become an attractive strategy to tailor the electron and phonon transport properties, as well. In this research, we focused on effects of defects on the crystal structure, band structure, and thermoelectric properties of CuGaTe2 chalcopyrite structure materials. Firstly, we will discuss defects induced by temperature. Te and CuTe were found to be precipitated from the CuGaTe2 matrix with elevated temperature. To analyze the effect of such defects on the crystal structure, temperature dependent tetragonal distortion and x-coordinate of Te were evaluated. Furthermore, 10 cycles of temperature dependent measurement of electrical conductivity and Seebeck coefficient was performed to reveal the thermal stability of CuGaTe2. Secondly, we will introduce defects induced by high-pressure treatment at room-temperature. Cation-disorder at Cu and Ga sites in CuGaTe2 were found to arise with pressure, which was determined by crystal structure analysis. We predict, from the calculated formation energy, that such disorder can be induced as a metastable structure The effects of defects on their thermal conductivity, electrical properties, and band structure will be also discussed.

Keywords: chalcopyrite structure, defect, band structure, transport properties

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Transition metals in ternary rocksalt-type tellurides – doping vs. precipitates

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Precipitates such as cobalt germanides have been shown to significantly increase the thermoelectric performance of germanium antimony tellurides (GST materials).[1] With respect to high-temperature and long-term stability of such composite materials, they benefit from low solubility of the transition metal in the ternary matrix material. A certain level of mutual doping between matrix and precipitates may also enhance ZT values. In case of copper telluride precipitates in GST, this is due to an enhancement of charge carrier mobility. Effective mass modelling based on Hall measurements shows that the charge carrier concentration is at its optimum in such composites; therefore, the reduction of lattice thermal conductivity kL due to the heterostructure is a decisive factor. According to such modelling, doping is also close to its optimum in GST / cobalt germanide materials. Melt-spinning followed by spark-plasma sintering further enhances ZT values; however, the influence of Co then becomes less pronounced. The interplay of different effects is very crucial and simple reasoning is prone to misinterpretations as shown by experiments with small amounts of NiTe2-x precipitates in rocksalt-type tin antimony tellurides. In contrast to GST, the latter have the advantage of not undergoing any phase transitions. Yet, despite the extremely small amount of Ni doping of the matrix, there is a pronounced increase of charge carrier density and thus electrical conductivity. This overcompensates any influence on kL. Despite the very close analogy to the Co-GST system, the influence of the transition metal is completely different. However, small precipitates are always expected to improve mechanical properties in analogy to dispersion hardening of alloys.

F. Fahrnbauer, D. Souchay, G. Wagner, O. Oeckler, *J. Am. Chem. Soc.* **2015**, *137*, 12633-12638.

Keywords: heterostructures, chalcogenides, precipitates, effective mass modelling

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Chalcogenide-based nanocomposites for thermoelectric applications

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Nanocomposites, made of nano-inclusions embedded in a uniform host matrix, have recently come at the forefront of materials research for thermoelectrics, due to the drastic reduction of the thermal conductivity with almost no effect on electronic properties, as reported by a number of theoretical investigations. Such reduction can be understood in terms of phonon scattering at the interfaces between the two phases, and the nanometric dimensions of one of the phases. However, Effective Medium Approaches taking into account these factors, while roughly reproducing the thermal conductivity decrease, cannot explain some results of molecular dynamic simulations, such as the high energy phonons filtering[1,2].
Here we report the first experimental investigation of the phonon dynamics in a nanocomposite made of nanocrystalline GeTe surrounded by amorphous carbon. Here a reduction of the thermal conductivity by a factor of 10 with respect to pure GeTe was recently reported[3] not explained by the changes in the electronic contribution alone, suggesting thus a dramatic modification of phonon properties.

We show that while phonon dispersions are not affected by the nanostructuration, the low energy part of the phonon density of states is strongly perturbed, giving rise to an excess of modes, reminiscent of a Boson Peak in glasses. Such results give hints of a disorder-dominated dynamics despite the amorphous component is minor.

A. Minnich et al., RSC Adv., 6, 105154 (2016)

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T. Damart, V. M. Giordano and A. Tanguy, PRB, 92, 094201 (2015)
A. Kusiak et al., J. Phys. Conf. Ser. **745**, 032104 (2016).

Keywords: nanocomposite, phonon dynamics, thermal transport, thermoelectric

Rapid oxidation in Mg2(Si-Sn) alloys ; optimization via tin reduction and nanostructuring approach

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Among the thermoelectric ecofriendly materials, Mg2Si1-xSnx (xbetween 0.4 and 0.6) have been known to demonstrate excellent thermoelectric figures of merit in the medium temperature regime.
Nonetheless a very fast disintegration of this material (identified as pesting effect) limits their application under air. In this work, a novel way to obtain a stable material thanks to a nano structuring approach and tin amount reduction (x inferior than 0.2) will presented. We demonstrated that mechanical alloying with high energy ball milling (HEBM) in inert atmosphere could be used for Mg2Si1-xSnx elaboration without long milling. Compatibility with large volume production is also demonstrated on 1kg kg/batch. The resulting HEBM powder is finely pre-alloyed and suitable for SPS. The high content of defects, induced by high energy impacts, confines the diffusion of elements during SPS in the nanometer range, leading to the formation of a specific microstructure, as shown in TEM and SEM analyses.
This process route leads to a Sb-doped Mg2Si0.87Sn0.13 composition, which demonstrated good stability under oxygen until 500∘C with a maximum of ZT equal to 0.9 at 500∘C.

Keywords: silicide, oxidation, ball, milling, sintering

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Exploit Si-kerf from Photovoltaics: A Promising Application on the Thermoelectrics

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Cutting Si wafers for photovoltaics has been a major issue since most of the 50% of the material is wasted as kerf. Efforts on making this kerf reusable are of increasing interest focusing on applications such as batteries, heat exchangers, color glasses etc. In this work, we explore the case of thermoelectrics as a potential field to exploit Si that comes from such type of waste and improve sustainability. Kerf slurry waste from cutting Si wafers was processed aiming to get powders with high Si concentration for the preparation of thermoelectric silicides. Mg2(Si,Sn) based materials were prepared using such starting powder and promising properties were found. Structural features as well as thermoelectric properties and performance of the silicides will be presented and compared to the known compositions prepared using Si of high purity.

Keywords: silicides, silicium, magnesium silicide

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Insight on band structure of p-type Mg2Si1-xSnx with x=0-1 using a single parabolic band

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Development of Mg2Si based thermoelectric generators requires both good n- and p-type materials. While n-type Mg2(Si,Sn) materials have good thermoelectric properties, the corresponding p-type does not. Therefore, optimizing p-type is highly desired. To this end, we have systematically varied the Si:Sn ratio experimentally and a SPB model is used to study the transport properties.
P-type Mg2Si1-xSnx with x = 0 - 1 was synthesized by high energy ball milling and current assisted sintering. The maximum achievable carrier concentration, power factor, and dopant efficiency increase with higher Sn content. Also, the carrier mobility increases strongly from Mg2Si to Mg2Sn. This is mainly caused by changing effective mass for the valence band which increases from 1.1 me to 2.2 me as we move from Mg2Sn to Mg2Si. The temperature dependence of the electrical conductivity can be modelled with good agreement taking into account acoustic phonon (AP) scattering and alloy scattering (AS). Estimation of deformation potential (Ed = 9.5 eV) and the alloy scattering potential constant (Ea = 0.4 eV) allows to predict the thermoelectric properties of any arbitrary composition. Hence, we can predict, first, an optimum material zT for x = 0.6, second, a maximum power factor achieved for Sn-rich compositions and third, a significant improvement of the thermoelectric properties of Si-rich compositions if the carrier concentration is experimentally increased.

Keywords: p, type Mg2(Si, Sn), single parabolic band (SPB)

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Contact development for n and p-type Mg2(Si,Sn)

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For the temperature range of 500 K to 800 K – where a large fraction of the waste heat is available – magnesium silicide based solid solutions are among the most promising thermoelectric materials for large scale waste heat recovery applications. They combine very good thermoelectric properties with a high material availability, low cost of raw materials and environmental compatibility. Alongside material improvement, the development of long-term stable contacts with low contact resistances is the most crucial challenge for a technological solution of magnesium silicide based thermoelectric generators.
We have evaluated Ni, Cu, constantan (CuNi), and Ag as electrode materials for magnesium silicide based solid solutions Mg2X (X=Si,Sn) trying to identify the key factors for good adhesion and low contact resistances. For most electrodes good mechanical adhesion could be obtained combined with relatively low local electrical contact resistances (), depending on joining conditions.

We can clearly show that the sintering temperature is one crucial parameter as it determines the interface thickness and composition. Adjusting the sintering temperature can be used to avoid the formation of phases that can lead to cracking formation as observed for Ag. Furthermore, as observed for Ni, optimizing the sintering temperature can also mitigate the cracking inside the thermoelectric material. With respect to CTE we can first show that while closely matching CTE is advantageous, less cracking is observed if the electrode has a larger (not smaller) CTE than Mg2(Si,Sn). The electrical contact resistances for n- and p-type thermoelectric materials are generally comparable, but can be significantly different if the electrode acts as a dopant for the TE-material.

Keywords: silicide, contact development, interfaces

*Speaker

Recent Progress in Silicide-based Thermoelectric Materials

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Silicide-based thermoelectric (TE) materials have recently attracted renewed interest as they consist of naturally abundant and less-toxic elements. Among the silicide TE materials, we are particularly interested in higher manganese silicides (HMSs; MnSi_˜1.7), CrSi2 and Mg2Si-based materials, as they exhibit reasonably high TE performance. In this contribution, we will review recent progress in TE properties of these silicides.
HMSs had a serious problem to form MnSi (monosilicide) striations during the solidification. We have discovered that a small amount of V-substitution effectively dissipates such striations as well as a moderate hole-doping which raises the TE power factor almost doubled at 800 K. The Cr- or Ru-substitution induces a sort of domain separation of Mn-rich and Mn-poor regions, with less than tens of micrometer-scale, which causes a significant reduction of lattice thermal conductivity. Unusual temperature evolution of lattice parameters, originates from the difference in the coefficient of thermal expansion of two sublattices, is another critical phenomenon to restrict the material for a wide use. We will discuss the solutions in terms of crystallographic knowledge.

CrSi2-based solid solutions are known to allow partial substitutions on the Cr sites and lots of partial substitutions with V, Mn, Mo or Nb have been performed. We have discovered that some metal atoms can also occupy the Si sites as hole-dopants and may shift the maximum operating temperature towards higher.

Interstitial Mg (MgI) plays a key role to dictate the conduction type in Mg2Si-based materials. We will demonstrate the effect of MgI on the TE properties in Mg2(Si1-xSnx) solid solutions.
This study is supported, in part, by New Energy and Industrial Technology Development Organization (NEDO) and JSPS KAKENHI (Grant Nos. 25289222, 17H03398 and 17H05207), Japan.

Keywords: higher manganese silicide, chromium silicide, magnesium silicide, valence electron counts, crystal structure

*Speaker

Mg2Si1-xSnx solid solutions: phase formation and challenges in their electrical contacting

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Mg2Si1-xSnx solid solutions are among the most investigated thermoelectric (TE) materials, not only due to their TE performance but also due to their low price, low density, non-toxicity and large natural abundance of their elements. The best TE properties have been found, experimentally and theoretically, for compositions with x = 0.6-0.7. However, a miscibility gap is featured in the reported Mg2S –Mg2Si pseudo binary phase diagrams which rules out the formation of stable ternary phases of certain compositions. The extension of the gap has not been conclusively determined. According to some reports, the optimal compositions (x = 0.6-0.7) would lie within the gap. It is therefore doubtful whether an efficient long-term operating TE generator based on Mg2Si0.3-0.4Sn0.6-0.7 is feasible. In this contribution I report on the phase formation of Mg2Si1-xSnx solid solutions (x = 0.5; 0.6; 0.7; 0.8) synthesized by field assisted sintering technology (FAST) under various regimes. The starting powder mixture is prepared by high energy disk milling of the elements. During this process, Mg2Sn is formed by mechanical alloying. The different stages of the reaction during the FAST process will be discussed. The parameters influencing the homogenization of the sample are the sintering temperature, the uniaxial pressure, the isothermal holding time and the particle size of the Si starting powder. In the course of homogenization, Mg2Si1-xSnx phases with compositions ranging over almost the entire Mg2Sn-Mg2Si pseudo-binary phase diagram are observed. The formation of single phase Mg2Si1-xSnx with x = 0.5; 0.6; 0.7 and 0.8 contrasts with the reports of a miscibility gap in the phase diagrams. Annealing of Mg2Si0.4Sn0.6 at 600 ∘C for 168 h does not lead to any phase separation. The possible influence of the direct pulsed current on the phase formation will be discussed. The affinity of Mg for oxygen and anions like For Cl (forming part of the solvent or flux in solder pastes) as well as the reactivity of Mg, Si and Sn with several metals used as diffusion barriers pose a big challenge for the contacting of Mg2Si1-xSnx with Cu substrates. Some progress on this topic will be also presented.

Keywords: fast, mangnesium silicide, tin

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Electron-poor Al-Ge narrow gap semiconductors: comparison with thermoelectric Zn-Sb compounds

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The Zn-Sb intermetallic compounds are well known for their excellent thermoelectric properties. This is mainly because of their low thermal conductivity due to their complex crystal structure and their favourable electronic band structure due to their complex bonding picture. These compounds have less than 4 electrons per atoms and can be seen as electron-poor semiconductors. This electron count leads to three types of chemical bonds: 2 electron-two centers Zn-Sb bonds, 2 electron-two centers Sb-Sb bonds and multi-center Zn-Sb bonds. It has been proposed that this peculiar bonding scheme is favourable for obtaining good electronic properties for TE applications. In order to verify this concept and to find new materials with similar crystal structure as Zn-Sb compounds, we have recently explored the family of metastable Al-Ge materials, which crystal and electronic structures was not well known. In the present communication, we report experimental and theoretical works on semiconducting rhombohedral Al6Ge5 and monoclinic AlGe compounds obtained using out-of-equilibrium synthesis techniques (mechanical alloying, ultrarapid quench). We have fully resolved their crystal structures and studied their stability, lattice dynamics and electronic properties in order to compare them to those of Zn-Sb compounds and to evaluate their potential for TE applications. Al6Ge5 has the same crystal structure as the ideal phase of Al4Ge3 without defect whereas the crystal structure of monoclinic AlGe is very similar to that of orthorhombic ZnSb. The Al-Ge compounds are thus electron poor semiconductors with the same complex bonding picture as the Zn-Sb compounds.

Keywords: Metastable, Semiconducting, Crystal structure, Lattice dynamics, Electronic properties,

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Stability

Structural analysis of beta- and gamma-phases of Zn4Sb3 thermoelectrics

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Beta-Zn4Sb3 is a promising thermoelectric material exhibiting $zT > 1$ at high temperature above 500 K. There is a problem in its synthesis process; cracks are formed in a beta-Zn4Sb3 sample during the cooling process after melting. It is considered that a phase transition from gamma-Zn4Sb3 to beta-Zn4Sb3 at 764 K accounts for the cracks. However, the crystal structure of gamma-Zn4Sb3 has not been reported yet.
In this study, we reconsidered the crystal structure of beta-Zn4Sb3. According to a previous study [1], beta-Zn4Sb3 has four Zn sites (Zn(1), Zn(2), Zn(3), and Zn(4)) and two Sb sites (Sb(1) and Sb(2)). Zn(1) is a normal site whose occupancy is approximately 90%, while Zn(2), Zn(3), and Zn(4) are interstitial sites where the occupancy of each site is approximately 5%. However, the Zn(2) and Zn(3) sites are quite close to the Zn(1) site. In addition, a summation of the occupancies of the Zn(1), Zn(2), and Zn(3) sites is approximately 100%. Therefore, we proposed a new crystal structure model in the framework of a composite crystal. The composite crystal consisted of [Zn3+dSb] and [Sb] subsystems with a superspace group of R-3m(00r)00s, i.e., its structure formula is represented as [Zn3+dSb][Sb]g. The former subsystem included the Zn(1), Zn(4), and Sb(1) sites, while the latter subsystem included the Sb(2) site. In this composite crystal structure model, the Zn(2) and Zn(3) sites were integrated with the Zn(1) normal site. Only, the Zn(4) site was remained as the interstitial site.

In the conference, we will present our experimental results on the structural analysis of beta- and gamma-Zn4Sb3 by using the composite crystal structure model, and discuss a reason for the cracks in the viewpoint of the difference in their crystal structures.
G. J. Snyder et al., Nature Mater., 3 (2004) 458.

Keywords: Zn4Sb3, composite crystal structure, X, ray diffraction

*Speaker

Kondo-like phonon scattering in thermoelectric clathrates

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Crystalline solids are generally known as excellent heat conductors, amorphous materials or glasses as thermal insulators. It has thus come as a surprise that certain crystal structures defy this paradigm. A prominent example are type-I clathrates and other materials with guest-host structures. They sustain low-energy Einstein-like modes in their phonon spectra, but are also prone to various types of disorder and phonon-electron scattering and thus the mechanism responsible for their ultralow thermal conductivities has remained elusive. While recent ab initio lattice dynamics simulations show that the Einstein-like modes enhance phonon-phonon Umklapp scattering, they reproduce experimental data only at low temperatures. Here we show that a new effect, an "all phononic Kondo effect", can resolve this discrepancy. This is evidenced by our thermodynamic and transport measurements on various clathrate single crystal series and their comparison with ab initio simulations [1]. Our new understanding devises design strategies to further suppress the thermal conductivity of clathrates and other related materials classes, with relevance for the field of thermoelectric waste heat recovery but also more generally for phononic applications. More fundamentally, it may trigger theoretical work on strong correlation effects in phonon systems. [1] M. Ikeda, H. Euchner, X. Yan, P. Tomes, A. Prokofiev, L. Prochaska, G. Lientschnig, R. Svagera, S. Hartmann, E. Gati, M. Lang, S. Paschen, arXiv:1711.08627

Keywords: clathrates, thermal conductivity, correlations

*Speaker

Looking for stable thermoelectric materials

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There is a perpetual hunt for new materials with higher performance and favorable elements. However, most of these new materials rarely end up being considered for actual applications. This can largely be attributed to a lack of confidence in the stability of the materials, as it is often only explored a little or not at all. Famously SnSe exhibits a record-breaking figure of merit in the b-direction, however SnSe is useless for applications as it starts decomposing at far lower temperatures than where the peak performance is observed. Even materials that have been thought to be stable and considered for applications have been demonstrated to decompose. An example of this is the clathrate Ba8Ga16Ge30, which has long been considered stable, but is now known to slowly decompose leaking pure gallium out of its structure as well as forming α-Ge at relatively modest temperatures. Even when the material does not decompose at higher temperatures it may start failing upon repeated heating cycles or in thermal gradients like β-Zn4Sb3. In the search for more stable materials that would actually be applicable for modules we could look to minerals. Some of the best-known and used materials are related to minerals themselves, such as Bi2Te3 (tellurobismuthite) and PbTe (altaite). It has been predicted from calculations that p-type RuAs2 (anduoite), should have high performance. While it does not have favorable elements, it is demonstrated to have high stability further supporting the idea of minerals as thermoelectrics.

Keywords: Mineral, Minerals, Stable, Stability, Decompose

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Thermoelectric Properties and Search for condition of insulator transition in Al-Ir based quasicrystalline approximants

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In recent decades, thermoelectric properties of aluminum based quasicrystals and approximants have been intensively investigated because of their degenerated semiconductor like electrical properties and low thermal conductivity. The highest ZT in these compounds are 0.26 for Al-Ga-Pd-Mn system quasicrystal. Since no quasicrystals discovered so far have band gap, their Seebeck coefficient are about 100 μVK-1 at highest. Therefore, discovery of quasicrystalline semiconductor is necessary for the breakthrough of quasicrystal as a thermoelectric material.
Recently, the computational study reported by Mihalkovič *et.al.* indicated that binary Al-Ir quasicrystalline approximant has an insulating electronic structure with a band gap of 40 meV if the appropriate composition and configuration is satisfied.
In this study, we will report the thermoelectric properties of Al-Ir approximant predicted to be semiconductor. Furthermore, we performed first principles calculations to characterize the electronic structure and thermoelectric properties and compared these with the experimental results. The temperature dependence of thermoelectric properties of the sample made by conventional sintering process didn't exhibit an insulating but metallic behavior due to large amount of vacancies. To control vacancy density and optimize carrier concentration, high pressure synthesis and carrier doping have been performed. We found that high pressure synthesis can reduce vacancy density and improve thermoelectric properties.

Keywords: thermoelectric properties, quasicrystal, metal insulator transition, vacancy, high pressure synthesis, intermetallic compounds

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Suppression of vacancies boosts thermoelectric performance in type-I clathrates

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Intermetallic type-I clathrates continue to attract attention as promising thermoelectric (TE) materials. Their peculiar structural characteristics as well as their ability to accommodate different types of atoms at the framework and guest sites make them interesting also for fundamental investigations. In this contribution, the composition-dependent structural and thermoelectric properties of single crystalline Ba8(Cu,Ga,Ge,)46, where denotes a vacancy, will be presented. In crystals without Ga, single crystal X-ray diffraction reveals clear evidence for the presence of vacancies at the 6c site in the structure. With increasing Ga content, vacancies are successively filled. This increases the charge carrier mobility strongly, even within a small range of Ga substitution, leading to a reduced electrical resistivity and enhanced thermoelectric performance. The largest figure of merit $ZT = 0.9$ at 900 K is found for a single crystal of approximate composition Ba8Cu4.6Ga1.0Ge40.4. This value, which may further increase at higher temperatures, is one of the largest to date found in transition metal element-based clathrates [1]. [1] X. Yan, M. Ikeda, L. Zhang, E. Bauer, P. Rogl, G. Giester, A. Prokofiev and S. Paschen J. Mater. Chem. A, 2018, **6**, 1727-1735

Keywords: Intermetallic type I clathrates, Crystal structure, Zintl phase, Single crystal X ray diffraction

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Understanding and tuning full-Heusler thermoelectric materials based on Fe2VAl

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Cubic full-Heusler, X2YZ, and half-Heusler XYZ systems have been proven to be very promising active thermoelectric materials because i) of their thermoelectric performance and ii) because of outstanding thermal and mechanical properties, important for applications in different domains. X and Y are (in general) transition metal elements and Z is a main group element. Although X, Y and Z elements are metallic in solid form, many of the full-Heusler and half-Heusler systems turn out to be semiconductors or, at least, the respective Fermi energy is located very near to a gap in the electronic density of states. Such a scenario is a pre-requisite for capable thermoelectric materials.
In this contribution, we report on tuning of full-Heusler systems based on Fe2VAl by substituting appropriate elements on all lattice sites of the Cu2MnAl type structure and a deeper understanding of the resulting relevant electronic and thermal properties by combining experiments carried out in a broad temperature range and first principles calculations in terms of the density functional theory (DFT) using the programme package VASP.

Depending whether these materials are manufactured as bulk or as thin films, a variety of unexpected features, like meta-stable states, behaviours reminiscent of high entropy alloys, huge logarithmic derivatives of the electronic density of states or certain types of protected states are observed (both latter from DFT calculations), which might positively influence the thermoelectric behaviour of this family of compounds.
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Keywords: Heusler, DFT, thin films, density of states, electron dispersion

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Thermoelectric properties of p- and n-type doped ScNiSb

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Crystallizing in the MgAgAs-type structure, ScNiSb belongs to a large family of half-Heusler (HH) compounds with promising thermoelectric properties. While many as-prepared HHs are n-type, arc melted ScNiSb exhibits p-type behavior which is comparable to the p-type conduction known for rare earths (RE) containing RENiSb-type alloys. Based on the transport data known for RENiSb-type alloys, one can expect a high hole mobility for ScNiSb. Further, our investigations show that the transport properties are tunable with appropriate dopants. While Co and Sn are p-type doants, Ti and Te substitutions readily give rise to n-type conduction behavior. High Seebeck coefficients with absolute values in the range 180 -240μV/K are noted for both p- and n-type alloys. The RT resistivity values are in the range of 0.5 -8.0 mΩ –cm.

Keywords: heusler

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Facile Synthesis of FeNbSb based Half-Heusler Thermoelectric Materials

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Half-Heusler materials are of growing interest for waste heat recovery applications with hot side temperatures ranging from 600 K to 900 K. These materials offer a wide range of compositions, which can be employed for fine tuning of thermoelectric (TE) properties via partial substitution and particularly reducing the lattice thermal conductivity through optimized phonon scattering.
A major challenge in the synthesis of commonly studied half-Heusler (HH) materials, such as (Ti,Zr,Hf)NiSn or FeNbSb, is posed by the high melting points of the constituent elements such as Hf, Zr, Nb, Fe and Ti. Most synthesis routes include a melting step. The problem associated with that arises from large differences in melting temperatures and vapour pressures of the individual elements, which may lead to evaporation and thus loss of some constituents, resulting in an undesired change in stoichiometry of the material. Furthermore, incomplete homogenization of the melt turns out to be an important issue, especially when using arc-melting. Therefore, several re-melting attempts of the ingot and subsequent long time annealing are generally required.

To overcome the obstacles linked with melting, we examine the possibility of direct ball-milling of pure elements in combination with current-assisted sintering of the powders to obtain high phase purity FeNbSb based TE materials, which will be addressed in this work. Moreover, the effect of doping and substitution by Ta on the TE properties of FeNbSb-based compounds is studied. Results of the phase and microstructure analyses, functional homogeneity together with thermoelectric properties will be presented and discussed.

Keywords: half Heusler, ball milling, FeNbSb, thermoelectric

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Phonon scattering by antiphase boundaries in Fe2VAl

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Fe2VAl is a semi-metal, which belongs to the family of Heusler alloys and crystallizes at 300K in the cubic L21 structure. Upon doping, its maximum power factor (PF) reaches PFmax = 4.0 - 6.0 mW m-1 K-2 at 300 K in *p*-type Fe2.04V0.86Ti0.1Al [1] and in *n*-type Fe2VTa0.05Al0.95 [2] respectively. These large values of PFmax, close or larger than in Bi2Te3 (PFmax = 4.9 mW m-1 K-2 at 300 K), combined with the low-cost and abundance of its constituting chemical elements could turn Fe2VAl into a competitive thermoelectric material. However, even after alloying, the thermal conductivity (lambda) remains large (e.g. lambda = 10 W m-1 K-1 in *n*-type Fe2VTa0.05Al0.95), restricting ZT to around 0.2 at 300K. The effect of phonon scattering by antiphase boundaries on the thermal conductivity was thus investigated in order to further reduce its phononic contribution in Fe2VAl.
Upon heating, Fe2VAl transforms structurally at 1080 ∘C into a disordered B2 structural variant (CsCl type) [3]. Upon cooling, the ordering transition from the B2- to the L21-structure results in the doubling of the lattice parameter as well as the formation of antiphase domains (APD). By increasing the cooling rate, it is possible to reduce the size of the antiphase domains and to increase the number of antiphase boundaries. Fe2VAl was thus furnace-cooled, water-quenched and melt-spun, leading to a decrease of the APD average size from > 10 mm to _˜700 nm and to _˜100 nm respectively. The phononic thermal conductivity decreases accordingly, from 28 to 17 W m-1 K-1. This work is among the first one to unambiguously unveil the scattering effect of antiphase boundaries on the phonon transport and it also paves the way to a larger ZT in Fe2VAl.

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Keywords: Heusler alloys, antiphase boundary, phonon scattering, thermal conductivity

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Industrialized Half-Heusler material and thermoelectric modules therefrom

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The industrialization and automation of material and module manufacturing technologies is one of the important topics to reduce the costs of thermoelectric technology. The company Isabellenhütte Heusler is engaged in the industrialization of Half-Heusler based thermoelectric technology.
The Isabellenhütte has a long tradition in Heusler compound research. Dr. Fritz Heusler found the first Heusler alloy in 1901 at Isabellenhütte. Since 2009 the Isabellenhütte has been actively involved in Heusler alloy research again. Since then we have been working on thermoelectric Half-Heusler compounds. Our purpose is the development of a melt metallurgical manufacturing process for these materials, which is able to be industrialized. We have also a focus on the development of thermoelectric modules using our Half-Heusler materials. In 2017 the Isabellenhütte built up an industrial pilot line production, which starts with the raw elements and ends up with thermoelectric modules. The ambition is to demonstrate an industrial scale material manufacturing and an automated assembling process of Half-Heusler modules in a constant high quality.

Now the project is in the process development phase. It has already succeeded to produce first 10 kilogram batches of P-type and N-type materials. In the framework of the H2020 funded project INTEGRAL it is planned to enlarge the production scale up to 50 Kg batches in 2019. Furthermore it is already possible to manufacture small single legs from these ingots with industrial processes. Concerning the modules first tests of an automated assembly by a self-developed production line are running. This work is a part of the German national funded project thermoHEUSLER[2].
Today the Isabellenhütte is able to show first results of P-type and N-type material from 10 kilogram ingots and results from thermoelectric modules made by these materials.

Keywords: Half, Heusler, halfheusler, heusler, industrial, Isabellenhütte, Module

*Speaker

High-Entropy Half-Heusler Thermoelectrics with High ZT_~1.5

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Half Heusler (HH) alloys currently are besides skutterudites and Zintl phases the most promising candidates for thermoelectric (TE) devices at elevated temperatures: they can be used in a wide temperature range and their starting materials are abundant and cheap. Particularly nanostructuring of TiNiSn-based thermoelectric materials - not only by ball-milling but also by preferably system-inherent phase separation - has accomplished multicomponent HH alloys with attractive ZTs for n-type TE materials based on (Ti,Zr)-Ni-Sn. These values could be achieved on the basis of a profound knowledge not only of isothermal phase relations, temperature dependent solubilities but also of the solidification behavior. The detailed experimental investigation of the constitution of the (Ti,Zr)-Ni-Sn systems including liquidus projections and Scheil solidification diagrams, as well as CALPHAD modelling, provided the necessary basis for an elaborate synthesis (annealing/hot-pressing) route in order to get a suitable and reproducible microstructure. Exploiting in addition the system inherent but coherent binodal/spinodal demixing at subsolidus temperatures within the sections TiNiSn-ZrNiSn and TiNiSn-HfNiSn we were able to achieve for the n-type half Heusler alloy Ti0.5Zr0.25Hf0.25NiSn a ZTmax = 1.5 at 825 K. The demixing is a balanced effect of destabilisation of the solid solution by a positive enthaphy of mixing compensated by elastic strain energy (coherent binodal) but also by the entropy of mixing. In this respect the five component thermoelectric material can be considered as a so-called pseudoternary high-entropy alloy system. The experimental data are backed by SEM/TEM analyses as well as by DFT results.

