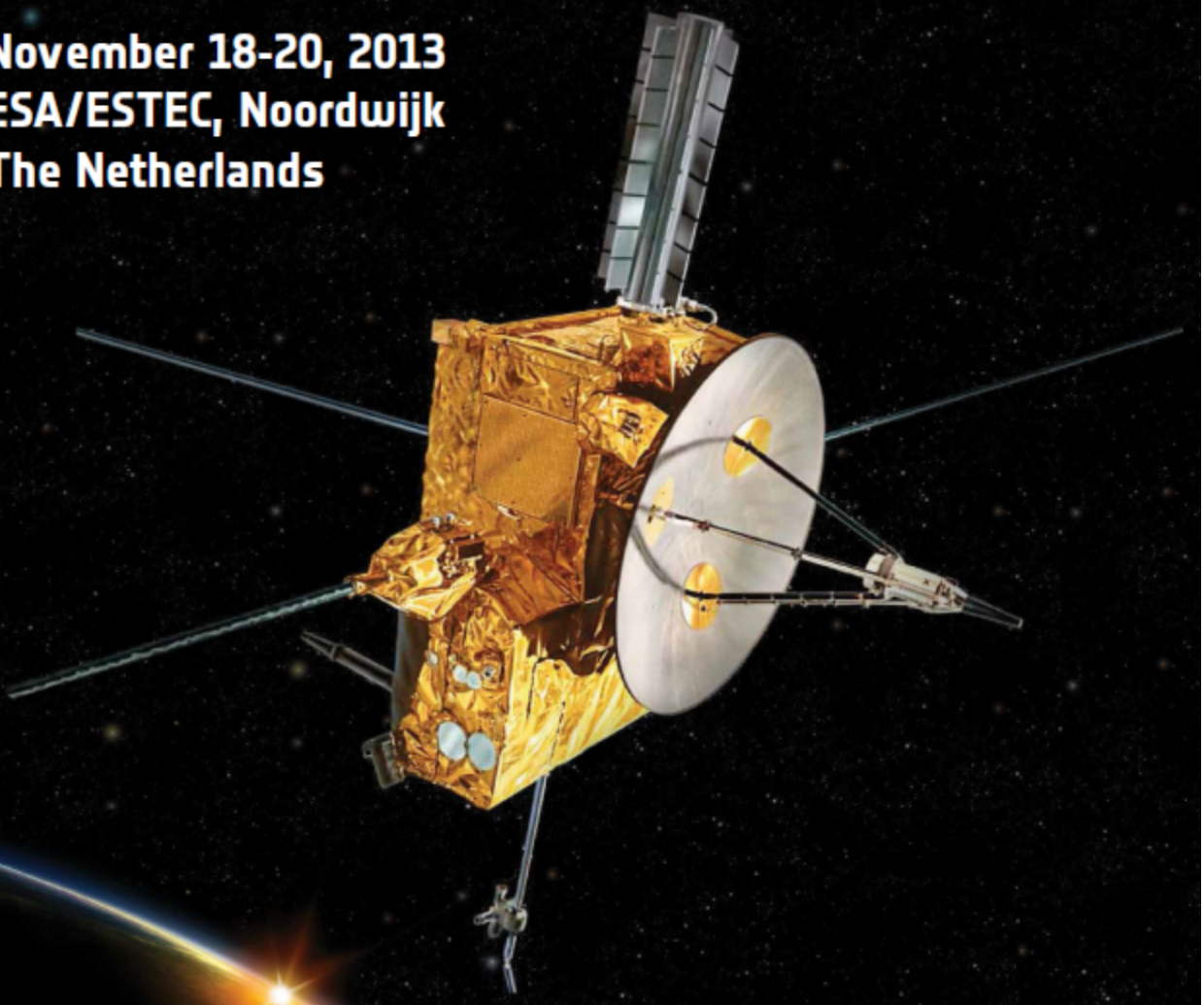
ECT 2013

esa

→ 11TH EUROPEAN CONFERENCE ON THERMOELECTRICS

November 18-20, 2013
ESA/ESTEC, Noordwijk
The Netherlands



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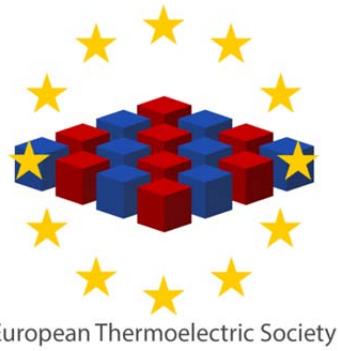
Organisation

ECT 2013 is organised by:



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** ESA/ESTEC (Noordwijk, The Netherlands)*

Invited Speakers

Mauro Brignone (Centro Ricerche FIAT, Italy)
Wednesday 20 November – 14:00

Mauro Brignone took his degree in Physics at the University of Torino and his PhD in Chemistry at the University of Piemonte Orientale. Mauro started to work at FIAT Research Centre in 2002, first in the "Micro and Nanotechnology" department and subsequently in the "Materials" department (Group Materials Labs) where is responsible for the "Advanced Metals" group. He is specialized in semiconductors physics and started his experience with organic, inorganic and hybrid light emitting devices. Since 2004 Mauro has been working on systems for energy production studying and developing photovoltaic cells (DSSC and thin film) and thermoelectric materials and systems. He is expert in materials characterization techniques (AFM, SEM, FIB, XRD, DSC) and in photovoltaic and thermoelectric characterization. Mauro has developed efficient skutterudites materials through low cost metallurgical synthesis and has designed and fabricated a full thermoelectric generator for gasoline passenger cars. Mauro has participated in several EU funded projects, is author or co-author of numerous scientific articles and international patents.

Sylvie Hébert (CRISMAT, France)
Monday 18 November – 16:40

Sylvie Hébert received her PhD in July 1998 on the pinning of vortices by columnar defects in high Tec superconductors (CRISMAT laboratory), and then did two post-doctoral stays at the Imperial College in London (1998 - 1999) and KULeuven in Leuven, Belgium (2000) on the pinning of vortices by columnar defects and by antidots respectively. Then she got her CNRS research position back in CRISMAT, Caen, in October 2000, to work on the magnetic and electrical properties of transition metal oxides, with a special emphasis on Seebeck coefficient. She has been mostly interested by the spin and orbital degeneracy impact on the Seebeck coefficient, and the thermoelectric properties in these strongly correlated materials. Since 2010, she is the director (together with Bertrand Lenoir, IJL Nancy) of the french CNRS network on Thermoelectricity (GDR Thermoélectricité).

Jan König (Fraunhofer-Institut für Physikalische Messtechnik IPM, Germany)
Wednesday 20 November – 09:00

Jan D. Koenig is leading the "Thermoelectric Energy Converters" group and is the deputy head of the department "Energy Systems" at Fraunhofer IPM (Institute for Physical Measurement Techniques), Freiburg, Germany. In parallel to the diploma and doctoral theses, advised by Dr. Harald Böttner, he started as project manager at Fraunhofer IPM in different projects regarding thermoelectric material research, measurement systems and module development. Remarkable projects were the design and fabrication of a fully automated material measurement setup and the development of a small scale production of thermoelectric modules. The current activities cover nanoscale bulk and thin film research on Bi2Te3, PbTe and silicide based materials. J. Koenig built up at Fraunhofer IPM a thermoelectric bulk material processing route as well as the high temperature generator fabrication. The development of a high temperature standard for thermoelectric metrology is as well a main topic including a worldwide round-robin test started in 2013.