Keywords: Half Heusler alloys, nanostructuring, spinodal decomposition, high ZT_~1.5

*Speaker

Half-Heuslers, a compound not as stable as one stipulate.

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Full-Heusler (FH) and Half-Heusler (HH) compounds are commonly referred as thermally stable and can reach ZTs up to 1.2 around 900 K. On track to improve the thermoelectric properties of a half-heusler compound, we included a dopant into the system, expecting it to get on the half-heusler interstitial position. Doing so, instead of obtaining the HF stoichiometry, we were expecting some additional nano-cristallites mixing in the half-Heusler matrix. The samples were studied by means of synchrotron X-ray diffraction and PDF analysis. At first, it is clear that all samples contain binary impurities. Full-Heuslers characteristic diffraction peaks are observable only for higher content of dopant. Additionally, unexplained diffraction intensity on the half-Heusler diffraction peaks brought the idea that a partial filling of the interstitial sites had to occur in some crystallites. When refining the data, that x-half-Heusler was necessary to get refinements to converge. After increasing the temperature to 1000 K, we can witness that the reflections related to the full-Heusler disappear above 800 K, and do not reappear when cooling down to RT. Applying additional heating-cooling cycles does not appear to further alter the material. Checking the stability of thermoelectric material should always be on the to-do list for future work.

Keywords: heusler, thermal stability, decomposition, synchrotron

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Composite Structures in Thermoelectric Materials

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Composite structures consist of at least two different structure motifs, which may exhibit a misfit resulting in incommensurate super structures. Earlier examples include layered misfits of rock-salt blocks TS (with T = Sn, Pb, Bi) and layers comprised of early transition metal disulfides such as TiS2 and NbS2. Such materials may very well constitute the epitome of the phonon-glass-electron crystal concept (PGEC), resulting in ultralow thermal conductivity, such as in layered misfits like [(PbSe)0.99]m(WSe2)n, (MS)1+x(TiS2)2 (M = Sn, Pb, Bi), Ca3Co4–xCuxO9+d, Bi2[AE]2Co2Oy, and in Nowotny chimney ladder phases such as FeGex. None of those materials, however, have attained large figure of merit values of the order of 1. Often the electrical conductivity was lacking, possibly because the mismatch causing low phonon mobility also resulted in low electron mobility. Here we report on a new one-dimensional misfit composite material, namely Tl2Ag12Te7+x that adopts an incommensurately modulated super cell of the Zr2Fe12P7 type. To our knowledge, Tl2Ag12Te7+x represents the first misfit material with a figure of merit above 1, along with an ultralow thermal conductivity.

Keywords: composite, incommensurate, low thermal conductivity

*Speaker

High ZT in MnTe via spin physics

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Thermal fluctuations of the magnetization greatly increase the thermoelectric power of Li-doped MnTe over its value due to classical electron diffusion effects, driving the ZT of the material to exceed 1 at T $\geq$ 800 K. MnTe is an antiferromagnet (AFM) with a Neel temperature between 303 and 318 K. The samples are thus paramagnetic (PM) in the technologically relevant temperature range. Classical magnon-drag theories [1,2] are not sufficient to explain the observed effect in the AFM range, and do not apply to the PM range. Experimental evidence will be presented for the contribution of short-lived local thermal fluctuations of the magnetization (*paramagnons*) to the electronic thermoelectric power in both the AFM and PM regime. This will be done in a series of samples prepared with different hole concentrations, via simultaneous measurements of thermoelectric power, resistivity, thermal conductivity, Hall and Nernst effects, specific heat, and magnetization. The new, theoretical model developed is based on the observation that the lifetime of the paramagnons is longer than the electron-paramagnon interaction time, but shorter than the time scale for magnetization measurements. Thus, the paramagnons can drag electrons effectively, adding to the electronic entropy, while leaving no experimental trace in the magnetization. The end result is a high-ZT material, a unique example of a system in which magnetic excitations contribute dominantly and usefully to electronic transport.
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Keywords: Magnetization, Antiferromagnet, Paramagnetic, Paramagnons, Electronic Transport

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Dopant Induced Impurity Bands and Carrier Concentration Control for Thermoelectric Enhancement in p-Type Cr2Ge2Te6

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Our previous work demonstrated that Cr2Ge2Te6 based compounds with a layered structure and high symmetry are good candidates for thermoelectric application. However, the power factor of ony _˜ 0.23mW/mK2 in undoped material is much lower than that of conventional thermoelectrics. This indicates the importance of an electronic performance optimization for further improvements. In this work, either Mn- or Fe-substitution on the Cr site is investigated, with expectations of both carrier concentration control and band structure engineering. First principle calculations indicate that an orbital hybridization between d orbitals of the doping atom and the p orbital of Te significantly increases the density of states (DOS) around the Fermi level. In addition, it is found that Mn doping is more favorable to improve the electrical properties than Fe doping. By tuning the carrier concentration via Mn doping, the peak power factor rises rapidly from 0.23 mW/mK2 to 0.57 mW/mK2 at 830 K with x = 0.05. Combined with the intrinsic low thermal conductivity, Cr1.9Mn0.1Ge2Te6 displays a decent zT of 0.63 at 833 K, a 2-fold value as compared to that of the undoped sample at the same direction and temperature.

Keywords: Cr2Ge2Te6, impurity level, thermoelectric

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Large Nernst power factor in polycrystalline topological semimetal NbP

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The energy crisis has sparked widespread research interests in sustainable energy technologies. In this context, there is a large boost in thermoelectric research, the base of which is the longitudinal thermoelectric response, the Seebeck effect. Recently, there is a growing interest in the Nernst effect, the transverse thermoelectric response produced by the orthogonal thermal gradient and magnetic field. The Nernst effect is an alternate and much simpler approach to conventional thermoelectric effect as there is no need for both n-type or p-type legs. Also, the transverse transport configuration allows for spatially separating the heat reservoirs from the electrical circuitry, while at the same time performing at high efficiencies. Recently there is a growing interest to study Nernst effect of topological semimetals, because their Nernst signal can exceed the signal of the longitudinal thermopower by orders of magnitudes. To date, the investigations are primarily focused on the single crystalline samples. However, the synthesis of large single crystals is the expensive, lengthy, and difficult processes which are unsuitable for mass production and practical applications. In contrast, polycrystalline samples are better choice because of its ease of production. We demonstrate that polycrystalline, spark plasma sintered Weyl semimetal NbP that crystallizes in a body-centred-tetragonal lattice (space group *I41md*) show a large Nernst thermopower value of _˜90 μV/K and power factor of _˜35×10-4 Wm-1K-2 at 9 Tesla. Our finding indicates the potential of polycrystalline Weyl semimetals for thermoelectric energy conversion.

Keywords: thermoelectric, Nernst effect, topological semimetal

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Development of high-performance thermoelectric materials guided by large-scale experimental data

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In searches for thermoelectric materials, screening of unstudied promising compositions is important. Combination of past experimental data and first-principles calculation will accelerate the development of high-performance thermoelectric properties.
In this study, we collected experimental thermoelectric properties of 454 samples of Pb(Te,Se,S) and SnTe, from 66 published papers. Temperature dependences of Seebeck coefficient (S), electrical conductivity (σ), thermal conductivity and hall carrier concentration (n) were collected. We investigated the consistence between experimental data and first-principles calculation. Among the unstudied compositions found by data analysis, we selected promising compositions by considering the results of first-principles calculations. Then we experimentally synthesized those samples, and evaluated their thermoelectric properties.

We found that n-dependence of S of n-type Pb(Te,Se,S) was successfully reproduced by Boltzmann transport calculation. The n-dependence of S for p-type Pb(Te,Se,S) and SnTe did not match with the calculation, implying the presence of some mechanisms that affect the electronic structure.
In our dataset, all reported SnTe samples were p-type, and no doping attempts were found to synthesize n-type SnTe. Our Boltzmann transport calculations suggested that the performance of n-type SnTe is 40% higher than n-type Pb-(Te,Se,S). During the presentation, we will report about our experimental attempts to synthesize n-type SnTe.

Keywords: Thermoelectric materials, Experimental database, Chalcogenides, Boltzmann transport theory

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Experimental force multipliers for accelerating thermoelectric material discovery

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Over the last decade, high throughput computational screening has generated a vast number of potential thermoelectric candidates. As such, the experimental assessment of these candidates is now a critical bottleneck due to the artisanal synthesis and characterization methods traditionally employed. Within this talk, we explore recent efforts to develop experimental force multipliers to accelerate this assessment process. For synthesis, these include weighing, reaction, densification, and annealing approaches that are amenable to high throughput automation. In these efforts, we are particularly focused on forming bulk (ie macroscopic) polycrystalline samples that are compatible with traditional measurement strategies. Likewise, the development of automated measurements systems is described and the validation of the results against traditional, single-sample systems is presented. From these efforts, we envision a future that is rich in experimental data that complements the strengths of computation. In particular, computation will provide insight into reciprocal space (eg electron and phonon group velocities) while high throughput experiment will illuminate scattering dynamics and the dependencies therein.

Keywords: automation robotics screening

*Speaker

A Valence Balanced Rule for Discovery of New Dimensions of Defective Half-Heuslers

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Stable defect-free half-Heusler (hH) compounds with the stoichiometric composition *XYZ* typically exhibit a valence electron count (VEC) of 18. Compounds reported with other electron counts are often thought of as outliers to this '18-electron rule'. However, emerging interest in VEC=19 hHs for their exciting thermoelectric properties demands a better understanding of their stability to reliably distinguish the stable compounds from the unstable ones. Using first-principles DFT we systematically investigate the thermodynamic stability and off-stoichiometry in 108 nominal 19-electron hH compounds. We demonstrate unambiguously that considering a cation deficiency towards the off-stoichiometric *valence balanced*, VEC=18 composition is *necessary* for explaining the stability of all previously reported nominal VEC=19 compounds. This is understandable in terms of an energy benefit from valence balance considering the valence of each atom using Zintl chemistry that offsets the energy penalty of forming defects in nearly all cases. Thus, we propose a *valence balanced rule* to understand the ground state stability of half-Heuslers irrespective of stoichiometry and nominal electron count (8, 18 or 19). Using this generalized rule we (a) predict 16 previously unreported nominal 19-electron *XYZ* half-Heuslers and (b) rationalize the reports of giant off-stoichiometries in compounds such as Ti(1-x)NiSb which has been known for over 50 years. Of the 16 new compounds predicted here, Ti(1-x)PtSb was synthesized and the hH phase confirmed through X-ray studies. The flexibility in stoichiometry of the hH systems to attain a stable valence balanced composition can be used in discovery of new dimensions of multi-component *defective* half-Heuslers based on intrinsic and extrinsic defects which compensate for the *nominally* non-18-electron count of the structure.

Keywords: 18 electron rule, half Heuslers, Zintl Concept

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Molecular dynamics simulations to understand phonon transport in nanoporous materials

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Nanoscale pores and voids have been found to significantly decrease the thermal conductivity of thermoelectric materials. Recent works on Si-based nanoporous materials have reported thermal conductivities at, or even below the amorphous limit [1,2]. However, understanding the microscopic details of phonon scattering on pores and voids of various sizes and configurations, from a few to several nanometers and from ordered to disordered, also accounting for possible coherent effects, is far from complete. Although a large number of theoretical investigations concerning rough surfaces and boundary scattering can be found, studies on nanoporous materials are less common.

In this work, we present thermal conductivity results for bulk crystalline Si with (spherical) nanovoids and (cylindrical) nanopores, computed with equilibrium molecular dynamics (MD) using the Green–Kubo formalism. We perform an exhaustive investigation on how void/pore size, concentration and distribution affect thermal conductivity. To comprehend the full picture of the phonon transport physics in these geometries, we further perform a qualitative analysis of how individual acoustic and optical modes are scattered, by means of a wavepacket approach. This approach can visually show how the phonon modes interact with voids/pores as they pass through them; moreover, it can be generalized to boundaries and interfaces, which are similarly used to achieve drastic reductions in thermal conductivity. Finally, we discuss how the knowledge acquired with MD can be used in tandem with large-scale Monte Carlo simulations, which can help to bridge the gap between nano- and mesoscale transport for better predictions of thermal conductivity in highly disordered materials.

J. A. P.-Taborda, et al., Nature Sci. Rep., 6, 32778, 2016

J. Tang, et al., Nano Letters, 10(10), 4279-4283, 2010

Keywords: Molecular dynamics, phonon wavepacket approach, nanoporous material, phonon transport in nanostructures

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Thermoelectric properties of TiNiSn and ZrNiSn half-Heusler alloys through ab-initio calculation and experiments

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A synergic computational/experimental work for the accurate characterization of half-Heusler alloys is presented.
The CRYSTAL program [1,2,3] is a powerful computational tool for the *ab initio* study of crystalline solids, that is here applied to the simulation of transport properties of alloys. Thanks to the use of a local (Gaussian) basis set, the band velocities are easily and accurately obtained as analytical derivatives of electronic bands [3], with a small computational cost, and the possibility to use hybrid functionals (such as PBE0) allows to obtain accurate results.

Electrical conductivity and Seebeck coefficient of half-Heusler phases, such as TiNiSn and ZrNiSn, were computed as a function of the charge carrier concentration at different temperatures.

Experimental thermoelectric characterization was performed on single phase TiNiSn and ZrNiSn half-Heusler alloys prepared by arc melting followed by suitable annealing.

The carrier concentration, that is key for the comparison with the theoretical result, was evaluated by measurement of the Hall effect between 4 K and 400 K. In the same temperature range, electrical conductivity and Seebeck coefficient were measured for a complete comparison with the computed thermoelectric properties.

R. Dovesi, A. Erba. R. Orlando, C. M. Zicovich-Wilson, B. Civalleri, L. Maschio, M. Rérat, S. Casassa, J. Baima, S. Salustro, B. Kirtman, WIREs: Comp. Mol. Sci. DOI: 10.1002/wcms.1360

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G. Sansone, A. Ferretti, L. Maschio, J. Chem. Phys. 147 114101 (2017)
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Keywords: half, Heusler, ab initio, transport properties, DFT

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Defects and their influence on the thermoelectric properties of materials: an ab initio study

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For thermoelectric applications, *ab initio* methods generally fail to predict the transport properties of materials because of their inability to predict properly the carrier concentrations that control the electronic properties. In this presentation, a methodology to fill in this gap is shown and applied in the NiTiSn half Heusler phase, an important material for thermoelectric applications. For that, we show that the main intrinsic defects act as donors of electrons and are responsible of the electronic properties of the material. Indeed, the presence of Nii interstitial defects explains the experimental valence band spectrum and its associated band gap reported in the literature. Moreover, combining the density of states of the solid solutions with the determination of the energy of formation of charged defects, we show that Nii defects are also responsible of the measured carrier concentration in experimentally supposed "pure" NiTiSn compounds. Subsequently the thermoelectric properties of NiTiSn can be calculated using a fully *ab initio* description and an overall correct agreement with experiments is obtained.
A similar methodology is applied to the Fe2VAl full Heusler compound and zinc antimony to predict the result of intrinsic/extrinsic doping in these compounds.

Keywords: heusler, ab initio, defects

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Quantum transport simulations of thermoelectric power factor in materials with hierarchical nanostructuring

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The need for multiscale hierarchical nanostructuring in increasing phonon scattering in bulk thermoelectrics is emphasized as one of the most promising routes to increase the ZT figure of merit [1]. Such materials contain macroscale grain boundaries, nanoinclusions, and atomic defects, each responsible for scattering phonons of different wavelengths. However, the power factor in materials with such complexities is usually overlooked and is much less theoretically studied, as it imposes the difficulty in accurately estimating both the conductivity and the Seebeck coefficient under such large degree of disorder.
In this work we employ the fully quantum mechanical non-equilibrium Green's function (NEGF) electronic transport method, which is particularly suitable for treating details of material geometrical features as well as electron-phonon scattering [2]. We investigate the thermoelectric power factor of nanocomposite materials with hierarchical nanostructuring; namely, embedded nanoinclusions, superlattice/nanocrystalline barriers, voids, and combinations of all within the same material. We identify cases, and present the conditions under which the power factor in these structures is: i) either resilient to the density of the embedded nanostructuring, ii) or even exhibits gains. Thus, we demonstrate how the materials can retain a high power factor in addition to the targeted suppressed thermal conductivity. Finally, we describe our efforts to relate our conclusions to real recently developed nanostructured material systems, which will prove experimentally useful and potentially further improve ZT.

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S. Foster, M. Thesberg, and N. Neophytou, *Phys. Rev. B* **96**, 195425 (2017).

Keywords: hierarchically nanostructured thermoelectrics, modelling, thermoelectric power factor, Non, equilibrium Green's function

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Defect-induced simultaneous increase of the conductivity and Seebeck coefficient in p-doped polycrystalline materials and enhanced thermoelectric power factor

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Simultaneous increase of the conductivity and the Seebeck coefficient has been rarely reported. It has been observed in highly B-doped polycrystalline Si upon thermal annealing above Ta=800 oC and resulted in high thermoelectric power factor reaching 18 mW/mK2. Understanding the origin of this behavior would be essential for the development of efficient thermoelectric applications. Our group has previously reported on these observations [1-3]. Here, we present for the first time a concise theoretical interpretation based on Boltzmann transport formalism extended to accommodate energy filtering, charge neutrality and T-dependent ionization of dopants and defects. We have performed a systematic analysis of new conductivity and Hall measurements over the temperature range 20–300 K, in samples annealed at different Ta. The underlying mechanisms have been identified and perfect quantitative interpretation of the measurements has been achieved. It is shown that the simultaneous increase of the conductivity and the Seebeck coefficient is induced by the presence of defects and their behavior upon thermal annealing. Thermal annealing above a critical Ta repairs defects and decreases ionized impurities concentration in the core of the grains. It simultaneously enhances charge trapping by defects at grain boundaries. Simultaneous increase of the mobility, the conductivity and the Seebeck coefficient is thereby provided. Our theoretical modelling has interpreted the observations in Si but provides generic physics insight that could be also useful for other polycrystalline semiconductors.

D. Narducci et al.MRS 2011 Proc.; J. Solid State Chem. 193, 19 (2012) ; ECT2015 Proc.

N. Neophytou, X. Zianni, H. Kosina, S. Frabboni, B. Lorenzi,D. Narducci, Nanotechnology 24, 205402 (2013)

X. Zianni, D. Narducci, JAP117, 035102 (2015); ibid ECT2017 Proc.

Keywords: polycrystalline, defects, grain boundaries, energy filtering, p, doping, silicon, thermoelectric properties

*Speaker

Metamaterials for Harnessing Thermoelectric Flow

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The ability to control electromagnetic fields, thermal currents, and heat currents by designing suitable metamaterials has resulted in many novel effects, including cloaking, field rotations and concentrations. Transformation optics has proven to be a versatile approach in achieving such unusual effects relying on materials with highly anisotropic and inhomogeneous properties. Most applications and designs have been with limited functionality within a single physical domain. Here I will discuss the application of transformation optics for thermoelectric phenomena, where thermal and electric currents are coupled via the Seebeck coefficient. Through coordinate transformations with suitable space stretching and compression a variety of effects can be achieved, including thermoelectric cloaks, rotators, concentrators, and diffusers. Using classical circuit theory, laminate metamaterials are proposed to mimic the required anisotropic and inhomogeneous systems for the operation of suitable devices. This design approach is quite general as it is not dependent on particular boundary conditions or initial medium properties. These efforts constitute a significant step forward towards finding new ways to control and manipulate thermoelectric transport at larger scale applications. Manmade highly inhomogeneous and anisotropic systems may prove useful towards effective separation of electric from thermal currents when Seebeck coefficient is significant.

Keywords: thermodynamics, cloak, rotator, concentrator, metamaterials, thermoelectrics

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Detailed Transient Multiphysics Model for Fast and Accurate Design, Simulation and Optimization of a Thermoelectric Generator (TEG) or Thermal Energy Harvesting Device

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Described herein is a transient multiphysics SPICE model of a thermoelectric generator module. When designing a thermoelectric generator (TEG), it is very desirable to utilize a TEG model that is fast and accurate. It is also desirable to use a model platform like SPICE with ability to model the complete electrical system including controls like maximum power point tracking (MPPT). These desirable features reduce the time needed to bring a new product to market and reduce the cost of expensive physical prototyping and tests. Less time is also needed to find the optimal design from many possible designs. There are many exemplary models found in the literature that run on various platforms. Some platforms run fast, and some take longer to run. Some published models include more physics detail than others. Some 3D models are typically more accurate but take longer to run and change. It was the objective herein to develop a TEG model with all desirable characteristics. This work describes a one-dimensional model created using thermal-electrical analogies and solved for transient response in SPICE. The comprehensive physics modeled include the Seebeck, Peltier, Thomson, Joule and Fourier effects. These effects are captured using distributed mass and heat flows in the thermoelements. Additionally, temperature dependent properties, thermal and electrical contact resistances, Joule heat generation within the thermoelement interconnects and electrical interfaces were modeled. The TEG model was correlated and compared with challenging experimental data that varied hot and cold side temperature and imposed an electrical current simultaneously. The model was in excellent agreement with the experimental data and exceeded expectations compared to the output of an existing 3D ANSYS model. The model herein takes 2.5 seconds to run a 4000 second transient simulation.

Keywords: Thermoelectric, Thermoelectric Generator, TEG, Thermal Energy Harvesting, SPICE, Thomson Effect, Seebeck Effect, Peltier Effect, Module, Transient, Device

*Speaker

μTEGs for Self-Powered Sensor Nodes: Device Optimization and System Integration

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Microfabricated thermoelectric energy harvesters (μTEGs) are devices designed to convert small amounts of heat into electrical power on the order of 10s to 100s of μWs. The μTEGs developed by Analog Devices, Inc. (ADI) are designed to power wireless sensor nodes or other small devices from thermal energy sources close to room temperature. These devices are based on bismuth telluride (Bi2Te3) and related compounds, and make use of an ADI-patented device architecture designed to achieve large device thermal resistances necessary for many targeted room temperature applications. In this talk, we will present the ADI device architecture and discuss work done around device design and thermoelectric material optimization. Process challenges associated with building μTEGs will also be highlighted, stressing the importance of looking beyond just thermoelectric material development towards integration with, for example, interconnects and adhesion layers. Finally, we will present a fully μTEG-powered machine health monitoring sensor node. Thermal and mechanical design of the sensor node around the μTEG as well as a description of the system architecture and component selection to enable ultra-low-power operation will be discussed.

Keywords: energy harvesting, bi2te3, uTEG, system integration

*Speaker

Human body-heat energy harvesters based on transverse thermoelectric effects

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As smart wearable devices gain popularity, their need for energy autonomy becomes crucial. Thermoelectric energy generators (TEGs) that can harvest human body heat, therefore, are very interesting for realization of energy autonomous wearable devices. The state-of-the-art wearable TEGs, however, are made with rigid and expensive inorganic materials. These wearable TEGs are based on the longitudinal thermoelectric effects with a Π-shape geometry, in which multiple stacks of electrodes and substrates required for the device increased difficulties in manufacturing and thus overall cost. Furthermore, a bulky and heavy fin-type heat exchanger needed to be attached on top of the TEG for enhanced heat transfer at the air side. In this work, we propose to use transverse-type TE energy harvesters for wearable applications. Transverse TEGs (transTEG) consist of tilted layers of alternating metallic and thermoelectric materials. TransTEGs utilize the voltage generated perpendicular to temperature gradients by the transverse Seebeck effect. We use 3D-printed tilted nickel layers as the metallic layers and castable polymer composites based on carbon nanotube:PDMS composites as the TE layers. In this approach, a simple device processing can be utilized; 3D printing the nickel layers and then casting the polymer composite solution into the gaps between nickel layers followed by a low temperature drying process to complete the flexible transTEG. In particular, we partially fill the gaps with polymer, leaving the top portion of the nickel layers directly exposed to air to promote air convection, thus eliminating the necessity of additional heat exchanger. Finite element simulation reveals temperature/voltage distribution in the device to explain the performance. Segmentation of transTEG is also discussed to further improve both voltage and power outputs.

Keywords: Wearable energy harvesting, transverse thermoelectric, flexible module, polymer composite

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Characterization of micro thermoelectric coolers with high packing density

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Micro thermoelectric modules have high potential as generators to power autonomous sensors in the internet of thinks as well as for cooling applications like local heat management of optoelectronic circuits. Especially, with the ongoing increase of network traffic, localized cooling of photonic integrated circuits (PICs) is a crucial topic, which can be addressed by integrating micro thermoelectric coolers (μTEG) at the chip component scale. In this work we report on the fabrication and characterization of highly integrated micro thermoelectric coolers with a packing density over 5000/cm2 and a maximum cooling over 10K at room temperature. The μTEGs are fabricated by a laser lithographic process in combination with electro-chemical deposition (ECD) of thermoelectric p- and n-type materials. The electrochemical deposition route offer full compatibility with existing integrated circuit technologies, large scalability and high deposition rates which allows to fabricate devices up to the micrometer range. We report on the device characteristics studied by thermoreflectance and electrical measurements. The study includes current and temperature dependent cooling performances, transient cooling response, cooling cycling, and long-term stability under constant current. Model simulations based on finite element method and analytical calculation are in good agreement with experimental results, indicating negligible contact resistances in the as-fabricated micro coolers.

Keywords: thermoelectric modul, cooler, generator, characterization, electrochemical deposition, micro TEC

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Thermoelectric nanogenerator array : a viable source of power for the autonomy of wireless sensors networks ?

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With the emergence of low power communication protocols, there is a real demand for autonomous micro-sources of energy that can deliver _˜ 100 μW. That range of power can easily be supplied by standard thermoelectric (TE) module under stationary operating conditions. However these conditions of use are not necessarily adapted for wireless sensors. For example, the energy input can be very intermittent, or the volume available too small to use a TE module and its heat sink. The expertise developed at the Institut Néel in the elaboration of suspended thermal sensors has been used to design membrane based nano-TEG. Planar nano-TEG are made of silicon nitride membranes suspended by means of several arms. Thermoelectric materials are deposited onto these arms. Since membranes have a negligible mass, their temperature can fluctuate contrary to the bulk silicon frame which conducts well the heat. Thus a temperature gradient appears between membranes and the bulk silicon frame. The proof of concept has been validated using poorly optimized Bi2Te3 TE thin films (ZT _˜ 0.2). In that case, for temperature gradient of 8 K the power generated by one membrane is about 1 nW. The duplication of this nano-TEG thanks to standard MEMS clean room techniques enabled us to obtain few thousand membranes which harvest 18 μW from a temperature gradient of 10∘C and a surface of 10 cm^2. For standard ZT values, that power may increase to hundreds of μW in the same conditions (10∘C ;10 cm^2). This power is enough for suppling sober sensors making them autonomous. The patented design of the nano-TEG array permits to arrange the nano-TEG in serial and/or in parallel depending of the final resistance expected. Prototypes have been built with two industrial groups and coupled to an ASIC in order to get an operational autonomous sensor. A start-up commercializing that solution is going to be created.

Keywords: MEMS, planar TEG, membrane, Start, up, autonomous sensor

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A High Efficient Thermoelectric Module with Heat Storage utilizing Sensible Heat for IoT Power Supply

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In 2016, a sewage water level sensing system where the thermoelectric power generating module (TEM) was used as a power source was commercialized by Fujitsu Ltd. This time, we have developed a new TEM, which has higher flexibility of installation than the solar cell, for river water level observation.

The power generation target for both sensing and radio transmission is set to a total of 20 J/day, even in the shaded.

For power generation utilizing the one-day temperature change, it is effective to arrange the heat storage on the cooling side of the TEM.

We investigated heat storage materials to ensure necessary power.

In our simulation, the water-based material under our recipe of is capable of generating power more than twice that generated using a phase change material (PCM), e.g. paraffin, in one year. Latent heat is available when the melting point of a PCM is approximately equal to the average temperature of the heat source. However, it's efficient only in a limited period of a year with narrow temperature range.

The newly developed TEM consists of a thermoelectric device (Model 254-200-12: Thermal-force.de), heat storage material, heat transfer fin, an Al part in contact with the heat source which is bridge steel frame, a box of dimension 15 × 15 × 10 cm for heat storage, and an outer box of dimension 20 × 20 × 13 cm for housing the entire module.

The TEM was installed on the north eastern side of the steel frames of the bridge, where the sunlight hits only for a few hours in the morning, in Yokohama City, and generated power was measured since September 8, 2017. An average power generation of around 55 J/day was recorded. This value was more than 2 times our target, and remained nearly the same from September 2017 to January 2018.

In conclusion, using our water-based material for heat storage, we were able to generate sufficient power, regardless of the season and location of installation.

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Keywords: power generation, water level sensing, radio transmission, heat storage, bridge steel frame, river water level observation

Fabrication and characterization of thermoelectric generators based on silicon nanowire forests

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The reduced thermal conductivity (kt) of silicon nanostructures has been largely demonstrated[1]. Nanostructuring offers, indeed, the opportunity of using silicon, which is a cheap, abundant, biocompatible, technologically feasible material, for thermoelectric applications. The exploitation of the potentialities of nanostructured silicon for thermoelectric purposes requires the development of simple processes for the fabrication, the interconnection and the assembly in thermoelectric modules of a large number of nanowires. We developed a cheap process, based on the Metal Assisted Etching Technique, for the fabrication of Si nanowire forests made of a large number of nanowires placed perpendicularly to a Si substrate. More than 10ˆ7 nanowires/mmˆ2, longer than 70 um, and with an average diameter between 60 and 80 nm, have been fabricated on surfaces of several cmˆ2. These nanowire forests, doped both n and p type, have been contacted by copper electrodeposition[2,3] and assembled in thermoelectric generator devices.
We will report:

1) The measurement of the electrical conductivity, of the Seebeck coefficient and, in particular, of the thermal conductivity of Si nanowire forests. Our measurements, made on the whole device, and hence averaged on a large number of nanowires, confirm the strong reduction of kt (down to few W/mK) already demonstrated on single nanowires.