Qiang Li (Brookhaven National Laboratory, USA)
Tuesday 19 November – 16:40

Qiang Li is a tenured physicist in the Condensed Matter Physics and Materials Science Department at US Department of Energy's Brookhaven National Laboratory, and an adjunct professor at Stony Brook University in New York. At Brookhaven Lab, he is the head of Advanced Energy Materials Group which studies microscopic and macroscopic properties of complex and nano-structured materials with a view to understanding and developing their application in different energy related technologies. His current research ranges from basic physics and material science studies to the applications of superconducting materials and thermoelectrics.

Tsutomu Iida (Tokyo University of Science, Japan)
Tuesday 19 November – 09:00

Tsutomu Iida obtained his Phd in electrical engineering from Meiji University in 1995 with regard to ion-beam and molecular-beam material synthesis. He obtained B.Eng. and M.Eng. from Meiji University in 1990 and 1992, respectively. He was then a research fellow of The Japan Society for Promotion of Science, and worked at Technical University of Darmstadt, Germany, as an invited researcher from The Volkswagen Foundation. Since 1997, he has been working at Tokyo University of Science as a research associate, he is currently a professor at Tokyo University of Science. His current research field is material science to develop appropriate energy conversion materials to avoid the effects of global warming. Since 2001, he started to work with the thermoelectric material synthesis especially environmentally-benign magnesium silicide (Mg2Si). He established the waste heat recovery technology consortium of Japan in 2009 composed of more than 30 industrial companies, 3 governmental sector institutes and 7 universities. His groups are also collaborating European automotive industries and institutes in the thermoelectric technology field.

Jeff Snyder (California Institute of Technology, USA)
Monday 18 November – 11:20

G. Jeffrey Snyder obtained his B.S. degree in physics, chemistry and mathematics at Cornell University (1991) focusing on solid state chemistry which he continued during a two year stay at the Max Planck Institut FKF (Festkörperrperforschung) in Stuttgart, Germany. He received his Ph.D. in applied physics from Stanford University (1997) where he studied magnetic and magneto-electrical transport properties of metallic perovskites as a Hertz Fellow. He was a Senior Member of the Technical Staff in the thermoelectrics group at NASA's Jet Propulsion Laboratory for 9 years (1997-2006) where he focused on thermoelectric materials and devices. He is currently a Faculty Associate in materials science at the California Institute of Technology (Caltech). His interests include the discovery of new Zintl phase thermoelectric materials and nanostructured thermoelectric composites using bulk processing, band structure engineering and thermoelectric performance optimization. Dr. Snyder has published over 200 articles, book chapters and patents. He serves as treasurer of the international thermoelectric society.

Since 2010 Dr. Snyder has become one of the world's most prominent scientists in the field of thermoelectrics, among the top cited authors and highest number of publications in the field (around 1000 citations and over 30 publications per year). His 2008 review article in Nature Materials, is the most cited review article in thermoelectrics.

Xanthippi Zianni (Technological Educational Institution of Chalkida, Greece)
Monday 18 November – 14:00

Xanthippi Zianni has received her First Degree in Physics from the Physics Department of the University of Athens (Greece) and her PhD in Theoretical Solid State Physics from the Physics Department of the University of Warwick (UK). She is currently Professor of Physics at the Technological Educational Institute (TEI) of Sterea Ellada and Research Associate at the Dept. of Microelectronics at the Greek National Research for Scientific Research (NCSR) 'Demokritos'. She is temporarily vising professor at MATEIS, INSA de Lyon (France).

Her research is in theoretical condensed matter physics and computational modelling. She has worked in: percolation theory, conductivity of disordered media, electrons and phonon properties of low-dimensional semiconductors, magnetic properties of nanoparticles, electronic, thermoelectric and optical properties of semiconductor nanowires and nanocrystals. Her current research focuses on the electronic and thermoelectric properties of nanostructures and on the energy conversion at the nanoscale.

Exhibition

1. Ulvac GmbH

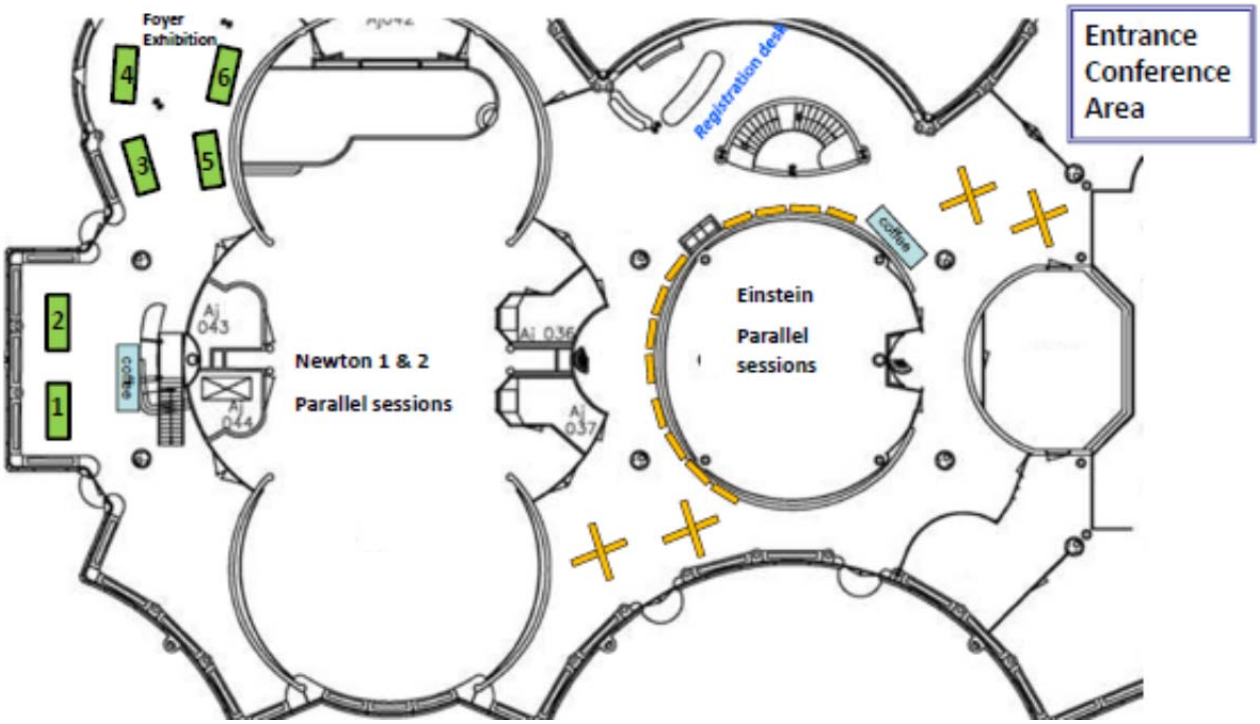
2. Quick Ohm Küpper & Co GmbH

3. Institute of Thermoelectricity

4. Toyota Tsusho Corporation

5. Linseis Messgeräte GmbH

6. Hot Disk AB



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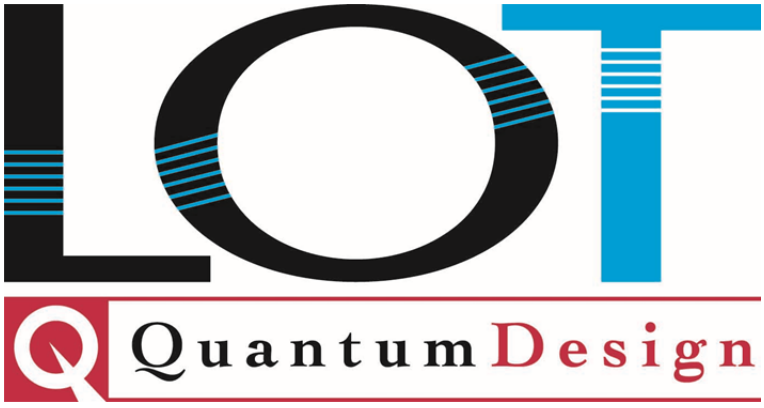


General Information

Wireless Internet

All pre-registered participants have received their log-in details by email, sent by the ESA ServDesk. A copy of your login details is also available in the back of your badge.