2) The assembly and characterization of simple prototypes of thermoelectric generators based on Si nanowire forests, with a total surface of few cmˆ2. In particular, the characterization of the figure of merit ZT, by means of impedance spectroscopy, will be presented and discussed.

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E.Dimaggio, G.Pennelli, Nano Lett. 16, 4348 (2016)

E.Dimaggio, G.Pennelli, Nanotech. 29, 135401 (2018)

Keywords: silicon nanowires, thermal conductivity, thermoelectric module

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Development of high durability substrate for thermoelectric module

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π-structure thermoelectric modules based on 4 types of substrates were fabricated and high temperature durability evaluated. A DBC (Direct Bonded Copper) substrate or a DBA (Direct Bonded Aluminum) substrate was fabricated by brazing bonding method in vacuum furnace. A pre-sintered silver layer on alumina substrate or a pre-sintered silver layer on DBA substrate was fabricated by firing in air atmosphere furnace after screen printing of glass containing silver paste on alumina or DBA. Thermoelectric materials were mounted on these substrates by die-bonding method. The increasing ratios of internal resistance after 100 thermal cycles (Tc=80°C, Th=150°C⇔450°C) of modules were measured in air as durability test. Cross-sections of after durability tested modules were analyzed by EPMA. The increasing ratio of a module used nickel/gold plating DBC or DBA greatly increased with oxidation of nickel. On the other hand, the increasing ratio of a module used pre-sintered silver layer on alumina substrate was 33%, and the increasing ratio of a module used pre-sintered silver layer on DBA substrate was 1%. These results indicate that the internal resistance increasing ratio at high temperature in air of thermoelectric module at the interface between the thermoelectric materials and the metal electrode can be decreased by application of silver as a non-oxidation electrode and aluminum as a buffer layer for stress relaxation.

Keywords: Substrate, module, durability

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Experimental evidence for separation of thermally generated bipolar charge carriers within a p-i-n-junction

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Thermoelectric generators (TEG) based on p-i-n structures are promising devices for heat-to-electricity conversion [Span et al.]. Beside the thermal diffusion of unipolar charge carrier in a conventional TEG, the pin-TEG provides the ability of harvesting the thermal energy of bipolar charge carriers. This leads to an enhancement of the extractable electric power. In this work we present the first experimental evidence of thermally generated and separated bipolar charge carriers in the built-in field of a p-n junction (i-region). Silicon p-i-n diodes are fabricated by laser sintering of highly doped boron and phosphorus silicon nanoparticles forming p- and n-layer on the sides of an intrinsic silicon wafer. The I-V characteristics were measured up to hot site temperature of about 300∘C. An equivalent circuit for the pin-TEG is developed to explain the device behavior. It is shown, that the generated electric power is caused by two different physical mechanisms. The first effect is based on the Seebeck effect that occurs mainly in the p- and n-legs of the pin structures. The second effect is attributed to the bipolar charge carrier generation and separation in the built-in field of the p-n junction. To investigate only this thermal generated current, the Seebeck effect is canceled by electrically short-circuiting the p- and n-leg, by extending the metallization layer over each leg. The output power of the short-circuited devices raises with the hot site temperature. This extracted electrical power is attributed to the mentioned effect. Only if both mechanism are taken into account, the measured device characteristic can be explained. This mechanism was already predicted ten years ago [Span et al.] but up to date was never demonstrated experimentally.

Keywords: thermoelectric generator, pin junction, charge separation, bipolar thermoelectric effect

*Speaker

Very long lifetime terrestrial RTG with Americium heat power source

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The storage of very long lifetime radioactive waste is an increasing social concern and a crucial issue for the nuclear industry. In this frame, in France, ANDRA - the French national agency for radioactive waste - is managing the CIGEO project (deep geological disposal facility) dedicated to the study of very long time underground radioactive waste storage. A major challenge related to this project is to power wireless sensors dedicated to radioactive waste monitoring for a long time period. In this context, ANDRA has started an ambitious collaborative project with our consortium to design and manufacture a prototype of a terrestrial Radioisotope Thermoelectric Generator (RTG) which will be the electric power source for the foreseen application. This RTG is design to operate in underground cavities with the goal of supplying electrical power to wireless sensors for one century.
Our consortium is composed of ORANO (formerly AREVA, nuclear industry), Hotblock Onboard (thermoelectric materials & devices), and LEMTA and IJL, two laboratories of the University of Lorraine (academic experts on thermoelectricity applications and thermoelectric materials).
In this project several issues have to be tackled: i) specific underground conditions, ii) the effects of radioactive waste in the vicinity of the RTG device and iii) the mandatory very long operating lifetime. All these points must be considered during the different steps of RTG design and assembly. In this *talk / paper*, we present the motivations that have governed technological choices to ensure the reliability of our RTG power source. Among them, we will briefly discuss the impact of using Americium Am241 as a heat source instead of a more conventional Pu source, as is commonly used in spacecraft RTGs; then, we will present some details about our 5W terrestrial RTG.

Keywords: RTG, Americium

*Speaker

Modeling and Simulation of a Thermoelectric Generator Using Bismuth Telluride for Waste Heat Recovery in Automotive Diesel Engine

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Waste heat recovery using thermoelectric power technology is a promising approach to reduce fuel consumption and CO2 emissions on passenger cars. However, possible application requires optimization of the heat exchangers and definition of adequate thermoelectric materials to improve efficiency. A dynamic model has been developed to investigate the application of a TEG for waste heat recovery in an automotive engine exhaust. The converted electrical energy is used to charge the 12V battery. The engine used is a 1.5 litre / 75 kW Diesel engine. The TEG is made up of counter-flow heat exchangers and commercial thermoelectric modules (TEM). The three tube heat exchangers of the TEG are installed downstream the turbine outlet while the engine coolant flows into the aluminium plates heat exchangers. The power output is measured for 30 Bi2Te3 TEM's (ZT of 0.9 at 390 K) connected in series. The model evaluates the amount of recovered energy over a prescribed drive-cycle. It also evaluates the effect of system integration such as fuel consumption, temperatures downstream the TEG and the relative counter pressure. Experiments are done on both a TEM test rig and a Diesel engine test rig equipped with the TEG prototype. Simulations of steady operating points show good agreement with experimental data. The results showed a maximum power generated by the TEG of 42 W, and a maximum 1.5 W per module (corresponding to 671 K TEM hot side temperature and 354 K TEM cold side temperature). At the end of the duty cycle, the energy recovered by the vehicle battery is around 27 KJ (7.5 Wh). The engine counter pressure exceeds the 30 mbar when the mass flow rate is higher than 36 g/s. The simulation results of temperatures, pressures, and output power show that the model can be used as a basis to develop a TEG with high performance that ensure safety operation of the engine and the after treatment system.

Keywords: Thermoelectric Generator, Waste Heat Recovery, Automotive application, Diesel En-

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gine, Engine Simulation model

RTGs: the enduring and the future

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NASA recently completed the Cassini mission, whose spacecraft was powered by three RTGs. Until the Cassini spacecraft plunged into the atmosphere of Jupiter after nearly 20 years in flight, NASA was simultaneously flying 11 RTGs powering five spacecraft. Of the four spacecraft powered by Radioisotope Thermoelectric Generator (RTGs) that NASA is presently flying, two have been in flight for over 40 years, the Voyagers, 1 and 2, with Voyager 1 now in interstellar space. The third, Pluto-New-Horizons, has completed its encounter with Pluto and is destined for the Kuiper Belt Object 2014 MU69 after nearly 13 years in flight. The fourth, the Mars Science Laboratory rover, *Curiosity*, is exploring Gale crater on Mars and about to begin its 2nd extended mission. Curiosity is powered by a Multi-Mission RTG (MMRTG) and was launched _˜6.5 years ago.
The future looks bright for radioisotope power systems (RPS). NASA is now planning to launch the Mars 2020 mission carrying a rover based on Curiosity and powered by an MMRTG. NASA recently announced, as a Step-1 candidate for a NASA New Frontiers mission, the Dragonfly mission concept, which would put an MMRTG-powered quad-copter into the atmosphere of Titan.

In addition, NASA has been funding the US Department of Energy to restart the production of fuel for RTGs, has been funding the technology maturation for an enhancement to the presently available MMRTG called the eMMRTG or enhanced MMRTG, and is now set to begin funding a project for the System Development of a potential Next-Generation RTG.
This paper will discuss the status of the operating RTGs and the recently concluded RTG-powered Cassini mission, and then look forward to the Mars 2020 and possible Dragonfly missions and describe the plans for the as-yet-to-be-built eMMRTG and Next-Generation RTG.

Keywords: Radioisotope Thermoelectric Generator, RTG, eMMRTG, MMRTG, GPHS RTG, Next, Generation RTG, planetary mission, science mission, RPS, power source

*Speaker

Power Enhancement of Si Membrane-based Thermoelectric Generator by Aluminium Ultrathin Layer Deposition

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In coming years, the Internet of Things (IoT) will expand to include many more remote devices requiring an ongoing energy source. On-chip thermoelectric generators (TEG) could provide a valid energy harvesting mechanism to IoT devices if the power-cost ratio could somehow be improved. Si membranes are innately inexpensive, but offer limited thermoelectric efficiency compared to expensive alternatives. Recent works have identified phonon surface scattering as an important factor in lowering thermal conductivity and improving the ZT of nanostructured Si. This work demonstrates a low-cost large-area method for enhancing the performance of simple Si membrane devices via single-nanometer Al thin film deposition. The TEG device that is proposed in this work was fabricated using only four photolithography steps, including etching windows for suspension, n- and p-type impurity doping and finally electrical contacts. Open-circuit voltage was measured for devices with 0, 1 and 10 nm of deposited Al, with an actual temperature difference range of ΔT_ACT = -9 to 27 mK. From these values, power density was then derived knowing the total bulk and contact resistance within the electrical circuit. A maximum of 17.4 nW/cmˆ2 was measured in 1 nm Al-deposited devices at $\Delta T = 27$ mK, which is a 42% increase compared to devices without an Al thinfilm.

Keywords: silicon, energy harvester, nanostructure

*Speaker

Holistic Optimization of Thermoelectric Generators for Automotive Applications Reaching a Cost Benefit Ratio of 81 /g/km

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At the automotive development one of the major future challenges is to achieve the required reduction of the CO2 emissions. Therefore, it is necessary to investigate all potential technologies for efficiency improvement. Regardless of whether a conventional or hybrid vehicle concept is used, approximately 2/3 of the fuels chemical energy dissipates as waste heat. The waste heat of the exhaust gas provides through its high temperature level the highest potential for waste heat recovery. The technology of thermoelectric generators (TEG) is very promising for waste heat recovery and under investigation for several years at the DLR Institute of Vehicle Concepts.
In this work the current results of a highly integrated system design with the highest power densities will be presented. With this design a gravimetric power density of more than 130 W/kg and a volumetric power density of more than 230 W/dm^3 are reached with Half-Heusler material.

A holistic method for optimization of TEG systems is developed. In this method the first widespread combined optimization of heat exchangers together with the thermoelectric modules (TEM) in column arrays is shown. The modelling is set up in a 3D-CFD simulation and this work also includes the development of a generic cost model. The simulativ study bases on measured values for the TEM and a validation of the temperatures within the TEG. The vehicle integration of TEG in a concept close to the engine is realized and all influences from the TEG to the vehicle overall system are considered. As boundary conditions the world-wide harmonized transient driving cycle (WLTC) is chosen. As reference vehicle the Volkswagen Golf VII (4 cylinder turbo engine, 1,2 L; 77 kW) is used with measured data of the roller dynamometer test bench.
With this holistic method in this work the cost benefit ratio is optimized. Result of this multi-objective optimization is a Pareto front. There the trade of between the maximal reduction of overall system CO2 emissions [g/km] and minimal system costs [] is shown. A cost benefit ratio of 81 /g/km is reached within the homologation cycle WLTC. The maximal overall system fuel reduction of 2,2 % is also reached in this driving cycle. The excessive methodical cost reduction leads for example to the use of only 20 grams of thermoelectric material per vehicle. The weight of the TEG is 3,7 kg including the power electronics of roughly 1 kg. In the overall system the weight and costs of the TEG system including power electronics and bypass are considered.

Keywords: thermoelectric generator, automotive

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A versatile system for Hall effect measurements at high temperature

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We present a fast Hall effect measurement system that can be used at high temperature. The use of a homogeneous high field permanent magnet in a Halbach configuration allows fast measurements in various DC and AC current fields with step and continuous measurement modes. The results are presented of measurements on platinum film at room temperature and Ge and BiCuSeO between 300K and 650K.

Keywords: Halbach magnet, Hall effect, galvanomagnetic

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Mechanochemistry for Thermoelectrics: Nanobulk Mawsonite Cu6Fe2SnS8 Synthesized in an Industrial Mill

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Copper based compounds have been frequently reported as good thermoelectric materials for mid-temperature range. They not only show high thermoelectric performance but they have many other advantages such as being environmentally friendly and low-cost due to high copper content in Earth crust. Recently, thirteen Cu-S based compounds were identified as potential thermoelectric materials among which mawsonite Cu6Fe2SnS8 and stannoidite Cu8Fe3Sn2S12 were mechanochemically synthesized in a laboratory mill. However, for industrial application up-scaling of milling process is urgently needed.

In this study we demonstrate the use of elemental precursors (Cu, Fe, Sn, S) to obtain mawsonite Cu6Fe2SnS8 by a solid state process at ambient temperature. For the synthesis an industrial eccentric vibration mill was utilized. The milling has been performed for 5-240 min in an argon atmosphere. The prepared samples have been characterized by various physic-chemical techniques such as XRD, SEM, Soxhlet analysis, etc. The results revealed that transformation of elemental precursors to mawsonite proceeds via several intermediate steps where binary (Cu2-xS, FeS2) and ternary (CuFeS2, Cu5FeS4) sulfides can be traced in various amounts. The mawsonite phase was obtained after 240 min of milling. The thermoelectric measurements performed on this sample after SPS treatment revealed figure-of-merit value zT of 0.514@623K. The high value of zT originates in low lattice thermal conductivity conductivity 0.29W/mK and moderate power factor 3.3μW/cm2K2. The obtained value of zT for mawsonite Cu6Fe2SnS8 synthesized in an industrial mill is comparable to the values obtained in a laboratory ball-mill.

Keywords: mawsonite, Cu6Fe2SnS8, mechanochemistry, advanced materials, thermoelectrics

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Copper rich complex Sulfides for Thermoelectric applications

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Copper-based sulfides became important thermoelectric materials for converting waste heat into electricity in recent times due to the presence of earth abundant and low cost constituents. Designing of copper rich sulfides by mimicking natural minerals allows to develop new synthetic minerals which are exhibiting promising p- type thermoelectric properties. Here in, we discuss the thermoelectric properties of stannoidite (Cu8Fe3Sn2S12), germanite (Cu22Fe8Ge4S32) and new type of colusite compounds. Above mentioned phases were successfully synthesized via mechanical alloying and SPS process. The X-ray diffraction analysis combined with 57Fe Mössbauer investigations has allowed the charge distribution of the cationic species on the various sites to be determined. In case of stannoidite Cu8+xFe3-xSn2S12 with $0 \leq x \leq 0.5$, copper hyper stoichiometry leads to a cross over from semiconducting to metallic state with maximum ZT of 0.35 for $x = 0.5$ at 630 K. This thermoelectric behaviour is interpreted on the basis of a model involving the Cu-S framework as the conducting electronic network where the Fe2+/Fe3+ species play the role of hole reservoir. The presence of low lattice thermal conductivity in these compounds is mainly attributed to their complex crystalline structures.

Keywords: Copper rich, complex sulfides, thermoelectric

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Low-temperature structure of tetrahedrite

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Tetrahedrites are promising *p*-type thermoelectric materials with extremely low lattice thermal conductivities (below 1 W m-1K-1 at 300 K). The understanding of the origin of low thermal conductivity in tetrahedrites remains limited, and may be related to a phonon instability arising from a low-temperature phase transition.
At 90 K, the electrical resistivity of Cu12Sb4S13 exhibits a marked anomaly, which is accompanied by a dip in magnetic susceptibility, and a sharp peak in heat capacity. Tetrahedrite is a mixed-valence compound, usually formulated as (Cu2+)2(Cu+)10(Sb3+)4(S2-)13, and the Curie-Weiss behaviour above 90 K, which shows evidence of strong antiferromagnetic correlations (Weiss constant = -170 K) is consistent with two Cu2+ per formula unit. The drop in magnetic susceptibility could hence be attributed to antiferromagnetic ordering of the magnetic moments of the Cu2+ ions.
We present here neutron diffraction data collected on Cu12Sb4S13 between 1 and 298 K on the WISH diffractometer (ISIS), which clearly indicate that the anomalies at 90 K are accompanied by a structural transition. Above the transition, Cu12Sb4S13 exhibits a cubic unit cell. Below 90 K, Cu12Sb4S13 adopts a tetragonal structure, and neutron data can be indexed on a primitive root 2 a x root 2 a x c supercell. The structure of the low temperature phase, which involves large displacements of the octahedrally coordinated sulphur and the trigonal planar copper atoms, was determined using ISODISTORT. The relationship between the structural transition and the magnetic and electronic behaviour will be discussed.

Keywords: tetrahedrite, thermal conductivity, structure

*Speaker

Nanoparticle-dispersed Cu12Sb4S13-based thermoelectric composites

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Fine-grained and nanostructured composites have long been demonstrated for its efficiency in enhancing thermoelectric property, but less concerned as a practical approach for Cu12Sb4S13 tetrahedrites hitherto probably due to its technical challenges. Here, we have designed and prepared superfine nanoparticles composited thermoelectric tetrahedrites. It was found that the lattice thermal conductivity can be largely reduced, benefiting from the formation of uniformly distributed nanoparticles/nanopores and additional interface scattering. In addition, the electrical conductivity and thermopower could be improved by a repeated mechanical alloying and spark plasma sintering process at entire temperatures due to the fine-graining nanostructures and enhanced alloying synthesis. This modified process and further introduced nanodispersions lead to high ZT value ≥ 1.10 at a relatively low temperature (723 K) in the Cu12Sb4S13-based composite, indicating the effectiveness of refining and nanostructuring as a promising technique also in tetrahedrites toward high thermoelectric conversion efficiency.

Keywords: nanoparticles, tetrahedrite, thermoelectric, MA and SPS

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Mineral-Related Sulphides and Selenides for Thermoelectric Energy Harvesting

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A significant fraction of waste heat from industrial processes is released at temperatures between 373 and 535 K. Metal sulphides are attractive candidates for thermoelectric energy recovery in this region, as the covalent character of the metal-sulphur bonding interaction leads to band broadening and increased charge-carrier mobility, while the high polarizability of the sulphide matrix, promotes the cation mobility required for phonon-liquid electron-crystal (PLEC) behaviour. Much of our recent work has focused on mineral-derived sulphides containing earth-abundant elements. We have exploited the relatively weak bonding of copper ions in synthetic analogues of tetrahedrite (Cu12Sb4S13) and bornite (Cu5FeS4), to achieve low thermal conductivities. Through suitable chemical substitution, figures of merit in excess of ZT = 0.5 at 573 K can be achieved. We have extended the work to sulphides and selenides with structures related to that of bornite, including quaternary phases with the kesterite structure. Neutron diffraction demonstrates that at elevated temperatures, a fraction of Cu ions becomes mobile in the region where anomalies in thermoelectric properties are observed, suggesting these may be related to the onset of PLEC behaviour in kesterite-type phases. Although the high electrical resistivity of the stoichiometric, semiconducting phases leads to low thermoelectric performance, chemical substitution produces significant enhancements (of up to 120 %) in the thermoelectric power factor.

Keywords: Sulphides, Minerals, Bornite, Kesterite

*Speaker

Thermoelectric Performance of Tetrahedrite Synthesized by a Solution-Phase Method

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Tetrahedrite materials demonstrate good thermoelectric properties while also being comprised of earth-abundant, non-toxic elements. A major drawback for these materials is the time and energy intensive synthesis by traditional solid-state furnace-ampoule techniques. Recently, the low energy solution-based modified polyol synthesis has been explored in our lab to alleviate the constraints of the conventional method. This technique can successfully synthesize the parent copper-based compound (Cu12Sb4S13) as well as tetrahedrite doped with transition metals (Zn and Fe). Nanoparticles ranging from 50-200 nm in size were obtained from the chemical synthesis, and nanostructuring was maintained after densification by spark plasma sintering. The nanostructured compounds exhibited lower thermal conductivity, higher electrical resistivity, and increased thermopower compared to bulk samples. Interestingly, Fe-doped samples demonstrated a unique crossover from n- to p-type behavior, showing n-type conductivity for the first time in these materials. Overall, this novel synthetic approach has provided groundbreaking results for tetrahedrite materials, both in terms of thermoelectric performance as well as synthetic versatility.

Keywords: Tetrahedrite, Solution Phase, Nanoparticle, Nanomaterial, Earth Abundant

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Structural phase transitions at high temperature of thermoelectric copper-based sulfides studied by in situ techniques

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Copper-based sulfides have attracted considerable interest since few years due to their high-efficiency conversion as absorbers for solar energy and promising thermoelectric materials. While their structure - properties relationships are relatively well understood, their stability and phase decomposition at high temperature, an essential knowledge for large scale applications especially in thermoelectricity, remains unknown or ambiguous.
We have then undertaken the structural phase transitions study at high temperature of ternary copper-based sulfides as bornite Cu5FeS4 (ZT _˜ 0.55@550 K [1-3]), tetrahedrite Cu12Sb4S13 (ZT _˜ 0.55@700 K [4-6]), and Cu4Sn7S16 (ZT _˜ 0.21@700 K [7]), [3,8] and of some quaternary copper-based sulfides including colusite Cu26V2Sn6S32 (ZT _˜ 0.93@675 K [9-10]), and germanite Cu22Fe8Ge4S32 (ZT _˜ 0.17@575 K [11]). The temperatures and chemical reactions associated with the phase transitions/decompositions determined by *in situ* differential scanning calorimetry, powder X-ray and neutron diffraction techniques will be presented and discussed in order to consider the real potential of these phases as thermoelectric materials.

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Keywords: sulfide materials, phase transition, in situ diffraction, DSC

Improving the thermoelectric efficiency of La3-xTe4 via f-orbital chemistry

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The state-of-the-art thermoelectric power system for space applications has typically been based up on either SiGe alloys or PbTe/TAGS for the past 50 years. Although reliable and robust, the thermoelectric performance of these systems remains low with a system level conversion efficiency of _˜6%. In recent years, complex materials such as n-type La3-xTe4 and p-type Yb14MnSb11 have emerged as new high efficiency, high temperature thermoelectric materials with ZTmax on the order of 1.2 at 1275 K. The high performance of these complex structures is attributed to their favorable characteristics such as semi-metallic behavior due to small band gaps, low glass-like lattice thermal conductivity values due to structural complexity and reasonably large thermopower values near their peak operating temperatures. Computational modelling indicates that the conduction band of La3-xTe4 is dominated by the La d-orbitals. Introduction of states near the Fermi level could potentially lead to a significant enhancement of the electronic transport properties. Praseodymium telluride (Pr3-xTe4) is a La3-xTe4 analogue with 3 f-electrons (whereas La has none). Density functional theory (DFT) calculations indicate that the f-electrons lead to a sharp peak in the conduction band edge near the fermi level. In order to verify the theoretical calculations, we utilized a mechanochemical approach to synthesize Pr3-xTe4 with various Pr:Te vacancy concentrations. The powders were compacted using spark plasma sintering (SPS) and the compacts were characterized using X-ray diffraction, scanning electron microscopy, and electron microprobe analysis. The temperature dependent electrical resistivity, Seebeck coefficient, and thermal conductivity will be presented and discussed.

Keywords: lanthanide, chalcogenide, Zintl

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Phase boundary mapping and phase discovery in a quaternary system: carrier density control in Cu2HgGeTe4

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Carrier density control is a persistent challenge in the optimization of thermoelectric materials. Phase boundary mapping is a promising new technique which has enabled dramatic increases in the zT of n-type Mg3Sb2 in the last few years. The application and extension of phase boundary mapping into higher dimensional spaces (e.g. ternaries, quaternaries) is no trivial task. Our prior work has shown that the quaternary diamond-like semicondctors (e.g. Cu2HgGeTe4) are expected to have zT $>$ 1.5 at 300C under optimized carrier densities. However, the materials present as near degenerately doped p-type materials which are notorously difficult to dope. Furthermore, computational defect calculations are often unreliable due to the small band gaps and spin-orbit coupling present in these materials. In this work, I demonstrate a rational method to apply phase boundary mapping to complex quaternary systems. I reveal the challenges in applying phase boundary mapping in systems where the phase diagram is unknown or sufficiently complex such that computational methods are hindered. I show how the presence of previously unknown ternary phases can dramatically influence the properties and (in some cases) provide a new means to optimize thermoelectric materials through selective scattering of phonons from antisite defects. Our work culminates in the discovery of several new phases, the optimization of an existing phase, and the realization of high p-type zT at 250-300C in a new material class.

Keywords: Phase boundary mapping, diamond like semiconductor, p, type, carrier density control, doping, material discovery, thermodynamics

*Speaker

Considerations for enhancement of the thermoelectric potential of semiconductors

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Thermoelectrics as a direct energy conversion method between heat and electricity is mainly used for electrical power generation and cooling applications.
A large variety of materials, such as intermetallic compounds (*e.g.* half-Heuslers), silicides and chalcogenides (*e.g.* PbTe and GeTe) have been investigated as thermoelectric materials due to high ZT values at different temperature ranges. Among these material classes, although currently showing lower ZTs, silicides and intermetallic compounds possess additional advantages due to improved mechanical properties, the ability to operate at higher temperatures and the potential for large scale commercialization, since they are composed of naturally abundant and less toxic elements.

Global trends for improving the thermoelectric efficiency via maximizing the ZT values include, electronic doping optimizations; generation of Functionally Graded Materials (FGMs) with an optimal maximal ZT envelope over a wide temperature range; and nanostructuring formation for reduction of the lattice thermal conductivity. Nanostructures generation can be achieved by nano-powdering using energetic ball-milling followed by a rapid consolidation method such as Spark Plasma Sintering (SPS). Yet, due to the demand for high stability characteristics, required for long operation periods at high temperatures, one approach for avoiding nano-features coarsening and thermoelectric properties degradation, is based on utilizing thermodynamically driven nanostructures, due to physical metallurgy based effects such as spinodal decomposition and nucleation and growth reactions.

All of the mentioned above general trends in thermoelectric will be discussed during the talk. A focus on the related activities in the department of Materials Engineering at BGU will be given.

Keywords: phase sepration, FGM, GeTe

*Speaker

Promising thermoelectric performances of Cu-excess a-Cu2+xSe for near-room-temperature applications

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Finding the alternatives for Bi2Te3, the only thermoelectric material for near-room temperature (RT) applications, is of great importance in thermoelectrics. Here, we report very promising near-RT thermoelectric figure of merit ($ZTmax$ = 0.9 at 390 K, $ZTave$ = 0.68 within RT _˜ 390 K) of Cu-excess α-Cu2+xSe, comprising of low-price, abundant, and non-toxic constituent elements. The addition of excess Cu led to the decrease in the hole concentration by suppressing the formation of Cu vacancy, resulting in the power factor optimization in the Cu-excess compounds. These effects of the Cu-addition were also elucidated by the calculations based on density functional theory and Boltzmann transport equation. Furthermore, we measured directly the Lorentz number (2.1210-8 V2 K-2 at RT) of α-Cu2Se for the first time, and also unveiled the origin of its very low lattice thermal conductivity (0.27 W m-1 K-1 at RT). Based on phonon calculation, it was suggested that its ultra-low lattice thermal conductivity is associated with structural instability of α-Cu2Se arising from interaction between Cu+ ions. Our results propose that Cu-excess α-Cu2Se is a very promising thermoelectric material to replace Bi2Te3 for near-RT applications.

Keywords: α, Cu2Se, Thermoelectric, Power factor optimization, Lorentz number, Thermal con-

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ductivity

Anomalous transport phenomena and thermoelectric performance enhancement in the Cu-overstuffed ferromagnetic spinel Cu1+xCu2Te4

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Recently magnetic semiconducting materials have been attracting attention due to various magnetic effects that could beneficially influence their thermoelectric properties [1]. The spinel phase CuCr2Te4 is a system that ferromagnetically orders above room temperature (TC = 325 K) but is however a poor p-type thermoelectric due to very low thermopower values (< 10 μV.K-1) It shows a moderate thermal conductivity (> 3 W.m-1.K-1) dominated by its electronic contribution, despite a low lattice contribution (< 1 W.m-1.K-1). In the cubic crystal structure of this compound (space group Fd-3m), two voids located at the tetrahedral 48f and octagonal 96g positions can be filled by excess Cu atoms in the case of non-stoichiometric compounds. Herein we report on the high temperature thermoelectric properties of the ferromagnetic compounds Cu1+xCr2Te4 for x=0, 0.5, 1 and 1.5, produced by solid state reaction and densified by Spark Plasma sintering. Here we demonstrate the possibility of making Cu-excess compounds above the previously attainted threshold by the use of SPS. Although a decrease of TC is also observed up to x=1.5, an anomalous change in temperature dependence of both electrical resistivity and thermopower is observed above x=1, both of them strongly increasing above 500K, resulting in a power factor improved by almost two orders of magnitude up to values $\approx$ 400 μW.m-1.K-2. The concomitant decrease of the thermal conductivity results in a ZT value of 0.10, which can be promising for a class of materials largely unexplored due to their too high metallicity. In addition, negative values of the anomalous Hall effect coefficient were measured in the paramagnetic phase for some values of x, further drawing attention to this interesting class of compounds. [1] Tsujii, N. and T. Mori (2013). Applied Physics Express **6**(4): 043001.