List of Participants

A list of participants is available for viewing on the message board at the registration desk. A final list will be sent by e-mail to all participants after the conference.

Proceedings

The proceedings of the conference will be published by Springer and will be made available online to conference participants.

Coffee Breaks & Lunches

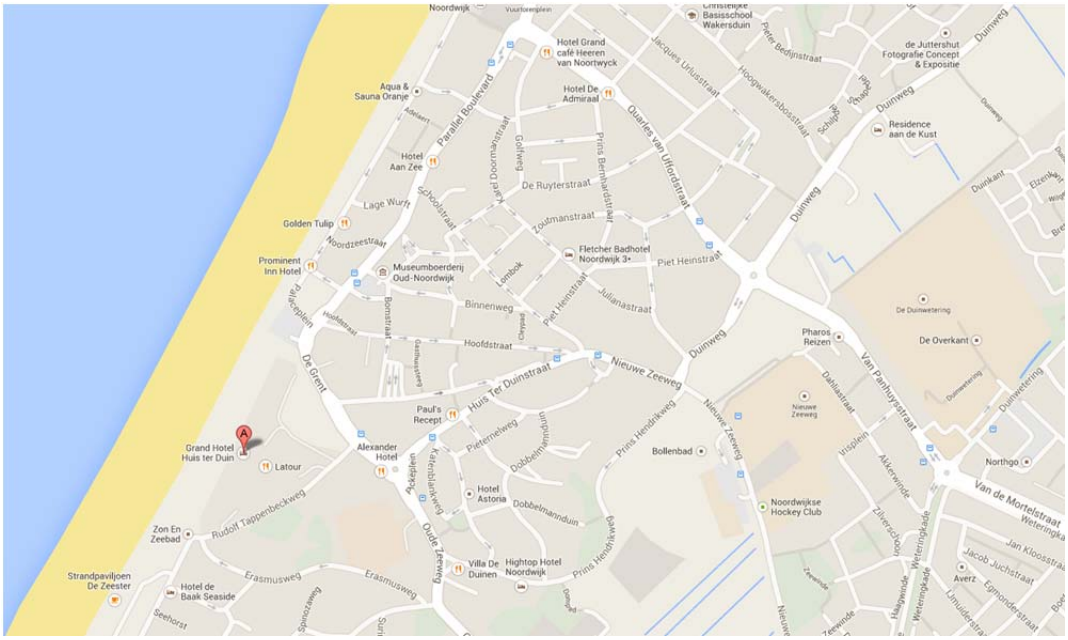
Each participant has received lunch vouchers to be used in the ESTEC self-service restaurant after 13:00.
Coffee will be served in the morning upon arrival and during the coffee breaks outside the meeting rooms.

Welcome Cocktail Monday 18 November 2013

The welcome cocktail will take place in the ESTEC main building, after the last session.

Conference Dinner Tuesday 19 November 2013

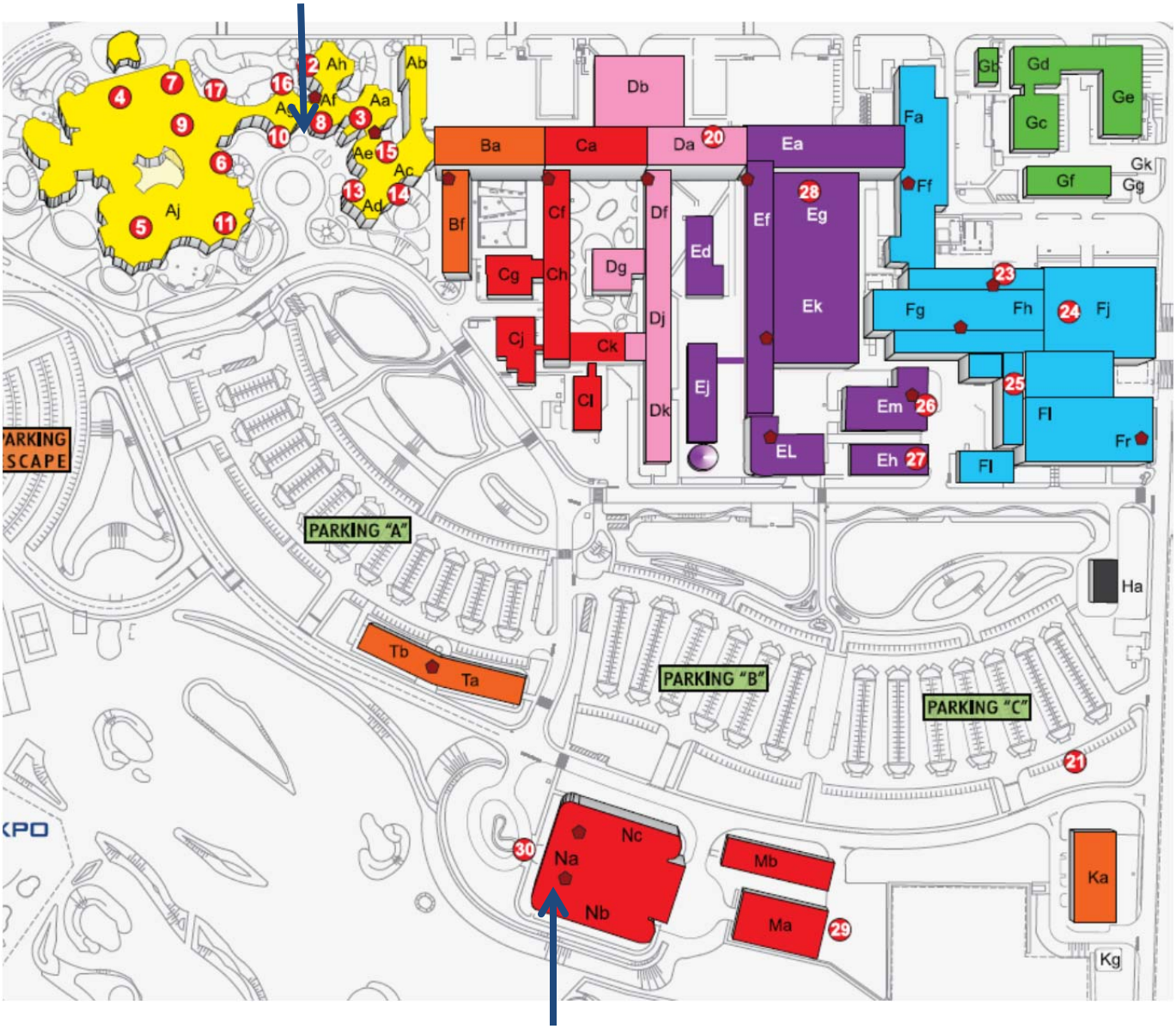
The conference dinner will take place at Breakers Beach House in Noordwijk aan Zee at 20:00. The Breakers Beach House can be reached through the Huis Ter Duin hotel; Koningin Astrid Boulevard 5, 2202 BK Noordwijk



Goodbye Drinks Wednesday 20 November 2013

The goodbye drinks will take place in the Erasmus Highbay, after the last session. The Erasmus Building is located on the other side of the ESTEC Premises, 5 minutes walking from the Conference Centre. Please follow directions from the Conference Organisation Team.