Keywords: thermoelectric, magnetic, stuffing

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Exploiting Interfaces to Enhance the Performance of Oxide Thermoelectrics

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In the last 15 years there has been growing interest in oxide thermoelectrics as alternatives to traditional metallic thermoelectrics which depend on rare, expensive, and sometimes toxic elements. The oxides are stable at high temperatures and generally lighter in weight and cheaper, and based on environmentally friendly materials. Many are based on perovskite structures and layer structures. A current limitation of oxides is the modest thermoelectric figure of merit (ZT), around 0.3 to 0.4, which comes from the low electrical conductivity and high thermal conductivity. In order to improve the material performance (by maximizing ZT) efforts have focussed on reducing thermal conductivity and electrical resistivity. One strategy is to employ microstructural engineering at the nanoscale to increase phonon scattering in order to reduce thermal conductivity. By taking examples from systems based on CaMnO3, (La,Sr)TiO3, ZnO and materials exhibiting self-assembly nanostructures, the nature and benefits of interface structures will be examined. Details of atom level structures revealed by use of high resolution TEM and information from DFT modelling can reveal important mechanisms. Finally, the potential benefits of oxide-carbon interactions will be outlined.

Keywords: DFT, TEM, perovskite, layer structures

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Redox-promoted enhancement of thermoelectric performance in strontium titanate-based materials

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Donor-substituted strontium titanate represents one of most promising n-type oxide thermoelectrics to seek high power factor, based on a specific electronic structure and prevailing lattice contribution to thermal conductivity, which can be tuned by substitution and/or micro/nanoengineering. SrTiO3-based materials also demonstrate excellent thermal and phase stability, both under oxidizing and reducing conditions, and possesses a unique redox flexibility and defect chemistry, which can be precisely set-up by controlled heat treatment combined with oxygen partial pressure changes. This work demonstrates how, by redox-sensitive substitutions, the thermoelectric properties of strontium titanate can be tuned and enhanced. The developed strategy is demonstrated for molybdenium-co-substituted SrTiO3, prepared under strongly-reducing conditions. In-situ formation of nanocomposite and atomic-scale inhomogeneities composed of SrMoO3-based insertions into SrTiO3 perovskite lattice promote simultaneous significant increase in the power factor and decrease in the thermal conductivity by decoupling the thermal and electrical properties. The proposed approaches show good prospects for tailoring thermoelectric performance in other oxide-based systems, containing redox-active cations.

Keywords: strontium titanate, redox activity, donor subsitution, nanostructuring, electrical properties, thermal conductivity

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Challenges to enhance the thermoelectric properties of ZnO-based ceramics

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Doped ZnO is a promising n-type TE oxide material with a reported zT value of 0.45–0.65 at 1000∘C. As well as being nontoxic, inexpensive and stable in air to high temperatures, it has a high S of about -400uV/K and excellent charge-carrier transport properties that are easily tunable via doping. Unfortunately, it also has a large lattice thermal conductivity due to its simple Wurtzite structure. The simultaneous optimization of compositional, structural and microstructural features, which would result in a high s while preserving a high S, and a drastically reduced k, remains a great challenge, despite many efforts. The sintering of ZnO in air results in intrinsic acceptor states (oxygen interstitials and Zn vacancies) at the grain boundaries, causing electrostatic Schottky barriers, which then decrease s. Our results showed that the conventional sintering of doped ZnO in a reducing atmosphere or under vacuum in an SPS eliminates the acceptor states at the grain boundaries and greatly increases the solubility of the dopants (Al, Mg, Ti) in ZnO, resulting in a s of 1.9x103S/cm and a maximum power factor of 8.2x10-4W/mK. However, due to the large concentration of point defects, k980K remained at 10W/mK, as in the sample sintered in air, having a several orders of magnitude lower s. In the case of In2O3-doping the highest zT values were reported for the homologous phase Zn5In2O8 with a high density of multiple planar defects. Our results showed, however, that already the addition of up to 0.5 at.% of In results in the formation of planar defects, increasing s to about 170S/cm and decreasing k to about 7.5W/mK, so indicating a broad window for further optimizations.

Keywords: ZnO, doping, processing, structure, microstructure, thermoelectric properties

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Thermoelectric properties of doubly substituted La0.95Sr0.05Co1-xCrxO3 ($0 \leq x \leq 0.5$) ceramics

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Dense La0.95Sr0.05Co1-xCrxO3 ($0 \leq x \leq 0.5$) ceramics were synthesized by solid-state reaction and conventional sintering. Room-temperature crystal structure and microstructure were investigated and the thermoelectric properties were measured in the temperature range 323 K – 1020 K. All compositions are single phase with rhombohedral structure, and the lattice parameter of La0.95Sr0.05Co1-xCrxO3 increases with increasing Cr content.
La0.95Sr0.05Co1-xCrxO3 is a p-type small polaron conductor. The charge carrier concentration is determined by both substitution of La3+ with Sr2+ and thermally-activated charge disproportionation of Co3+ and / or Cr3+. Above 550 K, the substitution of Co with Cr increases the Seebeck coefficient and reduces the electrical conductivity. Below 550 K, the trend of Seebeck coefficient with Cr content is not clear due to the thermally activated charge disproportionation. At low temperature, the electrical conductivity shows a minimum with Cr content of $x = 0.4$, as a result of trapped polarons in the Cr sites. By substituting Co with Cr, the power factor below 800 K is reduced and that above 800 K is improved.
The thermal conductivity is effectively reduced by doping Cr. The highest ZT value of 0.053 at 373 K is achieved for $x = 0$, but it decreases rapidly with increasing temperature. Substitution of Co with Cr can effectively improve the ZT values at high temperatures. In the temperature range 700 K – 1000 K, ZT increases with increasing Cr content, the highest being 0.04 at 1000 K for the composition with $x = 0.5$, more than 4 times the value of the La0.95Sr0.05CoO3 compound.

Keywords: thermoelectrics, p, type, perovskite, double substitution

*Speaker

Defect and Schottky Barrier Engineering in Thermoelectric SrTiO3-δ Ceramics

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Strontium titanate (SrTiO3) is one of the representative oxide thermoelectric materials. Especially, for n-type applications donor dopants have been used widely with controlling the sintering atmosphere. This work investigated the oxygen vacancy and Schottky barrier effects on the thermoelectric properties, and showed promising results to handle and design the oxide thermoelectrics. The undoped SrTiO3 (STO) samples were synthesized through traditional solid-state reaction method in air and then subsequently reduced through annealing under low oxygen partial pressures (pO2's) at 1573K. Controlling oxygen vacancy concentration in undoped SrTiO3 enhanced the phonon-glass electron-crystal (PGEC) behavior, showing that the oxygen vacancies act as phonon scattering centers and generate quasi-free electrons for the charge carrier, as a result significant increase of the figure of merit about 13 times larger as compared with the samples reduced under relatively high pO2. To engineer the Schottky barrier at the grain boundaries, reduced graphene oxide (RGO) and spark plasma sintering in vacuum at high temperatures were used. It was found that incorporation of RGO into undoped STO lowers the Schottky barrier height and enhances the band alignment of STO and RGO, and consequently increases both carrier concentration and mobility. In addition, it is anticipated that the STO/RGO interfaces play as a phonon scattering centers. Collectively, the controlling defect and Schottky barrier in undoped STO boosted the thermoelectric figure of merit in the STO ceramics.

Keywords: Thermoelectric, SrTiO3, Defect, Schottky barrier, Oxide

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Silicon and metal silicides nanocomposites as high-performance thermoelectric materials

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Conventional thermoelectric (TE) materials such as Bi2Te3 and PbTe contain highly-toxic and rare elements. Therefore, high-performance TE materials made from non-toxic and Earth-abundant elements need to be developed. Our group has focused on Si and metal silicides nanocomposites for such advanced TE materials. Although Si exhibits excellent power factor, the zT is not high as those of the conventional TE materials due to its high lattice thermal conductivity. When metal silicides disperse in the Si matrix in nanoscale, they scatter heat carrying phonons effectively, leading to enhancement in the zT of Si. Moreover, additional effects such as modulation doping and energy filtering for further enhancement of the power factor can be expected under several systems between Si and specific metal silicides. Here, VSi2, Mg2Si, NiSi2, TiSi2, CoSi2, ... are selected as the metal silicides. We synthesized the Si and metal silicides nanocomposites by a melt spinning method. The melt spinning enables us to control the size and the distribution of the metal silicides. In the nanocomposites, the metal silicides exist as nano-precipitates in the Si matrix with nano-dot or nano-lamellar structure. The experimental results on the microstructure and TE properties of the nanocomposites will be presented. This work was supported in part by JST, PRESTO Grant Number JPMJPR15R1.

Keywords: silicon, metal silicide, nanocomposite

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Thermoelectric and galvanomagnetic properties of topologically non-trivial (Co-M)Si "new fermion" semimetals (M=Fe, Ni)

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We present an overview of the experimental and theoretical results on electronic structure, galvanomagnetic, and thermoelectric properties (Hall coefficient, magnetoresistivity, electrical resistivity, thermal conductivity and thermoelectric power) of Co1–x Mx Si (M=Fe, Ni). CoSi and the alloys are the recent candidates to the family of materials with topologically non-trivial electronic structure. On the other hand CoSi is a well known promising thermoelectric compound.
Electronic structures of the compounds were calculated using density functional theory as implemented in VASP software package. The analysis of the electronic structure revealed that close to Fermi energy there are 4- and 6-fold degenerate "new fermion" nodes, located at G and R points of the Brillouin zone and carrying large topological charge. The non-trivial topological structure manifests itself by appearance of Fermi arcs of the surface states. Using results of these calculations, thermoelectric properties were analyzed in constant relaxation time approximation with the help of BoltzWann code.
Thermoelectric and galvanomagnetic properties were measured at temperatures from 2 K to 800 K. At low temperature in Fe-containing alloys resistivity reveals clear signs of weak antilocalization, which is suppressed by magnetic field. The longitudinal magnetoresistivity of CoSi is negative and small in magnitude. We discuss possible connection of observed peculiarities in the transport properties with topological features in electronic structure of the compounds.

Keywords: Silicide, thermoelectric and galvanomagnetic properties, topological materials

*Speaker

Screening silicide thermoelectric materials using ab initio transport calculations

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If thermoelectric technology is to conquer significant new markets, it is crucial to introduce materials based on cost-effective, abundant and non-toxic elements. Silicon is in this context an excellent starting point, with magnesium based silicides and higher manganese silicides being well-established thermoelectric materials. In this study a focused search for silicides with beneficial thermoelectric properties was performed, using a combination of ab-initio atomic-scale calculations and semi-classical Boltzmann transport theory. All known crystalline inorganic silicides were included in the search, excluding the expensive, rare, reactive, and toxic elements. The search only focused on intermetallic compounds and oxides were therefore excluded. The calculations were performed at a reasonably high level of accuracy, facilitated by efficient interpolation algorithms in the new transport software T4ME. The results are in excellent correspondence with the best known silicides studied experimentally in the literature. We also identify a small number of promising compounds that only have been scarcely studied.

Keywords: Mg2Si, silicides, DFT, modeling, manganese silicide

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Demonstration of thermoelectric generation in the metallurgic industry

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Energy intensive industries are continuously looking for technologies to harvest the enormous potential of high temperature waste heat. In order to fill this need, RGS Development introduces a fully stuffed thermoelectric panel – a ThermagyTM heat panel - allowing reliable and cost effective operations, as well as efficient implementation in industrial waste heat recovery situations.
Within the framework of H2020 project INTEGRAL (INitiative to bring 2d generation Thermo-Electric Generators into industrial ReALity) two pilot systems are established, one at ELKEM's silicon production facility in Salten Norway, and one at the rod mill line in ArcelorMittal's steel factory in Aviles Spain. The ELKEM pilot demonstrates the application of Thermagy at a silicon casting carrousel, powering a local suction hood. The ArcelorMittal pilot demonstrates a combination of electricity recovery and advanced temperature control, preparing for a full size cover over the milling transfer area.

For both demonstration projects, the project approach is discussed in detail. The first phase involves assessment of requirements, thermal modelling, and validation testing. Based on the information and practical experience during this phase, engineering and system installation is executed, and subsequent operation is prepared.

The INTEGRAL demonstrator projects can be considered as a template for application of thermoelectric systems in an industrial environment. In a broader sense the pilot projects will demonstrate the operational robustness and functionality of Thermagy panels for similar applications throughout the metallurgical industry.

Keywords: Waste heat recovery, Thermagy heat panels, metallurgic industry, Integral

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A thermal-shock resistant, high performance, SiGe thermoelectric generator for industrial waste heat applications

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Energy intensive industries (e.g. steel casting or float-glass) are looking for technologies to harvest the enormous potential of high temperature waste heat. However these reservoirs have remained untapped, because there is no reliable, cost efficient technology available today for temperatures above 800∘C.
For this application segment RGS Development has launched a thermoelectric panel - ThermagyTM heat panel - using silicide materials cast from the melt and shaped directly into legs. The advantages of these panels are the use of cost-effective, environmentally benign materials, a unique panel design that allows industrial manufacturing in combination with an "easy to handle" interface for large scale system integration.

The first generation devices were manufactured using higher manganese silicide (HMS) and silicon germanium legs with state of the art ZT values. However during tests in the steel industry it turned out that HMS thermoelectric elements failed due to thermal shock load and degradation of the thermoelectric properties. While the material degradation issue was overcome by using vanadium doping, the relatively low mechanical strength in combination with thermal cycling required unnecessary costly system solutions to permit the use of HMS in this environment. Consequently higher manganese silicide material was replaced by p-type SiGe.
For the second generation SiGe-based Thermagy panels an interconnection technology was developed for operation of the device at module temperatures above 700∘C under atmospheric conditions. In radiative environments, power outputs exceeding 3000 W/m2 (active area) are demonstrated. Combined with the excellent thermal stability over more than 1500 test hours and its resistance to thermal shock cycling, a reliable "solar panel for high temperature industrial waste heat" is available.

Keywords: silicon germanium, HMS, thermoelectric panel, industrial application, waste heat recovery

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Thermoelectric performance in nanocomposite bulk consisting of MnSi1.7 and SiGe

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Enhancing thermoelectric figure of merit ZT of cost effective materials is essential towards practical applications and nanocomposite structure is one of the promising solutions. We succeeded to reduce a lattice thermal conductivity to 1.0 W/Km in MnSi1.7-based nanocomposite thin films [1]. In this study, we fabricated nanocomposite bulk consisting of MnSi1.7 and SiGe and investigated the dependence of thermoelectric properties on the Ge amount.
The MnSi1.7-based powder was prepared from powders of Mn, Si, and Ge, whose composition ratio is 1.0, 1.9-g and g (g = 0.0, 0.05, 0.1, and 0.15), respectively. Mechanical alloying was carried out with a rotation speed of 300 rpm for 30 hours, following sintering process at 900°C for 10 minutes. The crystal structures were evaluated by X-ray diffraction and transmission electron microscopy analysis. The Seebeck coefficient (S), electrical resistivity (ρ), and thermal conductivity () were measured by 2-probe method, 4-probe method, and laser flash method, respectively.

The introduced Ge substitutes both the host of MnSi1.7 and the guest of Si. The grain size of the host ranges from 30 to 300 nm, comparable to the phonon mean free path. Both S and ρ monotonically decrease with the Ge addition resulting in increasing the power factor. On the other hand, the at first decreases when g is 0.05, but increases when Ge was added more because of the crystallization of SiGe. As a consequence, ZT increases from 0.34 to 0.56 at 530∘C by adding Ge owing to the reduction of the ρ.

This work is based on results obtained from the Future Pioneering Program "Research and Development of Thermal Management and Technology" commissioned by the New Energy and Industrial Technology Development Organization (NEDO). This work is also supported by ThermMAT.

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Keywords: higher manganese silicide, composite

*Speaker

Effect of element substitution on the phase stability of complex MnSiγ

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The Higher Manganese Silicide (HMS) is a promising thermoelectric material because of it is non-toxic, environmentally friendly, low cost, complex crystal structure (chimney ladder structure). The structure of HMS belongs to the group of chimney ladder crystal structure and was reported to have four different forms, Mn4Si7, Mn11Si19, Mn15Si26, and Mn27Si47. Mn sub-lattices and Si sub-lattices are arranged in such a way that they are stacked with Mn atoms forming chimney and Si atoms as helical ladder along the long c-axis. The four different structures were interpreted as the products of different incommensurate-length-ratios of two sub-lattices. In this study, we have analyzed the thermal stability of different higher manganese silicide (HMS) phases as the main motive was to understand the thermal degradation of thermoelectric properties which are strongly correlated with the phase stability.
The synthesis of Mn(1-x)TxSiγ (T = Re, Cr, W) was done by melting high purity elements in the arc melting furnace. Liquid quenching technique was used for the partially substituted HMS samples. All the processes mentioned above were carried out under pressurized Argon atmosphere. The samples were then sealed in the quartz tube and annealed at 1000∘C. The structural changes were analyzed from temperature dependent synchrotron X-ray diffraction data by using Rietveld refinement.
The systematic XRD data at 30∘C, 300 ∘C, and 600 ∘C showed that there is a phase transition for non-dope HMS at 600 ∘C, the structure transforms to Mn15Si26 from Mn27Si47. Notably, this phase transition behavior was not observed in Re substituted HMS in which no serious degradation was observable at high temperature. The time-dependent thermoelectric properties at the high temperature of non-doped and doped HMS will be shown in the presentation.

Keywords: Higher manganese silicide, Synchrotron X ray diffraction, Structural analysis

*Speaker

High temperature oxidation of higher manganese silicides and alloys

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Higher manganese silicides (HMSs) are among the most interesting materials for thermoelectric applications due to their mechanical properties, low toxicity and abundance in the Earth's crust. However, most terrestrial applications require stability at higher temperatures and durability under extreme environmental conditions. In the present work, high temperature oxidation of HMS compounds has been studied to understand the oxide composition, oxidation rates, as well as the reaction mechanisms. The oxidation behavior of HMS samples was carried out using a thermogravimetric analyzer (TGA) under controlled atmosphere and heating rates. The products were then analyzed by standard methods including XRD and SEM, to determine the compound phases, chemical composition, and crystal structures.

Keywords: High temperature oxidation, Higher Manganese Silicides, Thermoelectrics, Thermoelectric materials

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Mechanical Properties and Failure Analysis of Higher Manganese Silicide

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1

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This work focuses on the correlation between microstructure and mechanical properties of higher manganese silicide (HMS). A single crystal HMS ingot was cast from elemental Mn and Si with a nominal composition of Mn15Si26. The microstructure of the ingot was characterized, and its fracture strength was evaluated following ASTM C1161 bending test. The correlations between elastic modulus, fracture strain, fracture stress and toughness were studied, and Weibull distribution analysis was applied to fracture strength data. Statistical results show a wide distribution in the mechanical prosperities. Fractography reveals the profound effect of the minority MnSi phase on the failure mechanism of HMS. The negative effect of the minority second phase MnSi particles on the mechanical reliability of HMS is highlighted.

Keywords: Thermoelectric, elastic modulus, reliability, flexural strength, failure, cracks

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Thermoelectric characterization of n-type and p-type skutterudites fabricated in a up-scalable way

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Skuterudites (CoSb3) are one of the most used materials for thermoelectric applications in the range of medium temperatures. By nanostructuring the material, and increasing the number of grain boundaries, its thermal conductivity can be lowered while maintaining its high power factor values. A novel route, based on the nano-powder ball-milling fabrication method presented in Ref. [1] for n-type skutterudites. This method has been further developed, this time for obtaining both n- and p-type skutterudites. The sintering of these powders into nano-composites has been done by pressing and annealing treatments, obtaining nano-structured skutterudites and a complete characterization of their properties from a thermoelectric point of view has been performed, obtaining rather competitive materials for low-cost fabrication of thermoelectric devices for mid-range temperature applications.

Keywords: Skutterudites, upscaling

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Experimental and Computational Phase Boundary Mapping of Co-Sn-Te Phase Space for Skutterudites

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Historically, improved thermoelectric performance in skutterudites has been focused on the insertion of extrinsic dopants in the interstitial void known as "rattlers." While this approach decreases the intrinsically high thermal conductivity of skutterudites, optimization of the rattlers has plateaued. As a result, recent studies have considered mixed-anion skutterudites where the anion site is replaced with equal parts group 14 and 16 elements. Introducing the mixed-anion split to the framework results in the decrease of the overall symmetry from cubic to rhombohedral ordering and increases the valence band convergence in the electronic structure. In this work, we investigate the mixed-anion skutterudite system to aid in understanding the role the anion site plays in thermoelectric performance. We focus our investigations on the Co4Sn6Te6 mixed-anion skutterudite as it is closely related to the high-performing Co4Sb12 binary analog. We examine the phase stability of the single-phase region and its range of thermoelectric properties via the phase boundary mapping technique through traditional bulk synthesis and computational analysis. From this study, we conclude the anti-site defects control the intrinsic carrier concentration of the system. In addition, the extrinsic dopant concentrations necessary to optimize the thermal and electrical properties would be difficult for n-type samples albeit p-type Co4Sn6Te6 remains a promising avenue to explore.

Keywords: Skutterudite, defects, phase boundary mapping, experimental

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Analysis and Risk Mitigation of Raw Materials Sourcing and the Implications for eMMRTG Skutterudite Couple Performance

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The eMMRTG program seeks to enhance the performance of the Multi-Mission Radioisotope Thermoelectric Generator by exchanging the heritage thermoelectric couple materials and design with that of a more efficient skutterudite (SKD)-based thermoelectric (TE) couples. Both at the Jet Propulsion Lab-where the SKD materials were developed-and at TESI (Teledyne Energy Systems, Inc.)-where the technology is being matured under the Skutterudite Technology Maturation Program-many SKD material batches have been produced. A strong correlation has been observed between the TE performance of the materials and the particular lot numbers (same producer and vendor) of various raw materials used to produce the SKD materials. An analysis of the differences between lots, their effects on performance, and the current plan to mitigate the risk posed by these results will be presented.

Keywords: skutterudite, synthesis, purity, RTG

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Synergistically enhancement of thermoelectric properties in partially filled CoSb3 skutterudites through simultaneous doping and nanostructuring

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Because of the flexibility of fabrication and cost effectiveness, CoSb3 skutterudites are considered as promising thermoelectric (TE) materials with the objective of using them in TE modules for waste heat recovery at 573 K - 773K temperature range in automotive applications. We have investigated a series of partially filled Ni doped n-type skutterudite (Co1-xNixSb3, Dy0.1Co1-xNixSb3 (x=0, 0.1, 0.2) and Te0.1Co1-yNiySb3 (x=0, 0.3, 0.5)) materials processed by powder metallurgy route. Phase formation and optical phonon modes were investigated using X-ray diffraction and Raman spectroscopy. Microstructure investigation using high resolution transmission electron microscopy shows the non-uniform distribution of nanometer size grains. The selective area electron diffraction pattern confirms the co-existence of two skutterudite lattices having slightly different lattice parameters in Ni doped skutterudites (Dy0.1NixCo1-xSb3). Temperature dependent TE properties show substantial decrease of electrical resistivity and thermal conductivity in the Ni doped skutterudites. Filling element has negligible effect on the enhancement of electronic properties. Power factor _˜ 7 mW/mK2 is achieved in the Dy0.1Co0.8Ni0.2Sb3 sample which is the highest power factor in doped skutterdites reported so far. Dy0.1Co0.8Ni0.2Sb3 shows the lowest lattice thermal conductivity _˜ 0.3 W/mK at 773 K, which arises due to the enhancement of phonon scattering from lattice mismatch and impurity scattering centres. As a result, higher ZT _˜ 1.8 at 773 K is achieved in Dy0.1Co0.8Ni0.2Sb3. Detailed investigations of the co-relation of the microstructure, electron-phonon and phonon-phonon scattering to the enhancement of TE properties and thermomechanical properties in Ni doped skutterudites will be discussed within the scope of the presentation.

Keywords: Skutterudite, optical phonon modes, lattice thermal conductivity, phonon phonon scattering, thermoelectric properties, thermomechanical properties, microstructure

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Magnesioreduction : a low temperature synthesis route towards CoSb3-based skutterudites with improved thermoelectric properties

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Nanostructuration and rattler insertion into CoSb3 skutterudite were shown to be efficient strategies to significantly reduce the lattice thermal conductivity without greatly affecting its electronic properties [1]. Together with the optimization of the power factor by proper doping, these strategies result in ZT above 1.5 in the 750-850 K intermediate temperature range [2]. CoSb3 forms via a peritectic reaction below 1171 K. Its synthesis by conventional fusion-solidification process requires a subsequent annealing (typically two weeks long around 1100 K) including intermediate grindings to be brought to completion [3].

In order to save time and energy, magnesiothermic reduction (MTR), which consist in the coreduction of metal oxides by sacrificial magnesium metal, was used as an alternative route to produce phase-pure and doped CoSb3 powders. This one-step synthesis has the advantage to be realized in 4 days only at temperatures as low as 770K. The powders obtained by MTR are made of well crystallized (sub)micrometric grains which can be readily spark plasma sintered. This presentation will focus on the influence of the key parameters of the MTR process (morphologies/preparation of precursors, reduction temperature range , heat treatment duration), on the structural (XRD) and microstructural (SEM, EBSD, TEM) characteristics of skutterudite powders and subsequent improvement of their thermoelectric properties, especially their relatively low thermal conductivity.

B. C. Sales et al., Sciences, 272 (1996) 1325

X. Shi et al., J. Am. Chem. Soc., 133 (2011) 7837

E. Alleno et al, Rev. Sci. Instrum., 86 (2015)

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Keywords: Magnesioreduction, Skutterudite, Synthesis, EBSD

Optimisation Strategies for Double filled InxLa0.25Co4Sb12 ($0 \leq x \leq 0.5$) skutterudite material

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This paper present the contribution of In-addition into the La0.25Co4Sb12 skutterudite structure for the improvement of its thermoelectric properties. The InxLa0.25Co4Sb12 ($0 \leq x \leq 0.5$) samples were prepared through a combination of mechanical alloying followed by spark plasma sintering process. The characterization of phase structure and morphology of the sintered InxLa0.25Co4Sb12 bulk samples were examined by XRD and SEM-EDS analysis. Rietveld analysis of the XRD spectra indicated that double filling of the skutterudite voids with La and In was successfully achieved. Microstructural analysis also detected the presence of the secondary phase, InSb above x=0.1, which indicates that the maximum In filling in the voids beyond x=0.22. This has the impact of significantly improving the thermoelectric performance of the La0.25Co4Sb12 compound, through increase in the electrical conductivity. The electrical behavior changes from semiconducting to semimetallic for In > 0.1, which is likely due to the presence of excess In dopant and InSb secondary phase. Double filling also effectively reduced the lattice thermal conductivity. A maximum ZT value of 1.25 at 789 K was achieved for In0.5La0.25Co4Sb12. Summarily, the addition of In into La0.25Co4Sb12 provides a pathway to improve the overall thermoelectric performance of skutterudites through exploitation of double filling strategy to achieve significant improvement in its electrical conductivity and concurrent reduction of its thermal conductivity.

Keywords: Skutterudites, In addition, double filling, thermoelectric

*Speaker

Enhanced thermoelectric properties of In0.25Co4Sb12 with InSb nanoinclusions

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Uniform dispersion of nanoparticles in the bulk materials is one of the promising ways of enhancing the thermoelectric properties through increased phonon scattering at the interfaces. The influence of InSb nanoparticles on the thermoelectric properties of bulk In0.25Co4Sb12 was investigated in the temperature between 300 K and 723 K. InSb secondary phase was mixed with In0.25Co4Sb12 via high energy ball milling method and the composite powder was compacted by spark plasma sintering technique. The X-ray diffraction pattern of powder, as well as sintered pellets, showed the formation of single phase skutterudite structure for all the samples. The scanning electron micrographs showed the existence of three different phases in the samples and composition of the phases were determined using electron probe micro analyser. The presence of In2O3 phase in the samples indicates oxidation of In during synthesis of the parent compound and other two phases exhibit almost same composition having slight differences in In and Sb content. Therefore, it can be concluded that generation of two phases with slightly different compositions is due to the formation of solid solution of InSb nanoparticles with part of In0.25Co4Sb12 at the time of ball milling. The Seebeck coefficient (S) was negative for all the samples including a pristine compound which indicates n-type semiconducting behaviour. At room temperature, a decrease in S was observed in nanocomposites compared to In0.25Co4Sb12 due to enhanced carrier concentration. Addition of InSb nanoparticles in matrix improved electrical conductivity drastically. The thermal conductivity of (InSb)0.4In0.25Co4Sb12 decreased significantly due to enhanced phonon scattering at the interfaces. The above combined effects resulted in a maximum figure of merit of 1.26 at 645 K for (InSb)0.4In0.25Co4Sb12 composite.

Keywords: Seebeck coefficient, electrical resistivity, thermal conductivity, skutterudite

*Speaker

A new and fast SPD-method to produce high ZT (> 1.3) skutterudites

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For mass fabrication of thermoelectric generators a fast, cheap and easy method is necessary to produce high ZT leg material. It is well known that severe plastic deformation (SPD) introduces defects, enhances the dislocation density and refines the grains to nano size. SPD via high-pressure torsion (HPT) at elevated temperatures in argon atmosphere was used to directly consolidate commercial p-type cold pressed (CP) skutterudite powder (DD0.7Fe3CoSb12) into a solid.
The structural, physical and mechanical properties of the so generated compacted disc were investigated. The sample exhibited a very high figure of merit, ZT > 1.3 at 773 K, much higher than that of the hot pressed sample (HP) from the same powder, comparable with ZTs of high energy ball milled and hot pressed samples (BM-HP) as well as of ball milled, hot pressed and HPT processed skutterudites (BM-HP-HPT). The efficiency is even higher. Synchrotron measurements at temperatures from room temperature to 550 ∘C were performed in order to extract the transitions in grain size and dislocation density of the CP-HPT sample before and after annealing. The change of the dislocation density indicates a rearrangement of dislocations from statistically distributed ones to low angle grain boundaries, consuming the deformation-induced vacancies. SEM and TEM images help to give a better insight into the temperature dependent modifications of this new material. Due to grain refinement, the CP-HPT material exhibits higher hardness values and higher elastic moduli than the reference sample.

As already large high-pressure torsion facilities exist, which may be used for the processing of sheets, a new, fast and therefore cheap mass production of solid skutterudites directly from the powder is possible, without time and energy consuming ball milling and hot-pressing.

Keywords: Skutterudites, Severe Plastic Deformation, Mechanical Properties

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Realization of high figure of merit in Ni compensated double filled p-type skutterudites

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Harvesting waste heat into useful energy using thermoelectric materials for a wide range of applications has fascinated the scientific community for decades. Following the nano-structuring approach combined with fillers in cage like structure, researchers have reported a significant improvement on dimensionless figure of merit, ZT, of n-type skutterudites. However, the performance of p-type counterpart is inferior due to several reasons such as low Seebeck voltage and bipolar contribution in electrical and thermal conductivity at higher temperature, leading to low power factor and high thermal conductivity. In this work, we present the performance of Ni compensated double filled p-type skutterudites made via melting-quenching-ball milling-hot pressing under optimized physical conditions. By carefully adjusting the Fe/Ni ratio and fillers concentration, we suppressed the bipolar thermal conduction and achieved a high Seebeck voltage at elevated temperature leading to a ZT value above 1.1

Keywords: Skutterudites, nano, structuring approach, dimensionless figure of merit

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Filling Fraction Fluctuation in CoSb3-based Skutterudites Synthesized by High Pressure

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Pristine CoSb3 and rare earth-filled skutterudites RCo4Sb12 (R = La, Ce, Yb) have been synthesized and sintered in one step under high-pressure conditions at 3.5 GPa in a piston-cylinder hydrostatic press. The structural properties of the reaction products were characterized by synchrotron X-ray powder diffraction and high-resolution TEM.
Unfilled CoSb3 shows a surprisingly low thermal conductivity due to the point-defect and disorder phonon scattering caused by antimony vacancies for an actual composition CoSb2.90.1 Filled compounds clearly show an uneven filling factor of the skutterudite phases, confirmed by transmission electron microscopy. The non-homogeneous distribution of R filling atoms is adequate to produce a significant decrease in lattice thermal conductivity, mainly due to strain field scattering of high-energy phonons. Furthermore, the rare-earth filler primarily acts as an Einstein-like vibrational mode having a strong impact on the phonon scattering. Extra-low thermal conductivity values are measured for Ce0.5Co4Sb12 La0.25Co4Sb12 and La0.5Co4Sb12 nominal compositions. Besides that, filler atoms contributed increasing the charge carrier concentration in the samples, as for lanthanum and ytterbium there is an enhancement of the power factor.2

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Keywords: skutterudites, high, pressure, CoSb3, filling fluctuation, PGEC, lattice thermal conductivity

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Structure and bonding, and their role in thermal transport of materials for thermoelectrics applications: It's not just about skutterudites and clathrates anymore!

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Heat transport is not only of interest for thermoelectrics; it has, and continues to be, a topic of interest in basic and applied condensed matter physics. Materials with "open-framework" crystal structures, such as skutterudites and clathrates, have been shown to possess low thermal conductivities, and are therefore of continuing interest for potential thermoelectric applications. However, new materials with certain structural features and bonding can also possess low thermal conductivity. In some cases the thermal conductivity cannot be explained by conventional phonon transport theory. Moreover, certain compositions have only recently been realized and their transport properties are only now being investigated. Here theoretical first-principal calculations are not only invaluable in understanding the structure-properties relationships, but can also provide input for experimental direction. I will review a few of the mechanisms that lead to unique thermal properties, not only thermal conductivity. Several new compositions that have not previously been investigated will also be discussed. Certain phenomena may not be directly relevant to thermoelectrics; however, the intellectual merit of these investigations is very closely tied to the new and novel structure types and corresponding novel physical properties they exhibit, and aims to develop important fundamental research towards advances for thermoelectrics and other energy-related applications. An overview of some of the resent and ongoing research will be presented.

Keywords: thermal properties, crystal structures, transport

*Speaker

Shock-compression as a novel method of preparation of nanostructured CoSb3 skutterudite

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Shock compression method is a unique densification technique used for sintering of nanostructured materials. Unlike classical sintering methods, it preserves nanostructured properties of densified powders. Moreover, it is well known that this technique generates additional large numbers of micro- and nano-sized defects which act as phonon scattering centers, reducing the lattice component of thermal conductivity. The goal of the present work is to apply this new densification technique for preparation of CoSb3-based nanostructured materials in a fast, one-step process. We also study the influence of shock-compression parameters on structural, microstructural and transport properties of the newly obtained materials. Microstructured powders of CoSb3 were compressed under different pressures: 15, 20 and 30 GPa in time of few microseconds. The analysis of SEM and XRD data showed specific changes in the microstructure of the materials and a large broadening of XRD reflections, which indicates a significant lowering of crystallite size and the presence of huge internal strains. The new materials are also exhibit improved thermoelectric properties of materials in comparison to samples obtained by the classical SPS method.

Keywords: nanostructured materials, shock, compression, CoSb3

*Speaker

High-pressure synthesis of tetragonal iron aluminide FeAl2

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Tetragonal FeAl2 with MoSi2-type crystal structure (t-FeAl2, space group $I4/mmm$) is predicted to be a stable narrow bandgap semiconductor [1]. However, complex and disordered triclinic FeAl2 (a-FeAl2) with metallic behaviors is only synthesized under atmospheric pressure. We both theoretically and experimentally investigated thermal stability under high-pressure and high-temperature conditions, electronic structure, and thermoelectric properties of t-FeAl2. From total energy calculations, relative stability of t-FeAl2 against a-FeAl2 in terms of enthalpy increased with increasing pressure, indicating that high pressure is favorable to synthesize t-FeAl2. Boltzmann transport calculations implied that the large Seebeck coefficient of more than 150 μV/K is expected over a wide temperature range by carrier concentration tuning. In the experiment, we successfully synthesized t-FeAl2 both by laser-heated diamond-anvil cell (LHDAC) and by multi-anvil cell (MAC) techniques, under 10–20 GPa at 1273–2123 K. The experimental lattice parameters of the LHDAC sample were within 1.5% of the simulated lattice parameters at all pressures. More details of calculations and experiments on the LHDAC sample are shown in Ref. [2]. Thermoelectric properties of t-FeAl2 synthesized by MAC technique will be presented in the conference.

This work was partly performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2017G584)

M. Mihalkovič et al., Phys. Rev. B 85, 14113 (2012)

K. Tobita et al., Scr. Mater. 141, 107–110 (2017)

Keywords: iron aluminide, high, pressure synthesis

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Optimization of Thermoelectric Transport Properties on Weak Topological Insulator Bi14Rh3I9

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There has been a growing interest in exploring promising thermoelectric (TE) materials in the territory of topological insulators (TIs). In this work, we report the optimization of TE transport properties of a three-dimensional weak TI, Bi14Rh3I9. This compound represents a class of weak TIs with layered structure built by an alternating stack of two-dimensional (2D) quantum spin Hall (QSH) layers and normal insulator (NI) layers. The unique lattice dynamics of the NI layers renders this crystalline material extremely low lattice thermal conductivity (0.3_˜0.4 W m-1 K-1). The strong spin-orbit coupling effect in the QSH layers along with weak interlayer interaction generates a proper bulk band gap and a quasi-2D electronic structure. Significantly enhanced power factor stemmed from the optimized carrier concentration and enhanced mobility of the bulk state electrons is achieved by introducing Cu into Bi14Rh3I9. The enhanced electrical transport properties, together with the minimum thermal conductivity, give rise to largely improved figure of merit ZT. This layered weak TI suggests an interesting TE system in which the conducting electrons are confined inside the QSH layers while the heat-carrying phonons are strongly scattered by the NI layers.

Keywords: Thermoelectric transport properties, weak topological insulators, quasi, 2D electronic structure, minimum thermal conductivity

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Metal Phosphides as Overlooked Thermoelectric Materials

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The solution to the current energy dilemma rests on a concerted effort to broaden our renewable energy resources and increase our energy efficiency. Since almost two-third of the energy consumed worldwide is lost as waste heat, a new energy landscape would benefit from the use of thermoelectric materials to produce electricity through waste heat recovery. Although metal phosphides can exhibit excellent electronic properties, they have traditionally been overlooked as thermoelectrics due to expectations of displaying high thermal conductivity. In this study, we computed the electrical and thermal properties of various metal phosphides using first-principle calculations. The electronic band structures confirmed the excellent electrical properties in metal phosphides due to multiple band degeneracies and curved bands. In addition to the electrical properties, low-frequency acoustic modes were calculated for several metal phosphides suggesting a low lattice thermal conductivity and hence, a high thermoelectric performance. To test the reliability of these calculations, the computed properties were compared to experimental results indicating that the predicted properties are semi-quantitative. As an experimental study, the cubic-phase of NiP2 was synthesized and the low predicted lattice thermal conductivity was confirmed (1.2 W m-1 K-1 at 700 K). Furthermore, the experimental Seebeck coefficient and heat capacity of NiP2 agree well with the computed properties.

Keywords: Phospides, Thermoelectric, Thermal Conductivity

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A web application "Starrydata" for collecting and sharing plot data on published papers

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New materials have been discovered and designed by conventional concept-driven approaches based on the past experiences and knowledge. Lately, however, new approaches are expected because the complexity of new material discovery and design has a serious problem. In particular, Materials Informatics (MI), a data-driven approach to find new regularity and knowledge from an enormous data, is being rapidly developed.
In MI, first-principles calculations are used in many cases because data can be easily collected. In addition, as the enormous data have been shared on the Internet, MI has greatly contributed to the promotion of new material discovery and design. However, the values calculated under the ideal conditions by first-principles calculations are often different from the values obtained in experiments. Therefore, MI using experimental data is required, but hardly reported. Experimental data for MI are also hardly reported.
In this study, we have constructed an efficient web application named Starrydata, to collect and share experimental data on published papers. We extracted the experimental data as plotted, and comprehensively collected the sample compositions from the text. From 2,337 samples, experimental physical properties (electrical conductivity, thermal conductivity, Seebeck coefficient, etc.) have been obtained so far. We will introduce the details of this system and data, and application of this data for MI.

Keywords: thermoelectric materials, materials informatics, database, machine learning

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Phonons across the superionic transition in CuCrSe2 and AgCrSe2

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Superionic crystals exhibit ionic mobilities comparable to those of liquids while maintaining a periodic crystalline lattice, thus representing an unusual intermediate between two common states of matter. The atomic dynamics and fundamental mechanisms leading to such large ionic mobility have long been debated, and the behavior of phonon quasiparticles, which conduct heat in regular solids, is a central question. In particular, we wish to address whether these collective excitations survive in the superionic state, where a large fraction of the system exhibits liquid-like behavior. Here, we combine scattering studies and first-principles simulations to fully elucidate the lattice dynamical behavior in superionic conductors CuCrSe2 and AgCrSe2. Momentum-resolved inelastic neutron and x-ray scattering techniques, combined with first-principles simulations, allow us to definitely establish the co-existence of long-lived acoustic phonons with superionic diffusion. Furthermore, phonon dispersions and scattering rates reveal a deep connection between the low thermal conductivity and superionic behavior in these compounds. Below the superionic transition, anharmonic Cu/Ag vibrations act like 2D 'rattlers' and suppress the lattice thermal conductivity (klat) with a characteristic T dependence. Above the superionic transition, the mobile ions begin to diffuse within their layers, resulting in a disordered distribution of anharmonic rattlers and breakdown of corresponding phonon modes. In the superionic regime, scattering of the host lattice phonons by the disorder resulting from the half-filling of the delocalized Cu/Ag layer is a key mechanism to account for the very low and temperature-independent klat in the superionic phase. Most critically, we show that long-wavelength acoustic modes of the overall structure remain well defined in the superionic phase, ruling out a minimum klat picture. These fundamental insights regarding atomic dynamics in an intermediate state of matter shed new light on the role of lattice dynamics in fast diffusion for the design of high- performance solid-state electrolytes, and will facilitate the emergence of superionic compounds with ultralow thermal conductivities for thermoelectric applications. Neutron and x-ray scattering measurements and analysis supported by the S3TEC EFRC, DOE BES Award # DE-SC0001299. First-principles modeling supported by the US DOE BES Early Career Award No. DESC0016166. Sample synthesis supported by the US DOE BES, Materials Sciences and Engineering Division.

Keywords: selenide, phonons

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Direct Current Polarity-Reversal Technique to Measure the Thomson Coefficient to Determine the Absolute Seebeck Coefficient

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The absolute Seebeck coefficient is determined from the Thomson effect using the Kelvin relationship [1]. In 1985, the CODATA task group on key values for thermodynamics presented the recommended values for the absolute Seebeck coefficient of Pb, Cu, and Pt [2]. Nevertheless, discrepancies among the few reported cases have been known, and no remarkable progress has been made since the 1980s. One of the reasons for this discrepancy is that the measurement of the Thomson coefficient requires an accurate value of the thermal conductivity in a wide temperature range [3]. Therefore, an AC technique for Thomson coefficient measurement was proposed to eliminate the need for measuring the thermal conductivity [4]. However, a stray impedance such as a capacitance in the measurement circuit is inevitable. In the present study, we propose a DC polarity-reversal technique to measure the Thomson coefficient. In this technique, positive and negative DC currents are alternately applied to a sample. Thus, the Thomson effect is canceled out by averaging the temperature increases without using an AC current. As a result, the DC polarity-reversal method can eliminate the need for measuring the thermal conductivity as well as a stray impedance. The results from these heat-transfer analysis will be presented in the International Conference on Thermoelectrics 2018. We expect that the absolute Seebeck coefficient obtained from this simplified technique will become a useful tool for improving the accuracy of relative Seebeck coefficient measurements.

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Keywords: Measurement, Thermoelecteric peoperty, absolute Seebeck coefficient, Thomson coefficient

*Speaker

The Effective Mass: Our Stranger Friend

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The difficult task of striking the balance between thermal and charge transport is at the core of the search for improved thermoelectric materials. For several years, established guiding principles have been used with reasonable success in spite of many simplifying assumptions. Focusing on the electronic properties, I will discuss the importance of band structure warping in improving the electronic conductivity and illustrate a new way to build synergy between high-throughput electronic structure calculations and experiments. Examples will be drawn from recent results obtained in the AFLOW consortium (www.aflow.org) on a variety of materials ranging from oxides to complex sulfides.

Keywords: Electronic structure, electronic transport

*Speaker

A Study on the Reliability of Thermoelectric Couple Networks

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Thermoelectric generators (TEGs) rely on a network of individual thermoelectric (TE) couples, which collectively contribute to the overall power output of the system. As individual couples experience catastrophic failure, complete generator failure occurs when the power output fails to meet the required threshold. A series-parallel wiring arrangement accommodates failure of individual couples without catastrophic failure of the generator, however there exist failure paths in which the electrical continuity of the network is interrupted. In assessing the reliability of a TEG system, the probability of success is measured according to a network's ability to meet both the power level and electrical continuity criteria. A closed-form probabilistic model based on Karr's mathematical formulation is used to assess the implications of a hypothetical catastrophic TE couple failure on the reliability of a complete network. A system-level analysis is performed to evaluate the reliability effects of various network dimensions, based on the distribution of a finite number of TE couples across different numbers of series-parallel strings. Limiting the length of the strings by distributing the TE couples in parallel is found to improve the reliability of the TEG, but is bounded by the voltage requirement. The study includes an exploration into the trade between redundancy and reliability by assessing the effect of increasing the number of TE couples in a network with a defined number of strings. Reliability is found to reach a maximum for a particular level of TE couple redundancy, at which point the addition of further couples degrades the reliability of the TEG due to the increased probability of electrical discontinuity. This model is shown to be a useful tool for designing and understanding the wiring configurations of TEGs and other similar power devices.

Keywords: couple networks, systems engineering, reliability

*Speaker

Phonon transport across a Si/Ge interface: the role of inelastic scattering

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Controlling heat flow across material heterojunctions is important for nanostructured thermoelectric materials, thermoelectric devices, and for thermal management of various electronic devices. A clear physical understanding of what transport mechanism dominates near an interface can help benefit technology. We present a theoretical investigation of phonon transport across a semiconductor/semiconductor interface, specifically Si/Ge, and demonstrate how inelastic scattering and non-equilibrium effects play a key role. We treat phonon transport with the McKelvey-Shockley flux method, which is efficient, captures ballistic and non-equilibrium effects, inelastic scattering, and has shown excellent agreement with the more computationally-demanding Boltzmann equation. The Si and Ge phonon dispersions and 3-phonon scattering rates, serving as input for the transport modeling, are calculated from first-principles. The results show that, while the maximum phonon frequency in Si is nearly double that of Ge, significant heat currents are carried by the high-frequency Si phonons above the Ge cutoff. When approaching the interface, inelastic scattering redistributes energy to the phonon frequencies that can transfer elastically across the Si/Ge junction. We explain how this collective reorganization of phonons is driven by non-equilibrium effects near the interface. We also include a model for the contact resistance of an ideal interface, that depends on both phonon dispersions, which provides a lower limit for a given material combination. These results help provide clear physical insights into what controls phonon transport at semiconductor/semiconductor interfaces.

Keywords: Phonon transport, interface, scattering, first principles, density functional theory

*Speaker

The importance of considering parasitic heat losses in modelling TEG performance for high temperature application

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Adapting thermoelectric systems to high temperature ranges can have several reasons, i.e. performance maximizing or exploiting new applications. Keeping this in mind, our study is part of a current research project focusing on the development, manufacturing and testing of new thermoelectric generators (TEG) based on ceramics for operating temperatures up to 600 ∘C. In the presentation a strategy to define the constructional design of these modules is discussed. This strategy bases on computations to identify the most proper design variant.
When reviewing the literature for theoretical approaches applied to determining TEG behaviour, a vast number of mathematical models can be found. Often the sizing modification of TEG module components (e.g. legs, electrical contact bridge, substrate plates) is described as option to increase the electrical power output. That results in different TEG designs for various applications which is difficult to handle for manufacturers of those modules. Hence, the approach of our study is to modify a much easier adaptable parameter: the number of built-in thermoelectric legs, and thereby keeping the sizing of all module components constant.

The main focus of the presentation is on the influence of parasitic heat losses within the TEG module. It was found that for temperatures up to 600 ∘C parasitic inner heat bypasses have considerable impact on the performance. The heat losses are caused by radiation and heat conduction and are often neglected in the literature as the models were developed for low temperature ranges. Resulting deviations in the proposed performance are highlighted and the importance of the consideration of heat bypass effects are discussed by opposing common computation approaches at high temperatures.
The presentation closes with the selected high temperature TEG design for an illustrative example.

Keywords: parasitic heat bypass, heat loss, modelling, leg number, high temperature

*Speaker

Theoretical study on thermoelectric properties of metal/semiconductor multilayer with weak electron-phonon coupling

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Recently, it has been reported that a nanoscale metal/nonmetal multilayer is a potential structure to reduce the thermal conductivities in spite of using metallic materials when electron-phonon coupling of the metal is weak[1]. In this study, we focus on meal/semiconductor multilayers as a potential thermoelectric structure in order to investigate the effect on their thermoelectric properties. The effective Seebeck coefficients (Seff), effective electrical conductivity (σeff) and effective thermal conductivities (eff) of the multilayers were theoretically investigated by using two-temperature model (TTM) and single parabolic band model. Interfacial effects were estimated by diffuse mismatch model.
The temperature profiles of both electron and phonon of the multilayers are estimated by TTM in various thicknesses. We analyzed the eff based on TTM and Seff was evaluated by taking into account the electron-temperature profile. In the case that the metal layer with small electron-phonon coupling factor has a lower lattice thermal conductivity than that of semiconductor layer, the eff can be reduced remarkably when the thickness of both layers become thinner than the electron-phonon coupling length. Seff is attributed to that of semiconductor and σeff can be enhanced when the thicknesses and their ratio between constituents are optimal. Our theoretical study reveals that a nanoscale meal/semiconductor multilayer enables to enhance the σeff and remarkably reduce the eff, which lead to the enhancement of ZT.

This work is based on results obtained from the Future Pioneering Program "Research and Development of Thermal Management and Technology" commissioned by the New Energy and Industrial Technology Development Organization (NEDO). It is also supported by TherMAT.
A. Majumdar et al., Appl. Phys. Lett., 84, 4768 (2004).

Keywords: multilayer, electron phonon interaction, thermoelectric property

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Porous thermoelectric materials and their applications

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Thermoelectrics has been attracting much attention as one of technologies to overcome energy crisis. In order to expand use of thermoelectric conversion technologies and let them contribute to the improvement of energy efficiency of the society, cost-effectiveness needs to be enhanced. Number of researches are now going on from various perspectives. Since thermoelectric conversion efficiency is a monotonically increasing function of dimensionless thermoelectric figure of merit, zT, many of researches on thermoelectric materials targets enhanced zT. However, zT is not, of course, the only parameter that we have to take into account. zT is a parameter governing the conversion efficiency of the thermal energy which flows in the thermoelectric material. It is also a key, for example, how efficiently thermal energy is transferred into the thermoelectric material in a device.
Given that heat source is fluid, we propose thermoelectric conversion systems using porous thermoelectric materials. Porous materials have much larger specific surface area which could lead to enhanced transfer of thermal energy from fluidic heat source to thermoelectric materials.
In the presentation, fabrication technique of porous thermoelectric material will be presented as well as results from particle method simulations on the temperature distribution within the porous thermoelectric materials through which fluid as heat source flows.

Keywords: porous materials, specific surface area

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Fabrication of filled skutterudites with high thermoelectric performance using scanning laser melting method

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We developed a rapid scanning laser melting technique combined with subsequent spark plasma sintering to synthesize bulk n-type and p-type filled skutterudites. The kinetics process and microstructure evolution during the scanning laser melting and solid-reaction are systematically investigated. Due to the fast solidification in scanning laser melting, the peritectic segregation size of precusor reactants is confined within several microns, which leads to a great shorten of the fabrication period of filled skutterudites. The as-synthesized n-type and p-type filled skutterudites achieve very high dimensionless figure of merits, which are among the highest values of single filled skutterudites. The shortened processing period and the enhanced thermoelectric performance make this novel synthesis method suitable for industrial-level massive fabrication of skutterudite-based thermoelectric materials.

Keywords: filled skutterudites, scanning laser melting, thermoelectric properties

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Contact layer development on bismuth Telluride thermoelectric materials using novel light sintering technique

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Development of contact metal layer on Bi2Te3 based nanostructured materials using traditional methods such as electroplating, sputtering and evaporation has been challenging due to weak and inconsistent bonding strength and unstable contact interface between Bi2Te3 and contact metal. The poor contact layer is mainly due to severe damage of the top layer of the materials during surface preparation. Here, we report a novel and cost-effective way to prepare surface of thermoelectric materials (Bi2Te3) using light-sintering before going through electroplating of Nickel. The light sintering melts the top surface of the materials which not only enhances the electrical and thermal flow across the interface but also makes a consistent and stronger bonding between metal and thermoelectric materials. A contact resistance of around 5$\mu\Omega$-cm2 and pull strength of around 8MPa was consistently measured in both p-(Bi0.5Sb1.5Te3) and n-type (Bi2Te2.7Se3) compositions and electroplated Nickel layer. This novel technique of surface preparation for metallization can be used in all TE materials which eventually improves the performance of the TE modules.

Keywords: Thermoelectrics, contact resistance, bismuth tellurides, thermoelectric devices

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Near-net-shape fabrication of thermoelectric element by flash sintering

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The electric current assisted sintering (ECAS) is an effective method of microstructure refinement in sintered body because of its rapid densification of finely powdered material. In various kinds of functional material, its properties can be controlled by microstructure refinement in order to optimize its performance. Especially for a thermoelectric material, the reduction of thermal conductivity and the improvement of mechanical strength by the microstructure refinement can enhance utility for thermoelectric energy conversion devices. Recently, flash sintering (FS), which is categorized as ECAS of the order of seconds, is expected as an energy efficient sintering technique. In addition, from an application viewpoint, the high production rate of FS is expected to bring improved productivity to mass production of sintered parts. In this study, in order to enhance productivity of sintering process for thermoelectric element, the application of FS for thermoelectric materials was examined. Using the sintering apparatus specially designed for FS, the millimeter sized near-net-shape sintered Fe2VAl alloy was obtained by current feed within a second. The microstructure and transport properties of the sintered compact will be presented.

Keywords: Electric current assisted sintering, Flash sintering, Near net shape manufacturing, Finite element calculation

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Laser sintering of thermoelectric compounds

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Laser sintering has attracted great attention owing to the selective process being suitable for on-demand manufacturing. Here, we demonstrated the synthesis as well as sintering of thermoelectric compounds by using a continuous laser diode with a 940 nm light source. Owing to the high power density of the laser (60 W/mmˆ2 at the maximum), the precursor powders immediately melted and reacted when irradiated by the laser. Subsequent quenching led to the stabilization of high temperature phases in the compounds. As a result, thermoelectric compounds, including Bi-Sb and Mn-Si binary systems, Mn-Al-Si ternary system, rare-earth doped SrTiO3, has been synthesized, while nominal composition of Ca3Co4O9 resulted in multiphase of CaO and CoO due to the decomposition at high temperature. The variation in the thermopower caused by compositional differences agreed reasonably with reference data. As a feasible study of module fabrication, thick film (_˜40 um thickness) planer module of SnSe was sintered on quartz substrate. It was found that the fast scan rate during laser heating has desirable impact on the adhesion strength of the film. Finite element analysis of the laser heating revealed that the less heat leakage towards substrate in fast heating rate, resulting in homogeneous temperature distribution in the film. The trial test of power generation using SnSe (p-type) and Bi doped SnSe (n-type) resulted in reasonable output voltage with low power due to high resistivity of n-type legs. Phase decomposition during laser process was again found to be solved.
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Reference
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Keywords: laser sintering, module, chalcogenides, oxides, silicides

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Enhancing transport properties of Bi2Te3-xSex alloys via doping for thermoelectric power generation applications

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While trying to find new alternative energy resources new technological developments must be made to bring society one step closer to a cleaner environment. The rising awareness of the global warming effect as well as the steady decline in the quantity of current resources and subsequently the climb in their price drive the search for improving current energy usage and finding new energy resources. Thermoelectric devices take thermal heat, either directly from solar energy or as a byproduct of fuel burn, and transform it to electricity.
The performance of thermoelectric devices is assessed by the dimensionless figure of merit ZT of the material, defined as $ZT = \alpha 2 \sigma T/\mathrm{k}$, where α, σ, k and T are the Seebeck coefficient, the electrical and thermal conductivities, and the absolute temperature, respectively. The main difficulty in improvement of the efficiency of a thermoelectric device is due to the complex relation between σ, α and k.

Bismuth–telluride-based alloys are of great importance not only as the best thermoelectric materials with the maximal ZT values close to unity near room temperature, but also due to the potential for further performance improvement.
In this study Bi2Te3-xSex compositions were electronically optimized by various CHI3 doping levels, preferred alignment of the crystallographic orientation, and lattice thermal conductivity minimization. The synthesis route included rocking furnace melting, energetic ball milling and hot pressing under optimal conditions for enhancement of the thermoelectric figure of merit, ZT commonly applied in low temperature power generation applications. The transport properties in perpendicular to the pressing direction were examined.

Keywords: Bismuth, Telluride, Selenide, optimization

*Speaker

Advanced Protective Layers for Improved Chemical Stability in CoSb3, Mg2Si and Cu2X Based Thermoelectric Materials

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Despite the considerable success in recent years in thermoelectric materials development, their wide application in devices for energy conversion is still strongly limited by the problems related to chemical stability of these materials (resulting from *i.a.* corrosion processes undergoing during long-term heating at work temperatures of thermoelectric devices) and thus stability of their transport properties. The problems related to chemical stability of modern thermoelectric materials remain still - to a large extent - unsolved, making it the crucial obstacle on the way to their practical use and so an improvement of chemical stability of elements used in thermoelectric devices is currently one of the key issues which need to be solved in order to allow further development of thermoelectric energy conversion technology. In this context, the aim of our work was to develop new, effective amorphous protective layers for thermoelectric materials. The recent results of the application of such layers on the chemical stability of selected n and p-type doped Mg2Si, CoSb3 and Cu2X (X=S, Se) based thermoelectric materials are presented and analyzed in detail and the future advancements proposed.

Acknowledgments

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Keywords: amorphous protective layers, chemical stability, Mg2Si, CoSb3 and Cu2X thermoelectric materials

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Laser Additive Manufacturing with Bismuth Telluride and Magnesium Silicide

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Additive manufacturing offers the possibility of overcoming challenges such as limited geometries and material waste associated with traditional thermoelectric device manufacturing. In particular, laser additive manufacturing (also known as laser powder bed fusion or selective laser sintering/melting) has recently been applied to inorganic thermoelectric materials. This work describes our recent progress in laser processing of bismuth telluride and magnesium silicide. A custom-built laser processing setup enabled laser additive manufacturing of thermoelectric material powders in a layer-by-layer approach applied to loose powders – the same approach used in commercial additive manufacturing equipment. Three dimensional, bismuth telluride parts were built with relative densities _˜85-88%. The thermoelectric properties were characterized and compared to reference samples made via a traditional hot pressing technique, and X-ray diffraction results confirm the Bi2Te3 crystal structure is preserved during laser processing. Scanning electron microscopy confirmed complete through-thickness melting with no separation between fabrication layers although some micropores were present. The results indicate the rapid melting and re-solidification of the laser fabrication approach caused different effects of crystalline point defects compared to traditionally processed materials, causing a p- to n-type transition during annealing or characterization at elevated temperatures. Initial process-structure relationships for laser processing of magnesium silicide powders are also presented, and they constitute the first results of this additive manufacturing technique applied to Mg2Si, a lower cost thermoelectric material for mid- to high-temperature applications.