ESTEC Main Reception



Erasmus Building

Conference Bus Schedule

Date	Estimated pick-up time	Pick-up point	Destination
Monday, 18 November	09:45	Noordwijk hotels*	ESTEC Gate
Monday, 18 November	19:30	ESTEC Reception	Noordwijk hotels*
Tuesday, 19 November	08:00	Noordwijk hotels*	ESTEC Reception
Tuesday, 19 November	18:30	ESTEC Reception	Noordwijk Hotels*
Wednesday, 20 November	08:00	Noordwijk hotels*	ESTEC Reception

* Pick up points for Specific Hotels, please check below:

Hotel Admiraal	Quarles van Uffordstraat 81
Heeren van Noortwijck	Quarles van Uffordstraat 103
Hotels van Oranje & Beach Hotel	Kon. Wilhelmnaboulevard 20-31
Golden Tulip Beach Hotel	Kon. Wilhelmnaboulevard 8
Prominent Inn	Kon. Wilhelminaboulevard 4
Hotel Astoria	in front of the Alexander hotel, Oude Zeeweg 63
Palace Hotel	in front of the Alexander hotel, Oude Zeeweg 63
Huis ter Duin	in front of the Alexander hotel, Oude Zeeweg 63
Hotel Royal	Opposite the Old Post Office, Boekerslootlaan

Taxi / Getting to the airport

Reservations for the shuttle should be made at least one day in advance, taxi bookings one hour in advance directly with
ESTEC Reception: +31-71-565 4000, ESTEC.Reception@esa.int or
Taxi Brouwer: tel. +31-71-361 1000, info@taxibrouwer.nl

Schiphol Shuttle

Purchase a ticket at the ESTEC reception located in the A building (cash payment only). The costs for a one-way voucher are €13.50 (VAT included)

Schedule - Monday to Friday
- 14:30 hrs
- 15:30 hrs
- 16:30 hrs
- 18:00 hrs

Taxi Rates

Please note that there are fixed prices for any taxi of Taxi Brouwer from ESTEC to Noordwijk or Schiphol. These fixed all-in prices (VAT included) are :

Schiphol Airport – ESTEC	€53	Leiden – Schiphol Airport	€48
Schiphol Airport – Noordwijk	€53	ESTEC – Noordwijk	€11.50
Schiphol Airport – Leiden	€53	Noordwijk – ESTEC	€11.50
ESTEC – Schiphol Airport	€48	ESTEC – Leiden	€20
Noordwijk – Schiphol Airport	€48	Leiden – ESTEC	€20

On any other routes, there is a 15% discount.

Programme

Monday 18 November 2013

11:00 **Opening Ceremony** (Plenary)

11:20 **[Invited Speaker] Optimizing Performance in Thermoelectric Alloys** **33**

1n_X1_1 *Snyder , G.J.*
California Institute of Technology, (UNITED STATES)

Session X1: Oxides I

Chair: A. Maignan

Room: Newton

12:00 **Transport Properties of Misfit Layered Cobaltite Thin Films Synthesized by Polymer Assisted**

1n_X1_2 **Deposition** ***33***
Rivas-Murias, B. ; Vila-Fungueiriño , J. M. ; Rivadulla, F.
CIQUS-University of Santiago de Compostela, (SPAIN)

12:20 **High Temperature Thermoelectric Conversion Employing Calcium Manganates** **34**

1n_X1_3 *Thiel, P. ; Populoh, S. ; Saucke, G. ; Shkabko, A. ; Eilertsen, J. ; Rigort, R. ; Brunko, O. ; Trottmann, M. ; Sagarna, L. ; Karvonen, L. ; Weidenkaff, A.*
empa - Swiss Federal Laboratories for Materials Science and Technology, (SWITZERLAND)

12:40 **New Aspects in Oxide Thermoelectric Materials with Unconventionally Enhanced Phonon Scattering** **34**

1n_X1_4 *Ohtaki, M. ; Miyaishi, S. ; Mizuta, K.*
Kyushu University, (JAPAN)

Session F: Thin Films

Chair: K.M. Paraskevopoulos

Room: Einstein

11:20 **Novel Apparatus for Transport Properties Measurements of Thin Films under Sulphur Atmosphere at**

1e_F_1 **Moderate Temperatures (Room Temperature to 400°C)** **34**
Clamagirand, J.M. ; Ares, J.R. ; Ferrer, I.J. ; Sanchez, C.
Universidad Autónoma de Madrid, (SPAIN)

11:40 **Measurement of Thermal Conductivity on Nano Scaled Thin Film and Thin-Layered Materials** **35**

1e_F_2 *Marx, H.-W. [1]; Südmeyer, I. [2]; Rohde, M. [2]; Gaede, D. [2]; Seifert, H.J. [2]; Linseis, F. [1]; Linseis, C. [1];Renner, H. [1]*
[1]Linseis Messgeräte GmbH, (GERMANY); [2]Karlsruhe Institute of Technology, (GERMANY)

12:00 **Structural and Thermoelectric Properties of Binary and Ternary Skutterudite Thin Films** **36**

1e_F_3 *Daniel, M. [1]; Liebig, A. [1]; Gordan, O. D. [1]; Zahn, D. R. T. [1]; Plech, A. [2]; Albrecht, M. [1]*
[1]TU Chemnitz, (GERMANY); [2]Karlsruher Institut für Technologie (KIT) , Institute for Synchrotron Radiation (GERMANY)

12:20 **Multilayered Ge/SiGe Material in Microfabricated Thermoelectric Modules** **36**

1e_F_4 *Samarelli, A. [1]; Ferre Llin, L. [1]; Zhang, Y. [1]; Weaver, J.M.R. [1]; Dobson, P. [1]; Cecchi, S. [2]; Chrastina, D. [2]; Isella, G. [2]; Etzelstorfer, T. [3]; Stangl, J. [3]; Muller, E. [4]; Paul, D. [1]*
[1]University of Glasgow, (UNITED KINGDOM); [2]Politecnico di Milano, (ITALY); [3]Johannes Kepler Universitt, (AUSTRIA); [4]ETH Zurich, (SWITZERLAND)

12:40 **Development of Pulse Transient Hot Strip Method to Measure Thermal Transport Properties of Thin Film**

1e_F_5 **Materials** **37**
Ma, Y. [1]; Gustavsson, J. [2]; Gustafsson, S. [1]; Gustavsson, M. [1]
[1]Hot Disk AB, (SWEDEN); [2]Chalmers University of Technology, (SWEDEN)

13:00 ***Lunch Break***

Session X2: Oxides II

Chair: A. Weidenkaff

Room: Newton

Session T1: Theory I

Chair: J. Tobola

Room: Einstein

Session X3: Oxides III

Chair: J. Hejtmanek

Room: Newton

16:40 [Invited Speaker] From Oxides to Sulfides and Selenides: Optimization of the Power Factor 41

1n_X3_1 *Hébert, S. [1]; Takahashi, H. [2]; Raghavendra, N. [1]; Berthebaud, D. [1]; Guilmeau, E. [1]; Gascoin, F. [1]; Maignan, ...A. [1]; Pelloquin, D. [1]; Lebedev, O. [1]; Roddatis, V. [3]*