Keywords: additive manufacturing, bismuth telluride, magnesium silicide, laser processing

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Additive Printing and Photonic Sintering of High-Performance and Flexible Thermoelectric Materials and Devices Using Colloidal Nanocrystals

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The flexible thermoelectric generator (f-TEG) is a very promising technology for energy harvesting to enable self-powered wireless sensors and wearable devices, an area of exponential growth. Here, we present a scalable and cost-effective additive manufacturing process to fabricate f-TEGs using colloidal nanocrystals, and an innovative and highly efficient photonic sintering method to sinter large areas of printed films using pulsed light. Flexible TE films and devices were printed using screen printing and aerosol jet printing, followed by pulsed photonic sintering process. The pulsed sintering confines the delivered thermal energy within the printed film region without over heating the substrate, enabling TE film sintering on flexible polymer based substrates with relatively low melting point. In addition, the pulsed sintering limits grain size growth due to an ultrafast heating and cooling process, and lower thermal conductivity can be achieved than films sintered by conventional thermal processing. The p-type and n-type printed films demonstrate peak ZTs of 1 and 0.43 near room temperature along with superior flexibility, which is among the highest reported ZT values in flexible thermoelectric materials. A flexible thermoelectric device fabricated using the printed films produces a high power density above 19 mW/cm2 with 80 °C temperature difference between the hot side and cold side. The additive printing and photonic sintering can enable a highly scalable and low-cost roll-to-roll manufacturing process to transform high-efficiency colloidal nanocrystals into high-performance and flexible TEG devices for widespread applications.

Keywords: additive printing, Colloidal Nanocrystals, Flexible films

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On the Study of Electrospinning for Thermoelectric Devices

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Flexible thermoelectric generator (TEG) films which harvest energy from human body heat have attracted great focuses because it is a strong competitor to the battery for low power and wearable IoT devices. Different processes for flexible TEG are available, including thermal evaporation, dispenser printing, screen printing, inject printing, sputtering, and electrochemical deposition. Although the processes are different, each of the aforementioned technologies has its merits and drawbacks.
Nanowire thermoelectric modules for future flexible TEG were studied recently, and higher power were generated from the modules because stacking nanowire devices in series created larger temperature gradient. However, the expensive deposition process for nanowire is an obstacle for the new opportunity. Consequently, preparing thermoelectric nanowires through electrospinning is proposed. Electrospinning draws fibers due to electric force created by a very high voltage, and nanofibers with controlled diameter size are continuously produced. Electrospinning is a fast emerging technique and the process is simple, adaptable, cost-effective, and the materials are versatile. We have successfully electrospun our preliminary thermoelectric nanowires on a PET substrate. Our nanowires were generated under 11 KV, and fiber diameters are less than 1 micrometer.

After electrospinning process, we next extract properties of the samples through a self-developed measurement apparatus, which has been demonstrated to be a suitable tool for extracting Seebeck coefficients on flexible thin-film thermoelectric devices. With the new facility, simple, accurate, and direct measurement procedures are performed under stably controlled temperature gradient. In this study, about 100 micor-V per C of Seebeck coefficient was extracted from our current test samples.

Keywords: Electrospinning, Flexible TEG, New apparatus for Seebeck coefficient extraction

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Reliability Evaluation System for the Thermoelectric Power Generation Module Simulating Thermal Cycle

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To evaluate the reliability of thermoelectric generating modules it is essential to measure power and resistance changes under the temperature changing condition. For the practical durability test, the difference of temperature between the hot side and the cold side should be kept more than 500. Also, the hot side temperature should be controlled up and down and the cold side temperature should be stable during the thermal cycle test. Especially in case applying TEG to vehicles which the exhaust gas temperature is fluctuated rapidly from low to high temperature, the heating and cooling time to should be controlled and the hot side temperature reaches target point very quickly.

In this research, the thermoelectric module reliability evaluation system is introduced which simulate real temperature change condition. The Thermal cycle test profile was developed based on the exhaust gas temperature of passenger car under the real civil driving condition and the industrial generator natural gas engine gas temperature. The test profile temperature is adjustable, and the hot side can be heated up to 600 and cooled under 100 in 5 minutes with forced air cooling system while the cold side temperature can be maintained at 30 respectively. That can reduce the test cycle time for the high temperature operating TEGs so that researcher and company can estimate and guarantee module performance easily. The contact force is set up by the mechanical loader and during the test cycle, generated power and resistance are recorded and displayed continuously.

To verify the test system performance, thermal cycle tests based on the automobile exhaust gas temperature were performed with several TEG. The test result, the relationship between power output, resistance and thermal cycle time, shows the stability of temperature control system and the reliability evaluation system design adequacy.

Keywords: Reliability, thermoelectric power generation module, cycle time, power generation performance, exhaust gas

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Design of Thermal Contacts for High Performances Heusler-Based Thermoelectric Modules

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Most researches and developments presently dealing with thermoelectric materials and devices focus on high performances and/or low cost materials. However, for practical applications, thermoelectric modules based on these materials are needed. The main challenge in the design of thermoelectric modules is the development of efficient electrical and thermal contacts. Even though studies deal with electrical contacts [1], former work showed that thermal contacts present a stronger effect on the module performances [2], mostly in the base of commercial modules [3].
The present study deals with the design of thermal contacts for thermoelectric modules based on the low-cost Fe2VAl Heusler compound [4]. With low-cost thermoelectric materials, the cost of modules tends to be dominated by the ceramic insulators. Therefore, new low-cost substrates need to be developed. Innovative substrates for low and medium temperature modules have been investigated. Experimental results will be presented and unravelled by FEM simulations. Results show that the optimized thermal contacts significantly enhance the performances of the thermoelectric modules.

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Keywords: Thermoelectric Modules, thermal contacts, electrical contacts, Heusler

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Effect of electrical contact resistance on the performance of cascade thermoelectric coolers

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In this study the influence of electrical contact resistance on the performance of low-temperature cascade thermoelectric coolers (TECs) is analysed with emphasis on the resistance of commutating metal strips. Two key characteristics are under consideration: the maximum coefficient of performance (COP) at given temperature difference and the maximum obtainable cooling for the TECs with fixed configuration. The deterioration of these characteristics with increasing in the contact resistance is analysed for the TEC having from 2 to 6 stages that are optimized to achieving the temperature differences of 100-140 K with minimal power consumption. It is shown that the quality of electrical contacts is a crucial factor that greatly affects the performance of the cascade TECs. To keep the TEC efficacy at acceptable level, the contact resistance in the range from 10-7 to 10-6 ohm.cm should be provided whereas at greater resistance, a dramatic decrease in the TECs performance takes place, especially for the TECs with TE leg height of 0.5 mm and less. The irreversible losses caused by the connecting metal strips are analyzed and their thicknesses that should provide an acceptably low level of the contact resistance are determined for different TECs with typical TE leg dimensions and spacing.

Keywords: cascade thermoelectric coolers, performance, electrical contact resistance

*Speaker

Non-linear impedance spectroscopy: beyond the ZT estimation

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Thermoelectric characterization usually requires multiple measurements since the electrical conductivity (σ), the thermal conductivity () and the Seebeck coefficient (α) need to be measured. The use of multiple apparatus and the need of a precise temperature measurement increase the uncertainty in the evaluation of the figure of merit of the material ($zT = \alpha^2 T \sigma/$). Such measurements also do not provide any insight about the thermal coupling between thermoelectric system and thermal reservoirs that drastically modifies the performances of the system in real conditions [1].
Impedance spectroscopy consists of measuring the electrical impedance of the system as a function of the frequency. This measurement does not require any temperature measurement and can be used for a complete characterization of a thermoelectric material [2]. The difference between thermal and electrical time constants allows separating the electrical response from thermoelectric response.

This measurement is usually a small signal measurement, where only the linear response is considered. We extend the model of thermoelectric impedance spectroscopy to the non-linear response and give an experimental verification on a commercial Peltier module. Beyond the traditional response of small signals, the source of nonlinearities comes from the Joule effect. The presence of this non-linearity gives rise to second and third harmonic responses, which contain additional information beyond the evaluation of zT. The model also includes the thermal coupling with a thermostat, it follows that this measurement allows extracting many key parameters of the Peltier module including thermal coupling with the thermal reservoirs.

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Keywords: Impedance spectroscopy, thermoelectric measurement

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Detachable Contacts for Simultaneous Thermoelectric Characterization

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Determination of the thermoelectric (TE) figure of merit usually includes several measurements, more than one sample, specific sample preparations and, often, various sample geometries. We developed a Combined TE Measurement facility (CTEM) for the main TE materials' properties up to 600 ∘C – Seebeck coefficient, electrical and thermal conductivity and figure of merit using the Harman method – on one sample in one temperature sweep.
For high measurement accuracy, high quality soldered contacts between sample and sample holders are necessary. Besides low thermal and electrical contact resistances, the applied contact technique should allow for an easy dismounting of the sample from the holder after measurements for further use of the sample and sample holder.

This study presents results on tested contact systems for silicide and skutterudite TE materials. Several coating materials and techniques were tested on sample holders and TE samples as diffusion barriers or sacrificial layers. Low melting point solders based on Bi, In and Sn were used as bonds to allow suitable contacts and non-destructive detachment. For a selection of systems, electrical contact resistances were studied in dependence on temperature using an in house-built controlled heating station. Microstructure investigations show the contacting region before and after heat treatment, and reveal intermetallic reactions, interdiffusion zones and adhesion.
Promising contact solutions were found such as joints between Ni-coated Mo blocks and a FeSi2 sample bonded by BiIn solder (< 10% of the sample's resistance up to 600 ∘C) or uncoated Mo blocks bonded to CoSb3 using Bi-In-Sn solder (< 10% of the sample's resistance up to 450 ∘C). Investigations show a controlled influence of interdiffusion, good wetting behavior and suitable specific contact resistances.

Keywords: Contact development, barrier diffusion, interdiffusion layer, low melting solder, specific contact resistivity, characterization, wetting

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Thermoelectric performance of spark plasma-textured n-type polycrystalline SnSe

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Thermoelectric materials, which directly convert heat into electricity based on the TE effects, have long been investigated to use in semiconductor refrigeration or waste heat recovery. SnSe has attracted significant attention due to its high ZT in single crystals. The polycrystalline SnSe materials were then prepared to improve the mechanical performance for large-scaled application. However, the polycrystalline SnSe processes considerably low ZT due to their poor electrical properties. We aimed to improve the electrical and thermal transport properties of the n-type polycrystalline SnSe by doping and texturing. The effect of Br on the phase structure, electronic structure, microstructure and TE properties of SnSe was investigated. The spark plasma-textured structure boosts the electrical transport properties and the power factors as benefits of the layered microstructure. As a result, the ZT value is enhanced to be over 1.0, owing to the distinct improvement of electrical performance and maintenance of low lattice thermal conductivity. The present investigation indicates that the TE performance of the n-type SnSe compound can be markedly improved by the texture modulation.

Keywords: Thermoelectric, Polycrystalline SnSe, n type, Texture

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Ultra-high average figure of merit in synergistic band engineered Sn1-xNaxSe0.9S0.1 single crystals

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Thermal-electricity conversion is one of the most promising routes to harvest heat and convert it as easily storable and deliverable electric energy. Significant progress has been made since the discovery of Seebeck effect in 1821, particularly, the figure of merit zT approached a record high value of 2.6 in 2014. However, for thermoelectric devices, high average zT values (zTave) over the operating temperature range is more important as it is directly related to the conversion efficiency (g). Approaching highly stable and repeatable ultra-high zTave for Te-free materials has been historically challenging over the past century though exciting progress with zTave well above 1.10 was made recently. Here, through synergistic band engineering strategy for single crystalline SnSe, we report a series of record high zTave over a wide temperature range, approaching 1.60 in the range from 300 K to 923 K in Na-doped SnSe0.9S0.1 solid solution single crystals, with the maximum zT of 2.3 at 773 K. These ultra-high thermoelectric performance derive from the new multiple valence band extrema near the band edges in SnSe0.9S0.1 and the shift of Fermi level towards the multi-valley bands through Na doping which introduce additional carrier pockets to attend electrical transport. These effects result in an optimized ultrahigh power factor exceeding 4.0 mWm-1K-2 in Sn0.97Na0.03Se0.9S0.1 single crystals. Combined with the extremely lowered thermal conductivity attributed from the intrinsic anharmonicity and point defect phonon scattering, the series of ultra-high zTave and a record high calculated conversion efficiency of 21% over a wide temperature range are approached.

Keywords: Average zT, carrier pockets, band structure, lattice thermal conductivity

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Modification of bulk heterojunction and Cl doping for high thermoelectric performance SnSe2/SnSe nano-composites

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SnSe2 is a wide band gap semiconductor (Eg = 1.05 eV) with a typical two-dimensional hexagonal crystal structure of the prototype CdI2 phase, resulting in an intrinsically low thermal conductivity, which is favorable for thermoelectrics. Herein, we reported the remarkable role of Cl doping in SnSe2/SnSe nanocomposites. Doping with Cl in the system not only increased the carrier concentration by an order of magnitude but it also modified the heterojunction from that of the Schottky junction type (p-n junction) in undoped samples to junctions having an Ohmic contact (n-n junction) when the samples were doped with Cl, increasing their carrier mobility in the process. On account of the simultaneously boosted carrier concentration and carrier mobility upon Cl doping, the electrical conductivity and the power factor were greatly increased. Moreover, the enhanced point defect phonon scattering induced by Cl doping, coupled with the interface phonon scattering, resulted in a suppression of the thermal conductivity. As a consequence, the maximum ZT value of 0.56 at 773 K was achieved in the 6% Cl-doped SnSe2/SnSe nanocomposite measured in the direction parallel to the pressing direction. This is an almost 6 times larger value than measured on the undoped composite. In addition, unlike the conventional layered compounds (Bi2Te3, SnSe), the ZT value parallel to the pressing direction is much higher than the one measured perpendicular to the pressing direction. This study provides a new way for optimizing the thermoelectric properties of materials through interface regulation.

Keywords: SnSe2, SnSe nanoprecipitates, heterojunction, Cl doping, thermoelectric properties

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Structure and transport properties of nanostructured alloys of the novel thermoelectric material SnSe

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Single crystals of the orthorhombic semiconductor SnSe, was identified in 2014 as a mid-temperature thermoelectric material with record high figure of merit with high power factor and surprisingly low thermal conductivity. We have studied polycrystals of various alloys of SnSe prepared by arc-melting, a rapid synthesis that results in strongly nanostructured samples with low thermal conductivity – advantageous for thermoelectricity. The nanostructuring appears on various length scales: the sample consists of tens-of-nm thick crystalline platelets, and these in turn show structural inhomogeneities down to the _˜2nm scale. The thermal conductivity reaches the amorphous limit, with values around 0.3-0.5 W/mK. The Seebeck coefficient of some Ge-alloyed SnSe is record high, reaching 1000 μV/K. The electrical conductivity of pure SnSe and alloys with Ge, Sb, In or Pb is rather low, but alloying with transition metals such as Cu, Ag, Nb or Au provides a means to optimize the power factor.

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Keywords: SnSe, nanostructuring

Electrodeposition and thermoelectric characterizations of SnSe films

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Thermoelectric effect, which characterizes a reversible conversion of thermal differences to electric power, is more and more present in our daily life through various applications as Peltier micromodules including generators, coolers and sensors. If among thermoelectric materials, Bi2Te3 remains by far the most studied exhibiting a high figure of merit ZT at room temperature. However, the presence of the scarce element Te could be problematic for widespread deployment [1]. Therefore, SnSe could be a promising alternative as suggested by Zhao et al. [2]. SnSe is a narrow band gap binary IV–VI semiconductor, can also be used at room temperature with a promising power factor [3]. Focusing on an electrodeposition route, SnSe films were deposited at an optimized bath temperature using a dedicated chloride-based electrolyte. A preliminary study by CV on glassy carbon disk electrode was performed in order to understand the codeposition mechanism of SnSe. An operating potential window was defined, in which the electroplating of SnSe films was investigated. As a result, crystallized films according an orthorhombic structure (JCPDS card no. 14-0159) were obtained. EDX analysis showed an increase of Sn content in the films by increasing the value of the applied fixed cathodic potential. At -0.55V *Vs* Ag/AgCl, SnSe films exhibit an atomic composition of about 53% for Sn and 47% for Se, which is close to 1:1 stoichiometry. Finally, Seebeck coefficient and electrical properties of SnSe films were investigated exhibiting p-type behavior.

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Keywords: SnSe, film, electrodeposition

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Reassessment of thermoelectric potential of SnS

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Due to its environmental benignity and economic availability tin monosulfide, SnS, starts to be studied intensively as thermoelectric material with application potential in the medium-temperature domain [1]. Despite that studied since more than 60 years, the essential characteristics of pristine SnS are still not exhaustingly mapped. We have thus characterized concurrently the thermal, magnetic and electric properties of pristine SnS from cryogenic temperatures up to 750 K.
Furthermore, as the essential ingredient concerning the applicability of a thermoelectric material represents the stability of its thermoelectric properties, we reconsider the use of SnS with respect to its phase stability. In this respect, it is generally accepted that the p-type conductivity in SnS is the result of energetically favourable formation of tin vacancies. Considering such defects the comparative study of high temperature X-ray diffraction and electric resistivity performed up to 750 K either in static or dynamic inert atmosphere led to conclusion that already at temperatures above 500 K the tin, as formally "two valent" species, became unstable in the SnS structure. This fact may result, depending on sample morphology, surrounding atmosphere and concrete experimental conditions, in the formation of Sn2S3 phase. The detailed thermoelectric power data underpinning the electric transport measurements helped to understand both the phase relationships and doping mechanisms, respectively. We conclude that the stabilization of tin species in formally two - valent state represent one of the most important challenges considering the application potential of tin monochalcogenides.

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Keywords: phase stability, tin monosulfide, SnS

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Effect of resonant dopant In on the thermoelectric properties of Sn1.03Te

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The current research to replace the toxic, yet highly-efficient, PbTe for thermoelectric applications mainly focuses on SnTe compounds. In addition to being environment friendly, SnTe exhibits similar crystal structure and electronic band structure [1]. Amongst the many dopants used to enhance the thermoelectric properties of SnTe, In has been of great interest in recent years due to its ability to improve the thermopower of the system by creating resonant levels at the edge of the valence bands [2-4].

In this study, we present the synthesis as well as structural, chemical and physical characterizations of polycrystalline Sn1.03-xInxTe (x = 0, 0.0015, 0.0025, 0.0035). The transport properties were measured over a wide range of temperatures (300 – 800 K) in order to determine the concomitant role of excess Sn and In on the thermoelectric performances. The samples were synthesized by a conventional powder metallurgy route in sealed, evacuated glass silica tubes in a high temperature furnace. The resulting powders were then consolidated by spark plasma sintering to get bulk dense materials. Our results confirm the peculiar role of In on the thermopower with room-temperature values that are significantly higher than those measured in pristine Sn1.03Te. This beneficial influence of In results in a marked enhancement in the power factor which shows a fivefold increase for x = 0.0025 with respect to the x = 0 sample. At high temperatures, however, the impact of In is less pronounced leading to maximum ZT values of 0.6 at 800 K.

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Keywords: SnTe, Resonant level, Thermopower

Enhancement of Thermoelectric Performances in Topological Crystal Insulator Pb0.7Sn0.3Se via Weak Perturbation of the Topological State and Chemical Potential Tuning by Chlorine Doping

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Here we propose that a topological crystalline insulator (TCI) could exhibit a high thermoelectric performance by breaking its crystalline symmetry and tuning chemical potential by elemental doping. As a candidate material, we investigate thermoelectric properties of the Cl-doped topological crystalline insulator Pb0.7Sn0.3Se. The infrared absorption spectra reveal that the band gap is increased from 0.055 eV for Pb0.7Sn0.3Se to 0.075 eV for Pb0.7Sn0.3Se0.99Cl0.01, confirming that the Cl-doping can break the crystalline mirror symmetry of a topological crystalline insulator Pb0.7Sn0.3Se and thereby enlarges its bulk electronic band gap. The topological band inversion is confirmed by the extended X-ray absorption fine structure spectroscopy (EXAFS) showing that the TCI state is weakened in chlorine x = 0.05 doped compound. The small gap opening and partial linear band dispersion with massless and massive bands may have high power factor for high electrical conductivity with enhancement of Seebeck coefficient. As a result, the Pb0.7Sn0.3Se0.99Cl0.01 shows a considerably enhanced ZT of 0.64 at 823 K, which is about 1200 % enhancement in ZT compared to that of the undoped Pb0.7Sn0.3Se. This work demonstrates that the optimal n-type Cl-doping tunes the chemical potential together with breaking the state of topological crystalline insulator, suppresses a bipolar conduction at high temperatures, and thereby enables the Seebeck coefficient to keep increasing up to 823 K, resulting in a significantly enhanced power factor at high temperatures. We propose that breaking the crystalline mirror symmetry in topological crystalline insulators could be a new research direction for exploring high performance thermoelectric materials.

Keywords: Thermoelectric, Topological Crystal Insulator, Topological Semimetal, Chemical potential, Power factor.

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Self-compensating defects in AgSbTe2 from first principles studies

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AgSbTe2, which is an important component of high-performance thermoelectric materials such as TAGS (GeTe–AgSbTe2) or LAST (PbTe–AgSbTe2), tends to easily create VAg and SbAg defects. In this work, *ab initio* calculations for several structures with various compositions and ordering of these defects have been carried out. Relationship between the presence of particular defects in the system and its properties was analysed based on electronic structure changes. Calculated formation energies of VAg and SbAg indicated their preferable ordering in a system. Local impact of defects in a structure was described by means of Bader's approach to the topological analysis of the total electron density. AcknowledgementsThis research was financed by Polish Ministry of Science and Higher Education from the budget for science in the years 2015-2019, as a research project under the program "Diamond Grant" (grant no. DI2014 019144) and supported in part by PL-Grid Infrastructure.

Keywords: DFT calculations, chalcogenides, point defects, QTAiM analysis

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Quantum materials for thermoelectricity

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Research in thermoelectric (TE) quantum structures was greatly propelled by the prediction in the early 1990s of a signifi cant boost in TE efficiency by quantum size effects. Recently, research interest has shifted from quantum size effects in conventional semiconductors toward new types of quantum materials (e.g., topological insulators [TIs], Weyl and Dirac semimetals) characterized by their nontrivial electronic topology. Bi2Te3, Sb2Te3, and Bi2Se3, established TE materials, are also TIs exhibiting a bulk bandgap and highly conductive and robust gapless surface states. The signature of the nontrivial electronic band structure on the TE transport properties can be best verified in transport experiments using nanowires and thin films. However, even in nanograined bulk, the typical peculiarities in the transport properties of TIs can be seen. The signature of TI surface states on the thermoelectric properties of nanowire model systems will be discuss in depth and how these states can be modified by chemical modifications and in the vicinity of magnetic insulators. Finally, the remarkable transport properties of Dirac and Weyl semimetals like HfTe5 and NbP are discussed. We have measured the chiral magnetoresistance in the Weyl semimetal NbP and detected signatures of the mixed axial-gravitational anomaly in the transport experiment. This work has stimulated a scientific discussion about the application of theoretical models from High Energy Physics in the area of thermoelectric materials.

Keywords: Quantum Materials, Dirac Semimetal, Weyl Semimetal

*Speaker

Telluride based Thermoelectrics – from Glasses to Polycrystalline Materials

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The main paradigm in the present researches on thermoelectrics (TE) is focused on several approaches like phonon glass electron crystal model; concept of band structure engineering; and by achieving effective nanostructuring.
Recently it was found that 20% Cu-doping in arsenic telluride glasses increased σ by almost 5 orders of magnitude. Our results from X-ray Absorption Spectroscopy and multiple-scattering based theoretical model suggests there is a small charge-transfer from Te to Cu and σ is determined by the holes created in non-bonding Te 5p orbitals by Cu acceptors.

We replaced Ag in AgPb18SbTe20 (LAST) with more economically available Cu and compared their properties with different routes of synthesis. Irrespective of the synthesis route, σ and k of CuPb18SbTe20 were akin to that of LAST alloys. The Cu replaced samples with nanoscale dislocations and Cu-rich nanoprecipitates exhibits an ultra-low klatt, on par with that of LAST. Despite their comparable σ and k, the zT of Cu samples were low compared to LAST due to their contrasting thermopowers. DFT calculations attribute this variation in Seebeck to the dwindling of the energy gap between the valence and conduction bands when Cu replaces Ag in LAST.
GeTe based materials are of growing interest in the recent past due to their intriguing properties. Motivated by the resent results, where it was separately shown that the resonant levels induced by In and band convergence achieved by Sb leads to a reasonably high zT in GeTe, we tried to explore the effect of another Group IIIA element, Ga on the TE performance of GeTe and found that optimal doping of Ga improves the zT of GeTe, thanks to the resonant state created by Ga. With an aim to bring in synergistic band effects, we codoped Sb to the Ga-doped GeTe and successfully achieved the cumulative band effect, which ultimately increased the zT to 1.8 at 723 K.

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Keywords: Chalcogenide glasses, Cu replacement in LAST alloys, Synergistic band effects in GeTe

Effect of microstructure on the thermoelectric properties of bulk Ag16.7Sb30Te53.3 mosaic crystals.

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AgSbTe2 compounds with a rocksalt cubic crystal structure where Ag and Sb atoms are disordered, is a promising p-type semiconductor, suitable for thermoelectric power generation in the low-to mid-temperature range. In our study, we synthesized and characterized δ-phase Ag16.7Sb30Te53.3, bulk samples in the as-quenched state, which show a ZT of 0.5 at 300∘C [1]

The δ phase AgSbTe2 possesses low intrinsic lattice thermal conductivity , and we design the microstructure to achieve values as low as 0.5 Wm-1K-1. A laser flash analysis method was used to measure of the whole ingot, while the 3O-ω setup was taken to measure localy in well polished slices from the bulk. We will discuss the obtained results in particular regarding the differences obtained between the two methods.

Design of microstructures, such as introducing low angle grain boundaries [2], plays a big role to reduce , [2]. The as-quenched state of our material possesses a mosaic structure with abundant low angle grain boundaries (dislocation networks). Also, we observe many stacking faults. We analyzed the number densities of the different types of structural defects using electron channeling contrast imaging (ECCI) in the scanning electron microscope, and studied the atomic structure and chemistry of the defects using spherical aberration corrected scanning transmission electron microscopy. We observed a different chemical composition at the stacking faults compared to the bulk.

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Keywords: thermoelectric materials, silver–antimony–telluride compounds, thermal conductivity, electron microscopy

Extended Solubility Limit of ZnO on Binary Doping Leading to Anomalously Low Thermal Conductivity

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Zinc oxide has been one of the most promising n-type thermoelectric oxides with relatively large power factor competitive to major non-oxide candidates such as skutterudites and clathrate compounds. However, a quite high lattice thermal conductivity of ZnO has limit its ZT values below 0.7, despite a number of attempts to suppress the thermal conduction in the oxide. Very narrow solubility ranges of major n-type dopants such as Al and Ga in ZnO are the principal reason of the difficulties to reduce the thermal conductivity and to optimize the carrier concentration. In this paper, we report an extended solubility limit of ZnO on binary or parallel doping with equimolar amounts of Al and Cu.

The samples were prepared by conventional solid state reaction of reagent grade ZnO, CuO, and γ-alumina synthesized by hydrolysis of aluminum isopropoxide followed by calcination at 500 ∘C. The mixed raw oxide powders were pressed into pellets and fired at 1400 ∘C in nitrogen. The electrical conductivity and Seebeck coefficient were measured in air. The thermal conductivity was measured by laser flash technique in vacuum.

The ZnO samples doped with equimolar amounts (x at. % to Zn) of Al and Cu showed a significant peak shift in their XRD patterns, which has never been observed on single doping of Al or Ga. Moreover, the thermal conductivity of the samples at x = 8 was as low as 5 and 1.5 W/Km at room temperature and 800 ∘C, respectively. By comparing with the thermal conductivity of 40 and 8 W/Km for Al-doped ZnO at x = 2 at the corresponding temperatures, a drastic reduction of the thermal conductivity was obvious. It should also be noted that the value at 800 ∘C is very close to the theoretical lower limit of 1.2 W/Km for ZnO above room temperature.

Keywords: ZnO, thermal conductivity, solid solution, oxide thermoelectric material

*Speaker

Growth and characterization of thin film CaMnO3 and CaMn1-xNbxO3 for thermoelectrics.

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Oxides are promising as thermoelectric materials as they are a stable, cheap and environmentally friendly alternative to tellurides which are both rare, expensive and toxic. Thin films are interesting to study because of the possibility to characterize the effect of nano-structuring, e.g. grain size and multilayers. Additionally, thin films have potential applications where small dimensions are important, for example on chip cooling. In this study, CaMnO3 thin films have been grown by two step sputtering-annealing method. First rock salt structured Ca0.5Mn0.5O films were deposited by radio frequency (RF) reactive magnetron cosputtering from elemental targets of calcium (Ca) and manganese (Mn), followed by annealing at 700 ∘C for 3 h in oxygen flow to form the final phase of perovskite CaMnO3. For niobium (Nb) doping in CaMn1-xNbxO3 thin films cosputtering was performed from elemental targets of Nb, Ca, and Mn, with varying target power at Nb-target, while keeping constant power at Ca, and Mn-targets. The crystal structures of the films were assessed by X-ray diffraction
theta-2
theta, and pole figure analyses, and plan-view scanning electron microscopic studies. The grown films are confirmed to be textured and phase pure. Four point probe measurements at room temperature show a decrease in electrical resistivity from 2 cm for pure CaMnO3 film to 0.1 cm for CaMn1-xNbxO3 film. The decrease in resistivity is an effect from increased carrier concentration due to Nb-doping.

Keywords: CaMnO3, thin film, thermoelectrics

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Enhanced electronic conduction and phonon scattering in the Ga2O3(ZnO)m - In2O3(ZnO)m (m=9 and 15) solid solution by designing interfaces at the nanoscale level.

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The Ga2O3(ZnO)9 and In2O3(ZnO)9 homologous phases have attracted attention as thermoelectric (TE) oxides due to their layered structures. Ga2O3(ZnO)9 exhibits low thermal conductivity, while In2O3(ZnO)9 possesses higher electrical conductivity. The crystal structure and thermoelectric properties of the solid solution of Ga2O3(ZnO)9 - In2O3(ZnO)9 were studied to tune their TE performance.