[1]Laboratoire CRISMAT, (FRANCE); [2]Department of Physics, Nagoya University, (JAPAN); [3]CIC energiGUNE, (SPAIN)

17:20 Thermoelectric Properties and High-Temperature Stability of $Ca_3Co_4O_9$ Thin Films 41

1n_X3_2 *Brinks, P. [1]; Ihns, M. [1]; Van Nong, N. [2]; Breckenfeld, E. [3]; Martin, L. W. [3]; Pryds, N. [2]; Rijnders, G. [1]; ¨Huijben, M. [1]*

[1]University of Twente and MESA+ Institute for Nanotechnology, (NETHERLANDS); [2]Technical University of Denmark, (DENMARK); [3]University of Illinois, (UNITED STATES)

17:40 The $(ZnO)_k$ In_2O_3 System and its Microstructural, Structural and Thermoelectric Evaluation 41

1n_X3_3 *Kosir, M. [1]; Daneu, N. [1]; Reènik, A. [1]; Guilmeau, E. [2]; Bernik, S. [1]*

[1]Jozef Stefan Institute, (SLOVENIA); [2]Laboratoire CRISMAT/ENSICAEN, (FRANCE)

18:00 Synthesis of $Nd_{1-x}Ca_xCoO_3$ Perovskites Nanowires for Thermoelectric Applications 42

1n_X3_4 *Clara, M ; Culebras, M ; Gómez, A ; Sapiña, F ; Cantarero, A*

University of Valencia, (SPAIN)

Session T2: Theory II

Chair: X. Zianni

Room: Einstein

16:40 Theoretical Study of Point Defects in Mg_2X (X = Si, Ge, Sn) Thermoelectric Materials 42

1e_T2_1 *Zwolenski, P. ; Tobola, J. ; Kaprzyk, S.*

AGH University of Science and Technology, (POLAND)

17:00 Electronic Structure and Thermoelectric Properties of Pseudo-Quaternary Mg_2(Si,Sn,Ge)-Based

1e_T2_2 **Materials 43**

Kutorasinski, K. [1]; Tobola, J. [1]; Kaprzyk, S. [1]; Khan, A. U. [2]; Kyratsi, T. [2]

[1]AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Krakow, (POLAND); [2]Department of Mechanical and Manufacturing Engineering, University of Cyprus, (CYPRUS)

17:20 Computational Investigation of the Electronic and Thermoelectric Properties of Strained Bulk Mg_2Si..... 44

1e_T2_3 *Balout, H. ; Boulet, P. ; Record, M. C.*

Aix-Marseille University, (FRANCE)

17:40 Phonon Drag Effect in $FeGa_3$ 44

1e_T2_4 *Wagner-Reetz, M. [1]; Kasinathan, D. [1]; Schnelle, W. [1]; Cardoso-Gil, R. [1]; Rosner, H. [1]; Gille, P. [2]; Grin, Y. [1]*

[1]Max-Planck-Institut für Chemische Physik fester Stoffe, (GERMANY); [2]Ludwigs-Maximilians-Universität, (GERMANY)

18:00 A First-Principles Study of the Role of Lanthanum Substitution in Reducing Lattice Thermal

1e_T2_5 **Conductivity of the Thermoelectric Compound $AgSbTe_2$ (P4/mmm) 44**

Amouyal, Y.

Technion - Israel Institute of Technology, (ISRAEL)

18:20 Welcome Reception

Tuesday 19 November

Session B1: Silicides, Stannides and Germanides I
Chair: H. Böttner
Room: Newton

09:00 **[Invited Speaker] Current Status of Mg_2Si to Realize Practical Thermal-to-Electric Power Generation**
2n_B1_1 **Device 44**
Iida, T. [1]; Sakamoto, T. [2]; Taguchi, Y. [3]; Hirayama, N. [1]; Ishikawa, M. [1]; Nemoto, T. [4]; Kogo, Y. [1]; Nishio, K. [1]; Takanashi, Y. [1]
[1]Tokyo University of Science, (JAPAN); [2]JSPS postdoctoral research fellow, (JAPAN); [3]Yasunaga Corporation, (JAPAN); [4]Nippon Thermostat Co, (JAPAN)

09:40 **Thermoelectric Property of N-Type Mg_2Si Synthesized by the Convenient Melt-Growth Method..... 45**
2n_B1_2 *Udono, H. ; Kambe, K.*
Ibaraki University, (JAPAN)

10:00 **Mg and Mn Silicides : Material Development and Up Scaling, Thermoelectric Properties, Pre**
2n_B1_3 **Contacting and Module Assembling..... 46**
Pacheco, V. ; Recknagel, C. ; Pöhle, G. ; Senftleben, F. ; Wieland, S. ; Weissgaerber, T. ; Kieback, B.
Fraunhofer IFAM, (GERMANY)

10:20 **Thermoelectric Properties of P- and N-Type Mg_2Si Compounds Obtained by SHS 46**
2n_B1_4 *Mars, K. ; Godlewska, E.*
AGH University of Science and Technology, (POLAND)

10:40 **Optimizing Thermoelectric Properties of Mg_2Si: Fabrication Parameters and the Influence of MgO..... 47**
2n_B1_5 *de Boor, J. ; Compere, C. ; Dasgupta, T. ; Stiewe, C. ; Schmitz, A. ; Kolb, H. ; Kelm, K. ; Müller, E.*
German Aerospace Center (DLR), (GERMANY)

Session N1: Nano-Structures I
Chair: M. Martin-Gonzalez
Room: Einstein

09:00 **Electrodeposition of Composition-Controlled $(Bi_{1-x}Sbx)_2Te_3$ Nanowires in Polycarbonate**
2e_N1_1 **Membranes 47**
Schoenleber, J. [1]; Stein, N. [1]; Montaigne, F. [1]; Migot, S. [1]; Zhang, Y. [2]; Boulanger, C. [1]
[1]University of Lorraine/Institut Jean Lamour, (FRANCE); [2]University of Lorraine/LEM3, (FRANCE)

09:20 **Defect Engineering of Bi_2Te_3-Based Thermoelectric Nanowires and Topological Surface States 48**
2e_N1_2 *Nielsch, K. [1]; Bässler, S. [1]; Hamdou, B. [1]; Böhnert , T. [1]; Kimling, J. [1]; Gooth, J. [1]; Pippel, E. [2]*
[1]University of Hamburg, (GERMANY); [2]Max Planck Inst. of Microstructure Physics, (GERMANY)

09:40 **Thermal Conductivity of Bi_2Te_3 Nanowires Arrays: Theory, Fabrication and Measurements..... 48**
2e_N1_3 *Cantarero, A. [1]; Manzano, C. V. [2]; Martin, J. [2]; Caballero, O. [2]; Martín-González, M. [2]; de Lima Jr., M. M. [1]; de Tomás, C. [3]; Àlvarez, F. X. [3]*
[1]Uni. of Valencia, (SPAIN); [2]IMM-CNM-CSIC, (SPAIN); [3]Autonomous University of Barcelona, (SPAIN)

10:00 **Investigation of Thermal Transport in InAs Nanowires for Thermoelectric Applications..... 49**
2e_N1_4 *Swinkels, M.Y. ; Zardo, I. ; Cavalli, A. ; Plissard, S.R. ; van der Heijden, R.W. ; Bakkers, E.P.A.M.*
Eindhoven University of Technology, (NETHERLANDS)

10:20 **Thermal Transport Across Ultrathin Silicon Membranes and Asymmetric Nanowires 50**
2e_N1_5 *Ferrando, P. [1]; Lopeandía, A.F. [1]; Abad, L.I. [2]; Alvarez, F.X. [1]; Garcia, G. [1]; Muñoz-Pascual, F.X. [2]; Rodriguez-Viejo, J. [1]*
[1]Univ. Autònoma de Barcelona, (SPAIN); [2]Inst. de Microelectrónica de Barcelona, IMB-CNM, (SPAIN)

10:40 **Synthesis and Seebeck Measurements of Thermoelectric $Bi_{1-x}Sb_x$ Nanowire Array..... 50**
2e_N1_6 *Cassinelli, M. [12]; Müller, S. [2]; Voss, K.-O. [2]; Völklein, F. [3]; Trautmann, C. [12]; Toimil-Molares, M.E. [2]*
[1]Technische Universtät Darmstadt, (GERMANY); [2]GSI Helmholtz Centre for Heavy Ion Research, (GERMANY); [3]University of Applied Sciences Wiesbaden, (GERMANY)

11:00 ***Coffee Break***

Session B2: Silicides, Stannides and Germanides II

Chair: T. Kyratsi

Room: Newton

11:20 **Relation between Crystallographic Structure and Thermoelectric Properties of Undoped and Ag-**

2n_B2_1 **Doped $Mg_2Si_{1-x}Sn_x$ 50**

Bourgeois, J. [1]; Recour, Q. [1]; Chaput, L. [1]; Tobola, J. [2]; Berthebaud, D. [3]; Gascoin, F. [3]; Scherrer, H. [1]

[1]Université de Lorraine-Institut Jean Lamour, (FRANCE); [2]Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, (POLAND); [3]CRISMAT, (FRANCE)

11:40 **Synchrotron Study of Ag Doped Mg_2Si: Correlation Between Properties and Structure..... 51**

2n_B2_2 *Prytuliak, A. [1]; Godlewska, E. [2]; Mars, K. [2]*

[1]European Space Agency, (NETHERLANDS); [2]AGH University of science and technology, (POLAND)

12:00 **Evaluation of the Performance of a Two-Leg Unicouple (Bi-Doped $Mg_2Si_{0.6}Ge_{0.4}$ / Ge-Doped**

2n_B2_3 **$Mn_{1.75}Si$)..... *51***

Recour, Q. [1]; Ihou-Mouko, H. [1]; Bourgeois, J. [1]; Poli, G. [2]; Roux, J. P. [2]; Stephenson, K. [3]; Scherrer, H. [1]

[1]Université de Lorraine, (FRANCE); [2]AREVA TA, (FRANCE); [3]ESA-ESTEC, (NETHERLANDS)

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AGH University of Science and Technology, (POLAND)

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[1]Aristotle University of Thessaloniki, (GREECE); [2]University of Cyprus, (CYPRUS)

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Room: Einstein

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[1]Univ. of Milano Bicocca, (ITALY); [2]Univ. of Modena and Reggio Emilia, (ITALY); [4]CNR, Institute of Nanoscience−S3, (ITALY); [5]Technical Univ. of Vienna, (AUSTRIA); [6]Inst. of Chalkida, Psachna, and Inst. Microelectr.,(GREECE)

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[1]Universitat Autònoma de Barcelona, (SPAIN); [2]Intstituto de Ciencia de Materiales de Barcelona, (SPAIN); [3]Instituto de Nanociencia y Nanotecnología, ICN2, (SPAIN)

12:00 **Effect of Pore Sizes on the Reduction in Lattice Thermal Conductivity of Nano to Micro Scale Porous**

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Niarchos, D.; Tarkhanyan, R.

Institute for Advanced Materials, Physicochemical Processes, Nanotechnology & Microsystems, Demokrit, (GREECE)

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Institute for Microelectronics, Technical University of Vienna, (AUSTRIA)

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Wang, T. H. ; Jeng, H. T.

National Tsing Hua University, (TAIWAN)

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Session G1: TE Modules and Generators I

Chair: D. Narducci

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2n_W_1 **Properties** **59**
Li, Q.
Brookhaven National Laboratory, (UNITED STATES)

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2n_W_2 *Nielsch, K. [1]; Kimling, J. [1]; Böhnert, T. [1]; Gooth, J. [1]; Martens, S. [1]; Rott, K. [2]; Reiss, G. [2]*
[1]University of Hamburg, (GERMANY); [2]University of Bielefeld, Germany, (GERMANY)
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2n_W_3 *Feng, B. ; Martin, H.-P. ; Michaelis, A.*
Fraunhofer Institute for Ceramic Technologies and Systems, (GERMANY)
18:00 **High-Temperature Thermoelectric Properties of Tetrahedrites $Cu_{12}Sb_{4-x}Te_xS_{13}$** **60**
2n_W_4 *Bouyrie, Y. ; Candolfi, C. ; Masschelein, P. ; Ohorodniichuk , V. ; Daucher, A. ; Lenoir, B.*
Jean-Lamour Institut, (FRANCE)

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[1]Tokyo University of Science, (JAPAN); [2]Yasunaga Corporation, (JAPAN)
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2e_G2_2 *Min, G.*
School of Engineering, Cardiff University, (UNITED KINGDOM)
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2e_G2_3 *Semeniuk, V. ; Dekhtiaruk, R.*
Thermion Company, (UKRAINE)
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2e_G2_4 **Exploration Missions** **62**
Dimitriadou, I.A. [1]; Robbins, M.C. [1]; Williams, H.R. [2]; Freidman, U. [3]; Ambrosi, R.M. [2]; Reece, M.J [4]; Chen, K. [4]; Ning, H. [4]; Stephenson, K. [5]
[1]European Thermodynamics Limited, (UNITED KINGDOM); [2]University of Leicester, Department of ...Physics and Astronomy, (UNITED KINGDOM); [3]University of Leicester, Department of Engineering, (UNITED KINGDOM); [4]Queen Mary University of London, (UNITED KINGDOM); [5]European Space Agency, (NETHERLANDS)

20:00 ***Conference Dinner at Breakers Beach House in Noordwijk aan Zee***

Wednesday 20 November 2013

Session M1: Measurements I

Chair: E. Müller

Room: Newton

Session D: Skutterudites, Half Heusler and Zintls

Chair: J. Snyder

Room: Einstein

11:00 Coffee Break

Session M2: Measurements II

Chair: A. Burkov

Room: Newton

Session E: Sulfides and Clathrates

Chair: J. König

Room: Einstein

13:00 Lunch Break

Session A: Automotive Applications

Chair: M. Codecasa

Room: Newton

Session Y: Organics, Ionic and Liquids

Chair: G. Min

Room: Einstein

Session S: Space Applications *(Plenary)*
Chair: K. Stephenson
Room: Newton

Poster Session I – Monday 18 November 2013

Poster Session II – Tuesday 19 November 2013

Poster Session III – Wednesday 20 November 2013

Optimizing Performance in Thermoelectric Alloys

Snyder, G.J.
California Institute of Technology, UNITED STATES

Efficient operation of a thermoelectric device requires many variables to optimize. Achieving the maximum zT of a typical thermoelectric semiconductor requires optimization of the carrier concentration. Assuming the carrier concentration can be optimized the maximum zT is then determined by the quality factor which depends on the material parameters of the semiconductor – effective mass, carrier pocket degeneracy, deformation potential, lattice thermal conductivity which leads to a rational consideration of the trade-offs. For example, many unconventional electronic structures that increase effective mass are being studied or proposed for high efficiency thermoelectric materials. However high effective mass of the carriers due to flat bands results in low mobility, which leads to lower zT. Instead, high DOS effective mass due to high valley degeneracy leads to high zT. For example, utilizing the high degeneracy second valence band in PbTe leads to nearly twice the zT than that of the low degeneracy first valence band. Alloying with point defects is another example where both benefit and detriment occur from the same process. By analyzing the effect on the quality factor a rational criteria can be derived to determine and quantify the benefit of alloying. Finally these parameters are all temperature dependent and by considering the temperature dependence of the quality factor, band gap and optimal carrier concentration further advances in overall efficiency can be engineered. References Yanzhong Pei, Heng Wang and G. Jeffrey Snyder “Band Engineering of Thermoelectric Materials” Advanced Materials 24, 6125 (2012) Heng Wang, Yanzhong Pei, Aaron D. LaLonde and G. Jeffrey Snyder “The Criteria for Beneficial Disorder in Thermoelectric Solid Solutions” Advanced Functional Materials23, 1586 (2013)