We prepared high quality *(1-x)*Ga2O3(ZnO)m - xIn2O3(ZnO)m (x= 0.2, 0.4, 0.6, 0.8 and1.0 with m=9 and 15) ceramics by the solid-state route using B2O3 and Nd2O3 as additives. The crystal structures were analysed by XRD, HRTEM and atomic resolution STEM-HAADF-EDS. A layered structure with compositional modulations was observed in all samples in the ZnO-Ga2O3-In2O3 system. All the compositions exhibited nanoscale structural features identified as Ga- and In-rich inversion boundaries (IB's). Small In additions in the Ga2O3(ZnO)m compounds triggered basal and pyramidal In IB's typically found in the In2O3(ZnO)m system. The (Ga0.8In0.2)2O3(ZnO)m compounds do not exhibit the structural features of the *Cmcm* Ga2O3(ZnO)m compound, which is formed by a stacking of Ga rich IB's along the pyramidal plane of the wurtzite ZnO, but features resemble the crystal structure exhibited by the *R-3m* In2O3(ZnO)m with basal and pyramidal In IB's.

The structural changes led to improved thermoelectric performance. (Ga0.8In0.2)2O3(ZnO)9 showed low thermal conductivity of 2 W/mK and high-power factor of 150 μW/mK2 giving a ZT of 0.07 at 900 K.

The processing conditions of selected compositions were optimised to increase the ZT. Fast cooling rates increased the electrical conductivity without increasing the thermal conductivity due to improved microstructure and crystal structure. By combining the low thermal conductiv-

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ity of the Ga2O3(ZnO)9 and the high electrical conductivity of the In2O3(ZnO)m compounds led to a higher ZT in solid solution compounds.

Keywords: Oxides, homologous compounds, ZnO, thermoelectric

Transferable nanoporous Ca3Co4O9 thin films for flexible thermoelectric applications

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Nanoporous thin materials offer unique opportunity to independently tailor the electronic and phononic properties in the same material system leading to the high thermoelectric efficiency. The conventional methods for the growth of nanoporous films, being complex and time consuming, are not suitable for industrial upscaling. Here, we report a simple two-step sputtering-annealing method for the growth of nanoporous Ca3Co4O9 thin films. In this method, first the multilayered CaO/CoO films are sequentially deposited on mica substrates by rf-magnetron reactive sputtering from elemental Ca and Co targets, followed by annealing at 700 ∘C to form the final phase of Ca3Co4O9. The formation of nanopores in the postannealed films is the consequence of volume contraction during thermally induced phase transformation from as-deposited CaO/CoO film to the final film of Ca3Co4O9. Shape and size of the nanopores in the films are tunable by tuning the layer thickness in as-deposited CaO/CoO films. Despite high porosity the lowest electrical resistivity is obtained as _˜ 7 mOhm.cm, yielding a power factor of 0.23 mWm-1K-2 near room temperature, which is comparable to the undoped Ca3Co4O9 thin films without porosity. That is, electronic transport does not get affected by the nanoporous structure of the films. However, thermal conductivity is expected to be drastically reduced due to the enhanced scattering of phonons by the nanopores. Due to the weak adhesion of the films with the mica substrate via nanopillars, the films are easy transferable to arbitrary polymer platforms by simple dry transfer, and thus opening a new opportunity for transferable thermoelectrics.

Keywords: Thin film, nanoporous, transferable, Ca3Co4O9

*Speaker

Synthesis, sintering and thermoelectric properties of Sr1-xLaxCoO3 cubic perovskite ceramics

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La0.95Sr0.05CoO3 ceramics present the highest p-type thermoelectric properties at room temperature for oxide compounds [1]. According to Koshibae et al. [2], the SrCoO3 cubic perovskite counterpart should present high n-type properties. However, when synthesized by solid state reaction in air, stoichiometric composition does not lead to the formation of cubic perovskite structure but to hexagonal perovskite structure. Hancock & Slater [3] have recently shown that it is possible to stabilize the cubic perovskite structure by substituting 3 % of cobalt by silicon.
In this work, we have studied the lowest silicon amount required to stabilize the cubic perovskite structure. The Sr1-xLaxCoO3 samples ($0 < x < 1$) substituted with silicon have been sintered by conventional sintering. Several heat treatments with intermediate grindings are necessary to reach pure and dense ceramics. Evolution of the electrical conductivity and Seebeck coefficient has been studied from 330 to 1000 K.

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Keywords: thermoelectrics, n type, perovskite

*Speaker

Self-assembled oxide 2D nanocomposite with enhanced thermoelectric power factor and reduced thermal conductivity

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Sol-gel process was used to produce heavily doped misfit-layered cobaltate Ca3Co4O9 [1], which by subsequent heat treatment in suitable atmosphere self-assembled into 2D nanocomposite as confirmed by high-resolution transmission electron microscopy (HRTEM) [2,3]. Nanocomposite was preserved in sintered ceramic, which showed enhanced thermoelectric properties parallel to the cold-pressing direction as applied to the green body. This went along with the preferential alignment of multiphase misfit-layered oxide platelets as confirmed by scanning electron microscopy (SEM). The power factor was enhanced by increases in both the isothermal electrical conductivity and the Seebeck coefficient. In addition, the thermal conductivity was diminished by nanostructuring. All in all, the thermoelectric figure-of-merit was almost doubled compared to the starting compound and reached a value of 0.78 at 1073 K, which is among the highest observed for oxides so far.

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Keywords: Ca3Co4O9, oxide, doping, selfassembly, nanostructure, 2, dimensional, electrical conductivity, Seeebeck coefficient, power factor, figure of merit

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The Seebeck coefficient in some Ru oxides

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Different parameters can tune the value of the Seebeck coefficient, such as doping, spins and magnetism, coupling with the lattice and electronic correlations. The case of oxides is interesting as, depending on the crystallographic structure and on the nature of the transition metal, these different parameters can be strongly modified [1]. Here, we will show several examples of ruthenium oxides such as hollandites and magnetoplumbites, to highlight the diversity of these behaviors. The Seebeck coefficient in these ruthenates, presenting different electronic and magnetic backgrounds –antiferromagnetism, ferro- or ferri-magnetism– is investigated. In particular the coexistence of metallic carriers together with localized moments is focused on, and also the relative role played by transport and entropy [2]. Depending on the crystallographic structure, we will show that the transport of these metallic oxides can evolve from a simple Boltzmann transport model, to more complex behaviors developed for strong correlations, and with a large spin entropy term [3].

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Keywords: Seebeck, ruthenates, transport, spin entropy

*Speaker

Low-pressure chemical vapour deposition (LPCVD) synthesis of metal-chalcogenide materials for thermoelectric micro-generator applications

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Bi2Te3 is the archetypal thermoelectric material for near room temperature applications[1], with thin films of *Bi*2Te3 of particular interest from both enhanced device performance[2] and materials efficiency standpoints. We are investigating the impacts of various deposition experiment parameters on the quality, electrical properties and thermoelectric performance of *M*2E3 thin film materials. Our simple apparatus allows preliminary evaluation of experimental variables, including for instance; precursor volatilisation temperature, material deposition temperature, rate of delivery of precursor to the substrate, and deposition experiment time.
Materials of the type *M*2E3 *(M = Sb, Bi; E = Se, Te)* may be preferentially deposited onto specific regions of template-patterned substrates utilising low-pressure chemical vapour deposition techniques employing appropriate molecular precursors and deposition conditions[3]. We have studied flat thin film depositions in order to optimise conditions for materials growth; findings from these investigations have been applied to materials deposition onto template-patterned array substrates.

We present selected highlights of our flat thin film deposition studies and substrate-selectivity investigations.

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Keywords: Chalcogenide materials, chemical vapour deposition, LPCVD, materials synthesis, region specific selective deposition, thermoelectric microgenerator, thin films

Development of a ZT-Measurement system for thin films plus additional Hall constant determination in a temperature range from LN2 up to 300◦C

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Due to new research efforts in the field of thermoelectrics 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.
We report on the development of a new system to simultaneous measure electrical and thermal conductivity, Seebeck coefficient and Hall constant of thin films in the temperature range from LN2 up to 300◦C. Due to the nearly simultaneous measurement at only one sample, errors caused by different sample compositions, thicknesses and heat profiles can be avoided.

The system consists of a structured Si-wafer and a suitable measurement setup. To measure the el. conductivity and the Hall constant, the wafer owns a four-electrode-structure to use the Van-der-Pauw method. For the Seebeck measurement an additional temperature gradient can be applied on a membrane setup. The thermal conductivity can be measured in plane using the Völklein Method, doing a steady state or transient measurement. To get a correct result, the measurement has to be done under vacuum in a thermal stabilized and controlled chamber.

In order to meet these requirements a suitable vacuum chamber with sample holder has been designed. The sample holder can be cooled with liquid nitrogen and heated by Joule heating. To measure the Hall constant, the chamber is put between two spools of an electromagnet to apply a variable magnetic field with a maximum of ± 1 T.
As proof of concept, a showcase study of Bi87Sb13 thin films has been performed and compared to previously published data as well as results for metallic and organic samples.

Keywords: thermal conductivity, electrical conductivity, Seebeck coefficient, Hall constant, measurement instrument

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Transport measurements of bismuth nanowire embedded in quartz template by nano-fabrication

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We have developed single crystal bismuth nanowire embedded in quartz template. Recently, nano-fabrication technique has been introduced to fabricate local electrodes on the surface of the nanowire. The resistivity in the magnetic field and Hall measurements have already performed using 700 nm-diameter nanowire, and the temperature dependence of the mobility were analyzed [1-3]. Due to its long mean free path compared to its diameter, it obviously observed the mobility in lower temperature region was saturated because the collisions at the surface boundary were dominant. As a next step, we have developed the measurement of the Seebeck coefficient, which is key parameter to obtain semi-metal to semiconductor transition using narrower wire diameter; however, the measurement is very difficult task because the much narrower wire with a few milli-meter length brings much larger internal impedance, typically several M-Ohm, for measuring several-ten micro-V. Therefore, the nano-fabrication on the surface of the nanowire makes it possible to choose suitable impedance by selecting proper combination of the electrodes. We are presenting the overview of recent research results of our bismuth nanowire and measurement results not only the resistivity and Hall coefficient but also Seebeck coefficient to realize the transport phenomenon. Especially, techniques for the Seebeck coefficient measurement are developed and we discuss a plan to recognize the bismuth nanowire introduced quantum effect, bringing giant Seebeck coefficient, as near future work.

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M. Murata, A. Yamamoto, Y. Hasegawa, T. Komine, *Journal of Applied Physics*, 121, 014303 (2017).

M. Otsuka, R. Homma, Y. Hasegawa, *Journal of Electronic Materials*, Vol. 46, 2976 (2017)

Keywords: bismuth nanowire, nano, fabrication, transport measurements

*Speaker

Scalable, large-area and adaptable thermoelectric nanomaterials with high energy conversion efficiencies

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High cost materials and complex production techniques restrict the use of the conventional thermoelectric (TE) generators. Providing a low-cost TE device with a respectable performance is even more important than providing a very high-performance TE device which would cost an unexpected price.
We have established a versatile, cost-effective, reproducible and scalable synthesis route for the fabrication of thermoelectric materials based on nanostructured fibres. The architecture developed is self-supported and can easily be moulded to any shape.
As a proof of concept, we have developed p-silicon thermoelectric fibres with a figure of merit of 0.34 at T=823K and power densities of some tens of milliwatts per square centimetre when it is at 1000 k. The extension to other materials is also possible and will be shown.

Keywords: nanostructuration, cost, efficient, scalable, thermoelectric

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High-Performance Thermoelectric Properties of Multiwall Carbon Nanotubes Through Chemical Treatments

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Carbon nanotubes (CNTs) are being used for several years for a wide range of applications such as for biosensors, field-effect transistors and solar cells, also having an enormous potential in the field of Energy Harvesting (EH). Among several areas of EH, CNTs emerged as promising nanomaterials for thermoelectric (TE) applications due to their unique properties such as lightness, large charge carrier densities, mechanical, electrical and thermal properties at room temperature. Moreover, they are striking due to their high specific energy[1]. Several strategies are being developed to enhance their TE properties namely through their doping with heteroatoms or by inducing defects. Although an intense study is being pursued on CTNs, a major part of the focus has been devoted to single-walled carbon nanotubes. However, in commercial terms, these are much more difficult to produce, which substantially increases their cost. In this context, the ability to tune the TE properties of multi-walled CNTs (MWCTNs) emerged as an alternative solution, being this the main subject of the present work.
In this work, the TE properties of MWCTNs submitted to different oxidative treatments in liquid and gas phase, functionalizations or doping with heteroatoms will be presented. Our achievement unveils a substantial increase of the Seebeck effect from 4 uV/K (untreated MWCNTs) until up to 12.5uV/K (MWCNT treated with HNO3 and functionalized with urea). Concerning the power factor, an enhancement from 0.2uW m-1 K-1 (untreated MWCNTs) to up to 13 uW m-1 K-1 (MWCNTs functionalized with sulfonic groups). Moreover, depending on the type of functional groups we were able to change the electrical behavior from p-type to n-type. Finally, a micro-thermoelectric device based on MWCNTs will be presented using photolithography.
J. L. Blackburn et al. Adv. Mater. 2018, 1704386

Keywords: Multiwalled Carbon Nanotubes, Functionalization, Chemical Treatment, Seebeck, Photolitography

*Speaker

Integrated Silicon/Silicon Germanium Nanowires Thermo-Electric Generators

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The nanostructuring of thermoelectric materials is a promising approach for enhancing thermoelectric properties of existing abundant and inexpensive materials such as silicon and silicon-based compounds. Moreover, the compatibility of silicon compounds with mainstream technologies, such as microelectronics and micro- and nano-fabrication, has attracted the attention to the integration of some of these nanostructures in micro-Thermoelectric Generators for harvesting and thermal sensing applications.
In this work we have used a bottom-up approach to fabricate epitaxial Si, SiGe nanowires with controlled properties (diameter, length, doping level and alloy composition) fully integrated in silicon microdevices, i.e. monolithically grown with low contact resistances. The measurement of the thermoelectric figures of these nanostructures has been performed.
Different thermoelectric characterization of silicon micromachined structures were used for the assessment of the thermal and electrical properties of the integrated suspended single nanowires and arrays. As a result, it was possible to determine ZT from room temperature up to 350∘C. The epitaxial nature of the growth allows overcoming the possible artefacts coming from contact resistances. The results arisen from this study demonstrate the feasibility of a practical implementation of this technology in integrated thermoelectric power generators.

Keywords: Nanowires, Silicon, Silicon, Germanium, Thermoelectric micro, generator

*Speaker

Simulation, fabrication and measurements of thermoelectric transport properties of crystalline sub-micron silicon beams

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As it was already shown by different research groups thermoelectric properties are correlated not only to the dimensions, but also to the surface texture, e.g. for silicon nanowires or silicon nanoribbons. The micro platforms, we will show are developed and modified, based on the state of the art devices. They are fabricated in the same process with integrated individual beams from differently doped wafers. By dry etching and subsequent time controlled wet etching silicon beams are tailored, so it becomes possible to analyze the change of the thermoelectric properties continuously from bulk – to sub-micron-size. Measurement to determine electrical conductivity, thermal conductivity and Seebeck coefficient can be implemented. The measurement platform provides the opportunity to determine the electrical and thermal contact resistances and take them into account when evaluating the measurement results. In any case, the monolithic contacts between bulk silicon and the silicon beams to be analyzed are considered to be the best approach. Simultaneous fabrication of many devices on one wafer helps to achieve the required homogeneity of the layers and junctions. Also, as an important point, a high number of devices allows a good statistical evaluation of the results and the indication of the measurement related accuracies. We will present the simulations and fabrication of micro-sized platforms using SOI and bulk Silicon wafer to analyze the thermoelectric transport properties of top-down etched crystalline silicon beams. Additionally, first measurements will be shown.

Keywords: Thermoelectric, crystalline silicon, surface texture

*Speaker

Thin film Tin Selenide (SnSe) Thermoelectric Generators Exhibiting Ultra-Low Thermal Conductivity

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Tin selenide (SnSe) has attracted much attention in the field of thermoelectrics since the discovery of the record figure of merit (ZT) of 2.6 ± 0.3 along the *b*-axis of the material. The record ZT is attributed to an ultralow thermal conductivity that arises from anharmonicity in bonding. Whilst it is known that nanostructuring offers the prospect of enhanced thermoelectric performance, there has been minimal studies in the literature to date of the thermoelectric performance of thin films of SnSe. In this work, preferentially orientated porous networks of thin film SnSe nanosheets were fabricated using a simple thermal evaporation method, which exhibited an unprecedently low thermal conductivity of 0.08 W m-1 K-1 between 375 K and 450 K. In addition, the first known example of a working SnSe thermoelectric generator is presented and characterized.

Keywords: tin selenide, thermal conductivity, thin film, nanosheets, thermoelectric generator

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A Critical Assessment of the Impact of Excess Ni on the Thermoelectric Properties of ZrNiSn

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half-Heusler (HH) based materials have long been considered as promising thermoelectric materials for high-temperature waste heat recovery.These narrow band gap semiconductors with 18-valence electrons tend to have large power factors (S2/ρ).Their figures of merit (ZT), are limited by relatively large thermal conductivity ().Reductions in while retaining S2/ρ have been reported for TiNi1+ySn and were attributed to the occupancy of vacant tetrahedral sites, acting as phonon scattering centres [1]. Among HH alloys, pristine ZrNiSn itself exhibits alloy scattering dominated charge transport due to the presence of intrinsic interstitial Ni [2]. This raises the prospect of decreasing by excess Niatoms in ZrNiSn.
Here, we revisit the impact of excess Ni on S2/ρ and , along with Sb substitution to adjust the carrier concentration to optimize the thermoelectric properties of the ZrNi1+ySn1-zSbz HHs. Samples were prepared via solid-state reactions and characterized using neutron powder diffraction, transmission electron microscopy. In agreement with the literature, Sn/Sb substitution resulted in a semiconducting to metal-like transition with ρ is reduced by 2-orders of magnitude and S is only by a factor of two. This resulted in S2/ρ =5 mWm-1K-2 at 700 K. The introduction of excess Ni resulted in reduced S2/ρ =3 mWm-1K-2 at 700 K in compositions co-doped with Sb, caused by a reduction in carrier mobility. In terms of thermal transport, lat is decreased by 20% with excess Ni and does not compensate for the lower S2/ρ; results in a *ca.*50% reduction in ZT.The reduced ZT values contrast with TiNiSn, where improvements are generally observed. A comparison of the different impact of excess Ni in TiNiSn and ZrNiSn will be presented.

H. Hazama et al., J. Appl. Phys., 110, 063710 (2011); R.A. Downie et al., Chem. Commun., 49, 4184 (2013)
H. Xie et al., Sci. Reports, 4, 6888 (2014)

Keywords: half, Heusler, Thermoelectric, phonon scattering, ZrNiSn

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Half-Heusler Thermoelectrics: Stable or Unstable?

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Half-Heusler (HH) compounds with 18-valence electrons are narrow band gap semiconductors with a high effective mass and a large Seebeck coefficient. For this reason, HH compounds have attracted considerable attention as promising candidate materials for moderate and high temperature thermoelectric power generation applications. MNiSn (M = Ti, Zr, of Hf) compounds are among the best n-type half-Heusler thermoelectrics and the high ZT of 1.5 has been reported by several groups [1, 2]. One of the many advantages of MNiSn is its so-called good thermal stability at high temperature. However, utilizing X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) combined with thermal analysis, our studies show that the MNiSn compounds are not stable in the application temperature range. Results from repeated heating and cooling measurements of thermoelectric transport properties show partly irreversible changes in the local structure and composition. These data will enhance the knowledge on the high temperature dynamics for a regenerative device design of MNiSn half-Heusler thermoelectric converters.

S. Sakurada, N. Shutoh, Appl. Phys. Lett., 86 (2005) 2105.

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Keywords: half, Heusler, thermal stability

*Speaker

Efficient waste heat recovery in metal-rich TiNiCuySn half-Heusler alloys

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Half-Heusler alloys are promising thermoelectric materials which are limited by their large lattice thermal conductivity (lat). Several approaches have been used to reduce lat, including the introduction of excess Ni metal into the half-Heusler matrix [1]. It is also possible to use the excess metals to manipulate the electronic properties and we recently demonstrated that excess Co and Cu act as p- and n-type dopants in TiNiSn [2].
Here, we report on hot-pressed Cu-rich TiNiCuySn half-Heusler alloys ($0 \leq y \leq 0.25$) [3]. Detailed X-ray and neutron powder diffraction and transmission electron microscopy studies demonstrate that the materials are composed of metal-rich half-Heusler grains containing interstitials and segregated full-Heusler grains. This contrasts with other literature where nanoscale full-Heusler inclusions have been reported. Hot pressing results in a partial segregation of the excess Cu at the grain boundaries. This structural arrangement results in substantial reductions of lat. The reduction of lat is accompanied by an increase in $S2/\rho$ due to the efficient n-type doping caused by the additional 4s1 electron of Cu. This results in a much-improved thermoelectric performance with a ZTdevice = 0.4 and estimated power densities 6-7 W cm-2 in the 323-723 K temperature range.

In this contribution, we will discuss the link between the structure and thermoelectric properties of the TiNiCuySn half-Heusler alloys.

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S.A. Barczak et al., *ACS Applied Materials and Interfaces*, 10, (2018), 4786-4793.

Keywords: half, Heusler, TiNiSn

*Speaker

Low Temperature Magnetotransport Anomalies in Fe-Doped (Ti, Hf, Zr)NiSn Alloys

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Mixed refractory half-Heusler alloys, (Ti, Hf, Zr)NiSn, have been the focus of much thermoelectrics research for their promise in high temperature power generation [1]. Introducing magnetic elements or compounds, such as Fe, Mn, and BaFe12O19 [2], into the matrix or as a nanocomposite has been proposed, and in some cases, proven, to create temperature-dependent charge carrier traps. Tailoring the temperature dependence and strength of the magnetic interaction to the host material can help optimize the overall thermoelectric properties. In this work, we choose the simplest magnetic dopant, Fe, and add it to a phase-separated (Ti, Hf, Zr)NiSn system. Low temperature electrical resistivity in the Fe-doped samples below 10 K exhibits signatures of critical scattering characteristic of spin-fluctuation systems. Corresponding magnetoresistance measurements show decreased resistance with small applied fields at temperatures below 10 K and positive magnetoresistance above, as well as field-induced magnetic transitions near 2 K. Comparison of low temperature heat capacity data between the pure and Fe-doped samples allows for the separation of phonon and magnetic contributions, yielding insight into the short- and long-range magnetic ordering in Fe-doped (Ti, Hf, Zr)NiSn as a function of temperature and Fe concentration. The study physically details the correlation between magnetic and thermoelectric properties in a promising class of thermoelectric materials.

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Keywords: half, Heuslers, magnetotransport, low temperature, Fe, doped

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The decreases of the lattice thermal conductivity of the FeV0.955-xHf0.045TixSb half-Heusler phases

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The FeVSb HH-phase was studied as a new thermoelectric material. By using calculations, we found that the FeVSb HH-phase is capable of possessing a large ZT exceeding 0.80 as p-type at 700 K. To confirm this prediction, prepared FeV(1-x)TixSb HH-phases were found to possess almost the same ZT value as that predicted; $ZT = 0.63$ for FeV0.80Ti0.20Sb at 700 K. Besides, the partial element substitutions, such as (Ti, Nb) for V, were reported to be an efficient way to drastically reduce the lattice thermal conductivity. Otherwise, we realized that the influence of heavy element partial substitution such as Hf, Ta or W for V wasn't investigated yet. In this study, therefore, we fabricated HH-phases at the compositions of FeV(0.955-x)Hf0.045TixSb ($0 < x < 0.075$) to obtain a higher ZT value by decreasing the lattice thermal conductivity.
All the prepared samples contained the HH-phase as the dominant phase. We found that all the FeV(0.955-x)Hf0.045TixSb HH-phases showed a p-type behavior at $x > 0$ together with a moderately large Seebeck coefficient values of at least of 200 μV/ K at 600 K. However, the Seebeck coefficient was inhibited by bipolar effects at higher temperature and started to decrease at $T > 600$ K. In addition to that the FeV(0.955-x)Hf0.045TixSb HH-phases showed a low electrical resistivity value below 5 mΩ cm at overall temperature. The lattice thermal conductivity of samples monotonically decreased with increasing Ti concentration at $0.025 < x < 0.075$. The FeV0.88Hf0.045Ti0.075Sb ($x = 0.075$) HH-phase showed the minimal value of the lattice thermal conductivity of 2.1 W / m K at 700 K, that is less than a half of the value of 3.78 W / m K for the original FeVSb HH-phase.
As a result, we succeeded in effectively decreasing the lattice thermal conductivity of FeV(0.955-x)Hf0.045TixSb HH-phases. Unfortunately, bipolar effects degraded the Seebeck coefficient, that limited the magnitude of ZT to 0.55 at 700 K for FeV0.88Hf0.045Ti0.075Sb ($x = 0.75$).

Keywords: Lattice thermal conductivity, half Heusler phase

*Speaker

Unique role of refractory Ta alloying in enhancing the figure of merit of NbFeSb thermoelectric materials

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NbFeSb based half-Heusler alloys have been recently identified as promising high temperature thermoelectric materials with a figure of merit zT> 1, but their thermal conductivity is still relatively high. Alloying Ta at Nb site would be highly desirable because the large mass fluctuation between them could effectively scatter phonons and reduce the lattice thermal conductivity. However, practically it is a great challenge due to the high melting point of refractory Ta. Here we report on the successful synthesis of Ta alloyed (Nb1-xTax)0.8Ti0.2FeSb (x = 0-0.4) solid solutions with significantly reduced thermal conductivity by levitation melting. Because of the similar atomic sizes and chemistry of Nb and Ta, the solid solutions exhibit almost unaltered electrical properties. As a result, an overall zT enhancement from 300 K to 1200 K is realized in the single phase Ta alloyed solid solutions, and the compounds with x =0.36 and 0.4 reach a maximum zT of 1.6 at 1200K. This work also highlights that the isoelectronic substitution by atoms with similar size and chemical nature but large mass difference should reduce the lattice thermal conductivity but maintain good electrical properties in thermoelectric materials, which can be a guide for optimizing the figure of merit by alloying.

Keywords: thermoelectric materials, half, Heusler compound, solid solutions, thermal conductivity

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Ultra-fast fabrication of bulk ZrNiSn thermoelectric material through self-propagating high-temperature synthesis combined with in-situ quick pressing

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ZrNiSn, a member of the half-Heusler thermoelectric materials, shows great potential for mid-to-high-temperature power generation applications due to its excellent thermoelectric properties, robust mechanical properties, and good thermal stability. The conventional way to fabricate ZrNiSn bulk material usually adopts energy-intensive processes like arc-melting and long-time annealing. In this study, an efficient and ultra-fast method combined self-propagating high-temperature synthesis with in-situ quick pressing (SHS-QP) has been applied to the fabrication of ZrNiSn. In this method, a mixture of the constituent single elemental powders is loaded inside a stainless-steel mold, and the SHS process is then ignited by electric-arc. A quick and large mechanical force is applied to the mold immediately after SHS when the sample is still red-hot and soft. As a result, single-phase and full-dense bulk ZrNiSn can be obtained successfully in just one step, which greatly cuts down the synthesis period from days to minutes. The process parameters, such as time span between SHS and QP, pressure, have been analyzed and optimized to obtain ZrNiSn bulk samples with the relative density over 97%. The prepared sample comprises of rich nanostructures due to the large temperature gradient during the SHS-QP process, which lead to the observed reduction in the thermal conductivity. The obtained ZrNiSn exhibits a maximum thermoelectric figure of merit ZT of 0.65 at 900 K, which is comparable to those prepared by conventional methods. This study opens a new avenue for the ultra-fast and low-cost fabrication of half-Heusler thermoelectric materials.

Keywords: half Heusler, ZrNiSn, SHS, QP, thermoelectric

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Towards the Fabrication of Flexible and Efficient Organic Thermoelectric Generators by Inkjet Printing Technique

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Nowadays, commercial micro-thermoelectric generators based on thin film of Bi2Te3 demonstrate already the reliability of thermoelectric technology.[1] However, the requirement of sustainability and large-scale production made organic thermoelectric generators (OTEG) gaining high attention within the thermoelectric community as based for novel class of modules. In fact, OTEGs not only represent the alternative to the present metal-compound thermoelectric devices, but also fulfil prerequisites that the present technology does not satisfy, allowing the fabrication of flexible and lightweight modules implementable where adaptability to curved and irregular surfaces, and to surfaces changing in motion is needed. Moreover, flexibility results in easier adaptability of the devices, and therefore lower integration costs.
The overarching target of this project is the fabrication of thin-film OTEGs based on conjugated polymers by inkjet printing method. This manufacturing technique is suitable for low-cost and large-area fabrication of flexible organic devices.[2] Here, the studies towards screening and assessment of efficient and air-stable p- and n-type thermoelectric organic materials, and first OTEGs proof-of-concepts are presented. Both materials and devices are tested in homemade custom setups for the thermoelectric measurements.[3,4] The most efficient thermoelectric materials were then developed as ink for the printing technique, forming the legs of the thermoelectric generators during the fabrication process.

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Keywords: Organic, Polymer, Flexible, Module, Generator, Inkjet, Print

*Speaker

Enhanced Thermoelectric Properties of PEDOT/Te Quantum Dot Composite Films

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Conventional in-situ syntheses of PEDOT-based nanocomposite materials suffer major problems in inhomogeneous particle distribution, particle oxidation and ineffective loading that limit their application. New technologies are demanded in order to produce composite materials with a higher inorganic loading effectiveness that requires more uniform particle distribution, tunable particle sizes as well as better particle protection against oxidation. In this work, we developed a facile one-step synthesis to fabricate high quality small-sized anions codoped poly(3,4-ethylenedioxythiophene): dodecylbenzenesulfonate/Cl-tellurium (PEDOT:DBSA/Cl-Te) nanocomposite films using a series of novel Te (IV) based oxidants. The synchronized production of PEDOT and Te results in thick and homogeneous PEDOT-Te films containing Te quantum dots as small as $<$ 5 nm which are evenly distributed and well-protected in the polymer matrix. Owing to the Cl-/DBSA- heavily codoped crystalline PEDOT matrix as well as the nanoscale Te particle loading, at even low Te concentrations as 2.1 - 5.8 wt%, the composite films exhibits high power factors _˜ 100 μW/mK2, which is 50% higher compared to a pure DBSA doped PEDOT film.