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Transport Properties of Misfit Layered Cobaltite Thin Films Synthesized by Polymer Assisted Deposition

Rivas-Murias, B.; Vila-Fungueiriño, J. M.; Rivadulla, F.
CIQUS-University of Santiago de Compostela, SPAIN

Devices based on thermoelectric materials could play an important role in power generation and refrigeration if their efficiency is sufficiently increased. The efficiency of the device is determined by the figure of merit of the thermoelectric material z=S2/ñê, where ñ, S and ê are the electrical resistivity, the Seebeck coefficient, and the thermal conductivity, respectively [1,2]. Alloys and compounds of IVA to VIA elements show the highest values of z (=1-2 at their optimal operation temperature) but it seems that they already reached their maximum efficiency. Therefore, there is a demand of new materials for the next generation of thermoelectrics. In this respect, oxide-based nanostructures could accomplish many of these demands. For example, misfit layered cobalt oxides such as Ca3Co4O9 and Bi2Sr2Co2Oy [3,4], show a large power factor S2/ñ, and their thermal conductivity could be conviently reduced if they are prepared in the the form of thin-films or nanowires. Here we present the synthesis of high-quality thin-films of A3Co4O9 (A=Ca,Sr) and Bi2A2Co2Oy (A=Ca,Sr,Ba) by polymer assisted deposition (PAD) [5,6]. Aqueous solutions of EDTA-Metal complexes coordinated to polyethileneimine are spin-coated in single-crystalline substrates and subsequently annealed at high temperature. The result is high quality oriented thin-films whose stoichiometry and thickness can be easily controlled. Their structural, morfological and transport (S and ñ) properties have been characterized and compared with the literature. We show that this simple chemical method produces high-quality films over large areas, with transport properties comparable to these obtained in dense ceramic samples.

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[2] T. M. Tritt, M.A. Subramanian, MRS Bulletin 31, 188 (2006).
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[6] A. K. Burrell, T. M. McCleskey, Q. X. Jia, Chem. Commun., 1271 (2008).

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High Temperature Thermoelectric Conversion Employing Calcium Manganates

Thiel, P.; Populoh, S.; Saucke, G.; Shkabko, A.; Eilertsen, J.; Rigort, R.; Brunko, O.; Trottmann, M.; Sagarna, L.; Karvonen, L.; Weidenkaff, A.
empa - Swiss Federal Laboratories for Materials Science and Technology, SWITZERLAND

The polycrystalline tungsten-substituted $CaMn_{1-xW_x}O_{3-ä}$; x = 0.00-0.05 series was prepared from a combustible precursor and sintered to highly dense bodies. Substitution of manganese(IV) by tungsten(VI) is confirmed by powder X-ray diffraction and X-ray photoelectron spectroscopy studies. The impact of tungsten substitution on the crystal structure, thermal stability, phase transition, electronic and thermal transport properties is evaluated. Tungsten substitution leads to an increase of mobile negative charge carriers and strongly affects the oxygen deficiencies. In the high dimensionless figure-of-merit (ZT)-region starting from about T=1000 K "self-doping" due to the formation of oxygen vacancies dominates the electronic transport, diminishing the effect of tungsten substitution. The lattice thermal conductivity near room temperature is significantly reduced with increasing tungsten concentration due to mass-difference impurity scattering. The best ZT of 0.25 is found for x=0.04 at 1225 K. In a further step thermoelectric converters are manufactured and measured in a high-temperature testing rig up to 1098 K in ambient air. Power densities of 240 W/cm^2 are reached.

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New Aspects in Oxide Thermoelectric Materials with Unconventionally Enhanced Phonon Scattering

Ohtaki, M.; Miyaishi, S.; Mizuta, K.
Kyushu University, JAPAN

Recuperation of waste heat energy, which amounts to two-third of the total primary energy supply in our modern society, is attracting more and keener interests particularly in the manufacturing, energy, and transportation sectors in industry, because diversification of energy resources is becoming more and more of vital importance for better energy security options. Oxide materials, which are highly durable at high temperature in air, non-toxic, low cost with minimal environmental impact, are apparently promising for recuperation of decentralized waste heat energy at the temperature range of > 400 ←$B!←(BC, where all the non-oxide candidate materials will eventually be oxidized under aerobic conditions. Although strongly ionic characters of oxide materials has been regarded as an inherent disadvantage leading to low carrier mobility and high lattice thermal conductivity, it has been revealed that such disadvantages are not always the case with all oxides. Recent reports on reduced ferroelectric oxides [1] and cage-like structure oxides [2] are convincing that the simple picture of ionic compounds no longer holds for these oxides.

In this paper, some new aspects in metal oxides that show unconventionally enhanced phonon scattering will be highlighted in terms of their transport properties and crystal structures. In particular, ←$B&B←(B-pyrochlore oxides $ATaWO_6$ (A = K, Rb, Cs) show lower lattice thermal conductivity with decreasing the mass and size of the A-site alkali cations, clearly evidencing that the larger size mismatch between the A-site cations and the surrounding oversized cage framework enhances the ←$B!H←(Brattling←$B!I←(B motion of the A-site cations and thereby efficiently shortens the phonon mean free path more for the smaller A-site cations. As a consequence, the thermal conductivity of the oxide with the smallest A cation, $KTaWO_6$, was revealed to be virtually the same with its theoretical minimum, ←$B&J←($B_{min}$, as shown in Fig. 1.