Keywords: PEDOT/Te Quantum Dot Composite

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Energy filtering effect of PEDOT:PSS/Bi2Te3 nanowire composites

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Thermoelectric (TE) materials, which exhibit a capability to convert heat to electricity vice versa, can be used to develop power generation and cooling refrigeration without any moving parts. It is well known that the TE efficiency can be defined as the dimensionless figure of merit $zT = \sigma S\hat{}2T/k$, where S is the Seebeck coefficient, s is the electrical conductivity, k is the thermal conductivity, and T is absolute temperature. However, there has been a critical issue for TE efficiency arising from conflicting relationship of TE factors such as σ, S, and k. The energy filtering effect is a key component for solving conflicting relationship of TE factors due to enhancing the S without significant reduction of σ. The potential barrier formed at an interface between two materials scatters low energy carriers and allows to pass high energy carriers only. It leads to increase average heat transported per carrier by the high energy carriers and result in high S. These phenomena at an interface lead us to the high P value based on TE composites. We propose PEDOT:PSS/Bi2Te3 nanowire TE composite for introducing energy filtering effect. The SVA process increases s of PEDOT:PSS by inducing vertical phase separation between PEDOT and PSS in the film, resulting in electrons transported through a conducting PEDOT layer. Also, the SVA can change a work function of PEDOT:PSS due to different PEDOT to PSS ratio as various SVA time. The DMSO-SVA treated composite films form different potential barrier height between a PEDOT:PSS and Bi2Te3 nanowire as various SVA time. The best P, σ, and k are _˜203 mW/mK2, _˜1015 S/cm, and _˜44.7 mV/K respectively at 120 minute of SVA time corresponded to 0.1 eV of potential barrier in this experiment. Our study suggests that the potential barrier designed to maximize power factor in an organic-inorganic structure can provide the high thermoelectric performance.

Keywords: Energy filtering effect, Composite, PEDOT:PSS, Bi2Te3, PSVA

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Module Design for Organic Thermoelectric Materials

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There are large amounts of waste thermal energy in the environment, and the energy is usually at temperatures lower than 150 ∘C. To harvest the thermal energy, using thermoelectric devices which can directly converse heat energy to electricity is an effective means because of the simple structure and no moving parts. Organic materials are candidate thermoelectric devices in low temperature owing to its low thermal conductivity.
The organic material was Poly(3,4-ethylenedioxythiophene)/Poly(styrenesulfonate) (PEDOT/PSS), and the modules were composed of free standing PEDOT/PSS films as p-type thermoelectric material and nickel (Ni) metal foils as conducting material having n-type behavior. The thickness of PEDOT/PSS is ca.50 mm, and the thickness of Ni is ca.5 mm. The most important problem is the contact resistance between the organic films and metals. If the Ni foil is directly laminated on PEDOT/PSS films, the contact resistivity is higher than 105 mW×cm2. The total resistance of the devices is easily over 1000 W. To reduce the contact resistivity, the edge of both sides of Ni foil were coated by 20 nm Au. Polyvinyl butyral coating or polyimide film were used for insulators. All films and foils were cut into 2.2 cm × 2.2 cm square by a precision film cutter. The as-prepared Ni foils and free standing PEDOT/PSS films were stacked inside a mold for alignment, and laminated at 100 ∘C under 10 Mpa pressure for 60 min. The total resistant of the module with 50 layers was 31 W. The maximum power output was 37 mW, and the power density is ca. 24 mW/cm2.

In this talk, the fabrication of thermoelectric modules using composite materials with organic materials and carbon nanotube (CNT) will be discussed. The composite materials were p-type and n-type, and the feature of the composites was low contact resistance between p-type and n-type.

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Keywords: Organic Materials, Thermoelectric Module, PEDOT/PSS, Power Output, Contact Resistance

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Films of carbonaceous nanofillers and polymers as stable n-type materials for thermoelectric devices

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Materials such as graphene, carbon nanotubes and polymer-based organic nanocomposites have attracted the attention of the research community because of their promising applications for electronic devices: organic light emitting diodes, thermoelectric solar cells, transistors, thermoelectric generating devices. A thermoelectric module contains many alternating p-n junctions that are connected electrically in series and thermally in parallel. High values of power factor have been obtained for p-type organic and hybrids materials. However, for these materials, the electron transporters known as n-type have been rarely reported since the power factors are very low and the doping mechanisms involve states of unstable reduction to air or doping with insulating polymers. So, the building of thermoelectric devices has been restricted to single-carrier-type (p-type) legs. In this work, high-conductivity n-type films have been obtained from aqueous solutions of multi-walled carbon nanotubes (MWCNT) and graphene with different proportions of polymers, electron donating, such as: polyethyleneimine (PEI), polyvinylpyrrolidone (PVP) and polyvinyl acetate (PVAc). The films were subsequently doped with (4-(1,3-dimethyl-2,3-dihydro-1H-benzoimidazol-2-yl) phenyl)dimethylamine) (N-DMBI) to increase the conductivity. Transparent films have been obtained by spin coating, whereas non-transparent ones are obtained by drop casting. Properties such as the electrical conductivity, Seebeck coefficient, SEM images, Raman spectra and transparency have been determined as a function of the polymer type and concentration, reductor dopant and film formation procedure. Values of conductivity and Seebeck around 100 S/cm and -40 mV/K have been obtained. A thermoelectric module with the materials developed, p-n type legs, has been fabricated.

Keywords: Carbon nanotubes, graphene, n, type, electrodonating polymer

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Interfacial thermal resistance between Bismuth Telluride and PEDOT:PSS

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We have made a flexible thermoelectric generator of the Bi2Te3-PEDOT:PSS composite films by using a printing method. The measured thermal conductivity of the composite film was 0.2W(mK), and it is much lower than that of the predicted value by a conventinal effective medium theory. Here we focused on the interfacial thermal resisntace between inorganic and organic materials. The interfacial thermal resistance between inorganic-organic materials is in generally much higher than that of inorganic-inorganic materials due to their high physical properties contrast. We measured total thermal resistances of multi-layered Bi2Te3 and PEDOT:PSS films with different thicknesses in cross-plane by a differential 3 omega method. The Bismuth telluride films were deposited by a coaxial arc plasma method, and PEDOT:PSS was made by a spin coating. The measured interfacial resisntace was 10-7 W/(m2K) order, and the value was roughly10 times higher than that of the inorganic-inorganic materials. The composite of Bi2Te3-PEDOT:PSS thermal conductivity can be well explained by using the measured interfacial thermal resisntace in the present study.

Keywords: Interfacial thermal resisntance, Composite, Bismuth telluride, PEDOT:PSS

*Speaker

Thermopower of thermoelectric materials with resonant levels - beyond the constant scattering time approximation

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Resonant levels (RL) are formed by certain impurity atoms in semiconductors or metals, at energies, where in the absence of neighboring atoms a real bound state would be formed. A manifestation of RL is a sharp peak of the impurity's density of electronic states at the resonance energy, thus resonant impurities may significantly modify the host material's band structure. Electronic transport properties of thermoelectric materials containing resonant levels are discussed by analyzing two best known examples: cooper-nickel metallic alloy (Cu-Ni, constantan) and thallium-doped lead telluride (PbTe:Tl). As a contrasting example of a material with a non-resonant impurity, sodium-doped PbTe is considered.
Theoretical calculations of the electronic structure, Bloch spectral functions and energy-dependent electrical conductivity at T = 0 K are done using the Korringa-Kohn-Rostoker method with the coherent potential approximation (KKR-CPA), and the Kubo-Greenwood formalism. This allows to go beyond the constant scattering time approximation, most commonly used in literature. Effect of a resonance on the residual resistivity and electronic life times in PbTe may be then analyzed.
By using the full Fermi integrals, room-temperature thermopower is calculated, taking into account scattering of carriers by the resonant level. This confirms the increase in thermopower of PbTe:Tl *versus* PbTe:Na, due to the presence of RL. In addition, our calculations support the self-compensation model, in which the experimentally observed reduction of carrier concentration in PbTe:Tl against the nominal one is explained by the presence of n-type Te vacancies.

Keywords: lead telluride, resonant level, thermopower

*Speaker

Anharmonic and highly anisotropic low energy vibrational guest modes in the type IX chiral cubic barium-silicon clathrate

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The clathrate compounds are well known as archetypes of the concept of phonon glass – electron crystal because of their complex structure made of rigid cages in which the vibrations of the guest atom scatter the heat carrying acoustic phonons and hence reduce the lattice thermal conductivity. Among them, the type IX clathrate has quite interesting potential due to its unusual crystal structure made of three different cages of different sizes and symmetries but are still very few studied [1]. Its peculiar structure particularly attractive for studying the concept of rattling modes. In the present work, the vibrational dynamics of the Ba guest atoms in the type IX chiral cubic clathrate Ba24Si100 synthesized under HP-HT conditions [2] is investigated by means of high resolution powder inelastic neutron experiments and DFT calculations. The values of the vibrational energy and the degree of anharmonicity and anisotropy of the vibrational modes of the Ba guest atoms depend strongly of the size and shape of the cages where the guest atoms are intercalated. The vibrational modes involving motions of Ba guest atoms intercalated in large open Si20 cages are rather anharmonic and highly anisotropic with very low energy modes in the 3-4 meV energy range when the Ba guest atoms vibrate along the high symmetry direction where the cage is the largest. Thus, these vibrational modes can be seen as some kind of intrinsically anisotropic localized modes. This contrasts with the case of type 1 clathrate Ba8Si46 for which the vibrational modes of the Ba guest atoms intercalated in large Si24 cages are weakly anharmonic and anisotropic.

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Keywords: Clathrate, phonons, neutrons, DFT

Experimental validation of a 3D transient model of a Thermoelectric Generator

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Thermoelectric generators (TEGs) have become a promising approach for waste heat recovery as they can convert wasted thermal energy directly into electricity. Dynamic operation characteristics are important for design and optimization of TEGs in order to achieve the best performance especially in the case of time varying heat sources. This paper focuses on the experimental validation of a dynamic model of a TEG system which is composed of commercial thermoelectric modules (TEMs) and a finned heat exchanger. The model consists of a three-dimensional heat transfer transient model coupled to a thermoelectric power generation model. It implements a Maximum Power Point Tracker algorithm. The temperature dependence of the material properties is taken into account. The thermoelectric equations include the Thomson effect. Simulations of both steady-state and unsteady-state operating conditions are made and compared to experimental results. Different quantities and layout of the modules, inlet gas temperature and mass flow rates are tested. The comparison of numerical results to experimental data shows a good agreement. Based on these results, it is verified that the model can be used to simulate the behavior of a real TEG. This model gives then the possibility to optimize the TEG in order to maximize its performance and possibly reduce material cost.

Keywords: Thermoelectric Generator, TEG, Experimental, Validation, Transient, 3D modelling

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Angular Anisotropy of Thermoelectric Properties of a Periodic Composite Medium in the Presence of a Magnetic Field

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A calculational method based on Fourier expansion is developed and applied to a study of the strong-field galvano-magnetic thermoelectric properties of a free-electron metal, inside which is embedded a simple cubic array of identical spheres or cylinders, which have different thermoelectric and conductivity tensors. When the magnetic field is strong enough, the effective galvano-magnetic thermoelectric properties of such composites exhibit very strong variations with the direction of the applied magnetic field with respect to the symmetry axes of the composite microstructure. This is qualitatively similar to the predicted magneto-induced angular magnetoresistance anisotropy [D. J. Bergman and Y. M. Strelniker, Phys. Rev. B 49, 16256 (1994)] which was verified experimentaly [M. Tornow, et. al, Phys. Rev. Lett. 77, 147 (1996)]. This is a purely classical effect, even though it is qualitatively similar to what is observed in some metallic crystals which have a noncompact Fermi surface. The current results can be useful for studying the possibility of increasing the thermoelectric figure of merit in periodic composites by application of a strong magnetic field. As follows from our very preliminary results, the figure of merit can be increased by application of a strong magnetic field to the composite.

Keywords: magnetoinduced angular anisotropy, periodic composite medium, figure of merit

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Modeling and analysis of segmented thermoelectric generator performance using effective properties

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Development of new architectures for thermoelectric generators (TEGs) is crucial for optimal and efficient operation over a wide temperature range, from 200∘C to 700∘C. In addition, a comprehensive mathematical model that considers heat transfer and thermal losses needs to be developed to model and analyze the geometrical effects on the characteristics of TEG. The model should also account for the thermal and electrical contact resistances. In this study, an analytical and numerical model for a segmented TEG was developed which was validated using single couple devices. The model of the TEG was used to investigate steady state behavior as a function of geometric parameters as well as operating conditions. The performances under different geometric parameters was analyzed where the thickness of layers and area ratio of TEG's legs were varied. The analyses also quantify the effect of thermal losses such as conductive and radiative heat losses on performance of TEG using effective properties. Comparative studies revealed that the thermal losses of TEG predominantly increases heat transfer at the hot substrate and subsequently increases the power output, while the increase in heat input directly affects the efficiency of TEG. The results of parametric study showed that the efficiency increased as P-type and N-type leg area approaches a certain optimal ratio and each layer of the segmented TEG operates within optimal temperature range. In addition, the effective properties and compatibility factor of the device accounted for the improvement of performance with optimized geometric architectures.

Keywords: Modeling, effective methods, segmented thermoelectric generator, thermal loss, heat transfer

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Key Issues in Developing Viable PV/TE Hybrid Systems

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In principle, it is an excellent idea to integrate photovoltaic cells (PV) with thermoelectric modules (TE) to form a hybrid system for full-spectrum solar energy harvesting, where the photovoltaic cells convert the visible light directly into electricity while the infrared radiation is absorbed to produce heat for power generation by thermoelectric modules. However, in practice, many serious challenges exist, which need to be recognised and addressed in order develop truly economic PV/TE systems. In this talk, we will first present a theoretical outline that underpins the feasibility of hybrid PV/TE systems and then discuss the design requirements and system configurations that facilitate practical implementation of the hybrid PV/TE systems. Recent experimental results will also be presented, which provide the proof of principle and valuable insights into key mechanisms and parameters that are crucial to the development of economically viable hybrid PV/TE systems.

Keywords: hybrid system, PV/TE

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Harvesting Waste Heat from Cement Kiln by Thermoelectric System

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In cement industry approximately 25% of the system heat input is lost by dust, radiation and convection from the kiln, clinker discharge, and pre-heaters. The shell of the rotary kiln has a temperature of several hundred Celsius degrees. To reduce the heat loss, a novel heat recovery panel installed around the kiln shell is proposed to be used for generating electrical power. However, there will still remain a residual heat to harvest. Numerical simulations and analytical modelling are initially carried out to investigate how much energy is lost from the kiln. Then, the flow and heat transfer features are obtained in the presence of the heat recovery panel. Temperature distribution along the absorber circumference is obtained in order to design an efficient thermoelectric waste heat recovery system. The heat flux absorbed by the absorber is used as heat source in thermoelectric based heat recovery systems.

Keywords: Rotary Kiln, Absorber Temperature Distribution, Waste Heat Recovery, Computational Fluid Dynamic (CFD), Turbulent, Combined Heat Transfer

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Zonal thermoelectric passenger cooling: Simulation and Experiment

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As part of a EU project, JOSPEL – "Low energy passenger comfort systems based on the Joule and Peltier effects", European Thermodynamics Ltd is developing an air-to-liquid thermoelectric assembly to be employed in electric vehicles (EV) cabin climate control.
Electric vehicles in particular offer an interesting application for thermoelectric devices as part of a hybrid thermal management solution thanks to the potential to improve battery range without sacrificing passenger comfort. This can be achieved by exploiting thermoelectric devices advantages, including: zonal climate control, reduced weight, compactness, both cooling and heating function in the same unit with no moving parts and direct electric to thermal energy conversion.

The unit developed consists of four thermoelectric modules attached to a heat sink with an impinging fan. The waste heat of the thermoelectric assembly is dissipated into a liquid cold plate. Different heat sink configurations were explored during the project through CFD simulation and experimental validation. Both air temperature and air velocity must be considered in order to maximise comfort. Under these constraints, the outlet air temperature achieved in the more challenging mode of operation, i.e. cooling mode, was 5-10∘C lower than ambient thus meeting ASHRAE Standard 55 recommendations for a wide range of environmental conditions. The JOSPEL project aimed to evaluate the overall thermal comfort based on static models such as the PMV (Predicted Mean Vote) approach. A CFD study using ANSYS simulation software guided the most advantageous placement of the thermoelectric system for zonal climate cotrol.

Keywords: Electric vehicles, thermal comfort, zonal climate control, thermoelectric assembly

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A Study on Forest Soil Thermoelectric Energy Harvesting Method

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To solve the problem that in forestry area sensors and wireless nodes distribution wiring could not be widely distributed and are of poor reliability, in this paper, based on the Seebeck effect and combined with thermoelectric energy harvesting technology, a wireless node power supply system based on forest soil thermoelectric power generation was designed. We measured the performance of the thermoelectric collection system in an outdoor simulation experiment platform and obtained it's conversion efficiency and the change law of open circuit voltage and load current. LTC3108 DC booster circuit is used to boost the low voltage transformed by thermoelectric conversion module. Then the boosted voltage can be supplied for low power consumption devicesIn order to solve the electrical energy might be surplus or lack, this paper uses the lithium battery as energy storage elementsWhen the electricity is surplusthe rest of the electricity is stored into the lithium batteryAnd when the electricity is lackthe stored energy is released to equipment. Under outdoor condition, experiments were repeatedly carried out. The results show that the thermoelectric energy conversion system achieves a boost of 202 mV to 4.2 V and an energy output of 5.3 mW. The above parameters show that the system designed in this study provides an effective way to solve the problem of energy supply for wireless sensor.

Keywords: thermal power generation technology, LTC3108, booster circuit, lithium battery

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COMPARATIVE ANALYSIS OF DIFFERENT COOLING SYSTEMS FOR GEOTHERMAL THERMOELECTRIC GENERATORS

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Despite being one of the largest renewable sources, geothermal energy is not widely utilized for electricity generation due to the associated intrinsic difficulties: high initial investment, difficulties in modularizing and assessing the resource, as well as complexity in the implementation of cycles (the only installed technology nowadays). In this sense, thermoelectric generators can be considered an alternative in order to promote sustainable generation and contribute to the reduction of greenhouse gases. The present work presents the experimental development and the computational study of a project that aims to obtain electrical energy by means of thermoelectric generators in Lanzarote Island (Spain), where one of the most important hot dry rock fields in the world (with temperatures of 500∘C at only 3 meters deep) is located. In particular, different heat exchangers for the cold side of the thermoelectric modules have been analyzed: fin dissipators assisted by a ventilator, heat exchangers with water as heat carrier and fancoils, and biphasic thermosyphons. The heat exchangers have been experimentally characterized and subsequently used in a prototype that simulates the favorable conditions of the island. As a result, it has been demonstrated that biphasic thermosyphons are the best alternative due to their low thermal resistance and, especially, due to their lack of auxiliary consumption that deteriorates net generation, leading to a 12.5% higher generation than fin dissipators. Experimental results have served for the validation of a computational model, based on which it has been estimated that in Lanzarote almost 100 kW can be generated thanks to thermoelectric generators that use biphasic thermosyphons as heat exchangers in the cold side.

Keywords: geothermal energy, thermoelectric generator, heat exchanger, fin dissipator, ventilator, pump, thermosyphon, computational model, auxiliary consumption, net generation.

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Prototypical thermoelectric generator TEG for waste heat conversion from biogas-fired burner

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In our work we present the industrial thermoelectric generator (TEG) that was designed to work in an existing CHP (combined heat and power) plant at Novago company, Poland. Novago uses unique technology to produce energy from municipal waste in which one of the by-products is a biogas. The excess of the biogas has to be burned before being released into the atmosphere. In this work waste heat generated from a biogas burning is used as a heat source for the TEG heating. One of the aims of the project was to optimize a design of the hot and cold side of the heat exchanger to provide maximum efficiency. The installed gas burner with heat energy from 6 to 12 kW and a cooling system with 11 kW at RT were chosen. Thermoelectric modules with a nominal power of 400W were installed. Long term operational test at different conditions were conducted. The design of the heat exchanged at the cold side of the modules was investigated and confronted with results of energy calculations based on temperatures and fluxes of a cooling medium. The key parameters for TEG such as temperatures of the hot and cold side of the modules as well as the inlet and outlet gases temperatures were determined. The system possesses emergency bypass that could be activated in emergency situations. All parameters were controlled and collected in PC.Presented work was supported by the National Centre for Research and Development under the project "Innovative thermoelectric modules for energy harvesting" (PBS3/A5/49/2015). This scientific work has been partially financed as a research project no. UMO-2016/23/D/ST8/02686, National Science Centre, Poland.

Keywords: thermoelectric generator, waste heat recovery, performance characterization, industrial tests, biogas

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New Generation of Micro-Flexible Thermoelectric Devices to be Applied in Electronic Printing

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Thin and flexible micro thermoelectric generators (TEGs) are being envisaged in the last decade as alternative power sources, constituting a new business opportunity for the packaging industry such self-powered wearable electronics and/or to be used on remote places for low power consumption devices. The main strategies to obtain this goal are by depositing high performance thermoelectric materials onto the top of flexible substrate, organic polymeric materia or by combining both resulting in a composite. This last strategy unveil better achievements in the last years and the more promising due to low cost production and scalability to the market. Although a thorough search is being under pursuit, the results unveil to be always smaller than the direct inorganic material thin films. Thus, the main goal of this work is to conceive a flexible and easy printed TEG prototype for energy harvesting.
Towards this goal, Bi2Te3 thermoelectric material was synthetized by solid-state reaction using a close quartz-tube in a N2 atmosphere. The achieved material was submitted to a ball milling process to reduce the mean particle size down to 50 μ

Keywords: Thermoelectric Materials, Organic polymers, Bi2Te3, Power Output

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Complete characterization of bulk thermoelectric elements up to 250 °C by means of impedance spectroscopy

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Impedance spectroscopy has been shown as a promising method to characterize thermoelectric materials and devices [1]. In particular, the possibility to achieve a complete characterization of thermoelectric materials has been demonstrated, altough mainly for thermoelectric modules at room temperature [1]. However, this method has neither been extended to high temperatures nor has been evaluated in low-performance thermoelectric materials, which could be troublesome due to the very small impedance signals usually registered (in the m range).
Here, by employing a skutterudite material, which exhibit low thermoelectric performance at room temperature, we demonstrate the capability of the impedance method to determine with good accuracy all the thermoelectric properties of the material (electrical resistivity, thermal conductivity, Seebeck coefficient, and ZT) as a function of temperature up to 250 °C. This is achieved by attaching stainless steel contacts of known thermal conductivity at the edges of the sample. The results obtained, which are sensitive enough, are compared with measurements from commercial equipment (Linseis LSR-3 and the laser flash method) and the different sources of errors are analyzed. This approach offers a significant advantage with respect to the typically followed lengthy characterization procedure, which involves the use of two or three separate apparatus, which are reduced in this method to only one.

References

García-Cañadas, J.; Min, G. Impedance Spectroscopy Models for the Complete Characterization of Thermoelectric Materials. *J. Appl. Phys.* **2014**, *116*, 174510.

Keywords: Measurement technique, complete characterization, impedance spectroscopy

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Do high efficiency kW pulsed thermoelectric generators exist?

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Abstract

Thermoelectric generators pulsed in the 10 kW range have been built. The theory of Apostol [called Ultra Fast Conduction was published in 2001. It describes that under certain circumstances: In particular when the electrical circuit is very short with a very low electrical resistance (milli-ohm.) A very short pulse can go around the electrical circuit fast enough so that the pulse does not have time to disperse, so electrical energy can be transferred with a very low energy loss. The input energy is thermal, it is converted to electrical with the Seebeck effect. The electrical output power is chopped at around 50 kHz and extracted from the circuit through a transformer.

So far, many claims have been made. The authors have already presented papers reviewing the subject but never with experimental results.

The authors decided to build, as proposed by Marin Nedelcu, a generator with 4 H-Z14 modules in parallel.

James Glick designed and built an electronic circuit board with mosfets to pulse the current. A 10 kW transformer was built that can be used for TE generators. This unit enables verification and operation of the pulsing unit and to see the 4 Hi-Z modules in parallel, verification can detect any ultrafast conduction, as claimed by Marin Nedelcu (private communication). Results will be presented.

The square assembly is optimum dimensioned unit for verification of Ultrafast conduction has been designed with 24 TE discs of bismuth telluride D=24 mm thickness 1 mm. The square assembly has 6 TE discs on each side.
This is a stable structure in time with no shear stress between operation conditions and shutdowns. Results will be presented. We hope that we can now confirm the existence of ultrafast conduction.

Keywords: generators, pulsed, experimental

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Maximum Power Point Tracking on a TEG operated under constant heat conditions

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Optimization of the electrical operating point of thermoelectric generators (TEGs) is important to improve the overall efficiency of TEG systems. Previous literature focused mostly on characterizing the maximum power point (MPP) of TEGs when operating at constant temperature difference. However, in most practical applications TEGs operate under constant or limited heat conditions. As a matter of fact, in waste heat recovery systems the amount of thermal energy is limited. Under these circumstances, the MPP is different from that occurring under constant temperature difference because the Peltier effect changes the effective thermal resistance of the TEG and the temperature difference across it with variations of the output current. This work presents control electronics that operates a TEG system with limited heat flux at the optimum point. The control architecture is based on perturb and observe and modified to take into consideration the thermal transient response of the TEG. The sampling time and step size of the MPPT algorithm is adapted dynamically to provide fast response during transients and precise accuracy at steady-state. A Boost dc-dc converter is used to step-up the TEG voltage to 28V for connection to an eight-cell Lithium-Ion (Li-Ion) battery. A microcontroller implements the control algorithm that drives the power converter. Experimental results are provided to compare the MPPT performance of the proposed converter against the MPP obtained by characterizing the TEG used.

Keywords: MPPT, Constant Heat

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A new thermoelectric generator concept for maximizing waste heat recovery under highly variable thermal load

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It is virtually impossible to optimize a thermoelectric generator for a wide range of thermal input conditions when using conventional heat exchangers. The system will either operate efficiently under low loads but suffer a bypass to avoid overheating under high loads, or it will operate efficiently under high loads, but have a very low efficiency under low loads due to thermal dilution.
The authors have been exploring the concept of a temperature-controlled thermoelectric generator (TCTG) operating efficiently under the highly variable temperatures and flow rates encountered in the exhaust heat recovery of vehicle driving cycles. The concept relies on the addition of a thermal buffer between the heat source and the modules so that there is control over the thermal level achieved by them irrespective of the thermal input variability. This allows to maximize the usage of the waste heat source without the risk of overheating or thermal dilution. The TCTG concept presented thus far relied on gravity for operating properly and there were limitations regarding the system compactness and form factor, which is critical for mobile applications. A new TCTG concept without such limitations and a form factor similar to conventional generators is presented and its performance is explored in a vehicle application under realistic driving conditions.

Keywords: Thermoelectric generator, temperature control, variable thermal load, exhaust heat exchanger, waste heat recovery

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Preview Certified Reference Material Data, Measurement Protocols, and Uncertainty Analysis for p-Type Polycrystalline Silicon Germanium at High Temperature

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Certified Reference Materials (CRMs) and Standard Reference Materials (SRMs®) provide unchanging and accessible starting points that can support the development, production and reliability of materials and devices related to thermal energy conversion and harvesting applications. Only a small number of SRMs® and CRMs are available for bulk transport properties relevant to thermoelectric research. For example, National Institute of Standards and Technology (NIST) SRM® 3451 Low Temperature Seebeck Coefficient Standard enables instrument validation, interlaboratory comparisons, and protocol studies between 10 K and 390 K. A complementary standard for high temperature is now in the final stages of development. We report the synthesis, preparation, and anneal treatment of boron-doped polycrystalline silicon germanium for use as a Seebeck coefficient SRM® at high temperature (300 K to 900 K). We will present preview certified reference material data, measurement protocols, and uncertainty analysis, as well as chemical and thermocyclic transport property data that indicate the homogeneity and stability of the material. Optimal measurement protocols were identified by comparing commonly applied probe arrangements and measurement techniques using our custom built high temperature thermoelectric measurement apparatus. Based on our studies, we have determined that thermal contact errors for different probe arrangements are the primary influence on measurement accuracy at high temperature. Corroborating data will be presented.

Keywords: metrology, Seebeck coefficient, standards, thermal contact, measurement techniques

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Wearable Electrocardiography System Powered by a Flexible Thermoelectric Power Generation Module

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With the emergence of the Internet of Things (IoT) era, wearable electronics have already had a diverse effect on human life, especially for the use of various medical sensors for mobile healthcare system. The electrocardiography (ECG), which provides information on the cardiovascular system, is one of the most important wearable sensors. The wearable ECG can acquire the ECG signal of a patent over a certain period of time while the patent is having usual daily life. In this application, a self-powered system using a semi-permanent energy harvester such as thermoelectric generator is very useful because it can significantly reduce the inconvenience of the users.

In this work, a self-powered wearable ECG system is demonstrated using a flexible thermoelectric power generation (f-TEG) module. The f-TEG was successfully fabricated, with a size of 70 mm * 70 mm, the module ZT of _˜ 0.7, and the minimum bending radius less than 10 mm. A polymer-based flexible heat sink (PHS) was newly devised, which can help maintain a large temperature gradient across the f-TEG. The PHS was comprised of a superabsorbent polymer and a xylitol-coated fiber that promotes liquid evaporation. The polymer heatsink and the f-TEG were carefully optimized for the maximum power generation using body heat. The ECG sensing circuit was fabricated also in the form of a bracelet using a flexible PCB. The power management IC was also newly designed and fabricated for this particular application using 65 nm standard CMOS foundry service, because the commercially available PMICs are not suitable for the low output voltage of the f-TEG using body heat. The fabricated self-powered ECG system could successfully monitor the ECG signal in easy and wearable manner. This work will pave the way for the commercialization of the self-powered mobile healthcare system using thermoelectric power generation.

Keywords: Wearable thermoelectric devices, Flexible heatsink, Power generation, Body heat, Wearable ECG sensor

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