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[2] M. Ohtaki, S. Miyaishi, *J. Electron. Mater.*, **42**, 1299-1302 (2013).
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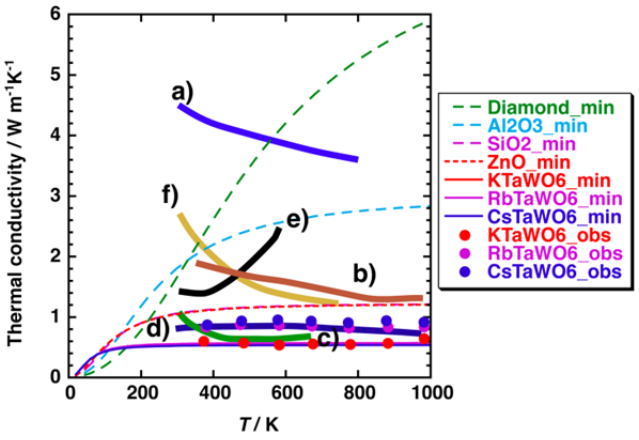

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Novel Apparatus for Transport Properties Measurements of Thin Films under Sulphur Atmosphere at Moderate Temperatures (Room Temperature to 400°C)

Clamagirand, J.M.; Ares, J.R.; Ferrer, I.J.; Sanchez, C.
Universidad Autónoma de Madrid, SPAIN

Metal-based chalcogenides form an important group considered to be used in thermoelectric application due to their adequate transport properties and its wide

number of compounds. However, it is needed to find less expensive and non toxic chalcogenides with better transport properties in the near-room temperature range to achieve a major implementation at different applications. To this aim, research is focused on metal sulphide compounds [1,2] due to the abundance, low toxicity and cheapness of sulphur compared to other chalcogenides. Sulphides are frequently formed by a solid-gas reaction controlled by the sulphur pressure (P(S2)) and metal temperature (T) that define the formed phase (according to thermodynamic and kinetic of the reaction) and subsequently, the thermoelectric properties. Therefore, an "in situ" measurement system of the transport properties during the sulphidation process is required to investigate, in accurately way, the thermoelectric properties of the sulphides phases formed at different P(S2) and T as well as the formation mechanism.

However, experimental set-up built up to measure "in situ" thermoelectric properties are frequently performed under an inert gas (He, N2) or vacuum [3] but not under gases like sulphur due to its very high reactivity, complicated pressure control, ..etc. In this work, we present a novel experimental system able to monitored the transport properties of metallic thin films under a sulphur atmosphere. Resistance and thermopower could be measured up to 400 °C and P(S2) < 10 mb. Film temperature and sulphur pressure are controlled in an independent way. Experimental set-up was calibrated by measuring the transport properties of palladium and several semiconductors films ("n" and "p" type) under different atmospheres (He and air), pressures and temperatures. "In situ" transport properties measurements obtained during sulphuration of palladium films will be shown and compared to previous results [2]. Results provide useful information about the metal sulphuration process (phases formed and their thermoelectric properties) and they may be extended to other "chalcogenization" formation processes.

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Acknowledgements

Authors thanks to F. Moreno for technical support and MAT-2011-22780 from MINECO for financial support.

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Measurement of Thermal Conductivity on Nano Scaled Thin Film and Thin-Layered Materials

Marx, H.-W.[1]; Südmeyer, I.[2]; Rohde, M.[2]; Gaede, D.[2]; Seifert, H.J.[2]; Linseis, F.[1]; Linseis, C.[1]; Renner, H.[1]
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In recent years thin film and thin-layered materials become more and more important in research and industry (LEDs, phase change memories, thermo-electric materials, semiconductors ...). Reliable thermophysical data of those materials are needed, particularly thermal conductivity.

The standard method for thermal diffusivity measurement, the so called Laser Flash Method, is well suited for bulk materials, but it can be only restrictively used for thin materials (i.e. thin foils depending on the thermal transport properties of the material). Therefore, this method is not suited for measurement of thin layers and thin films in the sub-micrometer range because of limited rise time of the IR-detectors.

In recent years, a transient thermoreflectance method (Time Domain Thermoreflectance, TDTR) has been introduced enabling thermal conductivity measurement on nanometer scaled thin layers with high accuracy. As reflectance of light depends on the temperature of the reflecting material, reflected light can be used for temperature change measurement. This is a much faster method than the classical method by IR-detectors and thus enables measurement on thin films and layers.

Using this TDTR-technique, it has been proved on various samples, that thermal conductivity is strongly dependent on sample thickness. Thermal conductivity decreases with decreasing sample thickness by one or two orders of magnitude compared to those of the corresponding bulk materials.

A new instrument, the so called Nano Laserflash, has been developed in order to allow measurement of such nano scaled materials under different geometries and in temperature controlled environment. Measurement can be done either in front heating front detection (FF) or in rear heating front detection (RF) mode. The latter one which is also called "high speed laserflash method" is suitable only for transparent substrates; the FF-method can be used also for opaque substrates.

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Structural and Thermoelectric Properties of Binary and Ternary Skutterudite Thin Films

Daniel, M.[1]; Liebig, A.[1]; Gordan, O. D.[1]; Zahn, D. R. T.[1]; Plech, A.[2]; Albrecht, M.[1]

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Increasing interest in an efficiency enhancement of existing energy sources led to an extended research in the field of thermoelectricity. Especially skutterudites with its high power factor (electric conductivity times Seebeck coefficient) are suitable thermoelectric materials. The relatively high thermal conductivity can be further decreased by introducing loosely bound guest ions into the voids of the lattice of these materials. This yield to the well accepted concept for optimizing the efficiency of thermoelectric materials is Slack´s idea of phonon-glass electron-crystal [1].

In this work 30 nm thick thin films of the binary skutterudite compounds $CoSb_3$ and $FeSb_3$ have been deposited via MBE technique onto thermally oxidized Si(100) substrates at room temperature. The samples were post-annealed in ultra-high vacuum for one hour at 450°C to form the desired crystalline phase. Structural and electrical properties were investigated and compared for both compounds. The results agree with the work of J. R. Williams et al. [2], who reported on the formation of the metastable $FeSb_3$ compound.

Additionally 30 nm thin films of the ternary compound $Yb_x(CoSb_3)_4$ were deposited in the same way. Yb is situated in the voids of the $CoSb_3$ skutterudite phase, which was verified by X-ray diffraction combined with Rietveld refinement to extract the Yb filling fraction. The achieved maximum filling fraction of 0.68 is higher than the expected equilibrium value of x = 0.12 for bulk samples and the films exhibit a decrease of thermal conductivity with higher filling fraction. Moreover the electrical properties are drastically changed with respect to the binary $CoSb_3$.

[1] G. S. Nolas, D. T. Morelli, T. M. Tritt, Annu. Rev. Mater. Sci., 29: 89–116, 1999

[2] J. R. Williams, M. Johnson, and D. C. Johnson, J. Am. Chem. Soc., 123: 1645-1649, 2001

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Multilayered Ge/SiGe Material in Microfabricated Thermoelectric Modules

Samarelli, A.[1]; Ferre Llin, L.[1]; Zhang, Y.[1]; Weaver, J.M.R.[1]; Dobson, P.[1]; Cecchi, S.[2]; Chrastina, D.[2]; Isella, G.[2]; Etzelstorfer, T.[3]; Stangl, J.[3]; Muller, E.[4]; Paul, D.[1]

[1]University of Glasgow, UNITED KINGDOM; [2]Politecnico di Milano, ITALY; [3]Johannes Kepler Universitt, AUSTRIA; [4]ETH Zurich, SWITZERLAND

Commercial thermoelectric modules are still dominated by bulk Bi2Te3 alloys below 100 °C and PbTe is still one of the best performance thermoelectrics for applications below 500 °C. Te, however, is a rare and unsustainable material and Pb is banned from consumer devices due to its toxicity. Hence there is substantial interest in replacing these materials with more sustainable alternatives. The thermoelectric properties of major semiconductors such as Si, Ge and SiGe are poor compared to Bi2Te3 in commercial thermoelectric generators and Peltier coolers close to room temperature. The presence of low dimensional structure, however, such as quantum wells, quantum wires or quantum dots can dramatically enhance the thermoelectric performances of a material. Mature Si/SiGe and Ge/SiGe heteroepitaxial growth technology potentially allows engineered thermoelectric materials which would be compatible and integrable with CMOS and Si photonics circuits used in a range of applications. In this contribution, we report on low dimensional n- and p-type Ge/SiGe superlattices with Seebeck coefficients up to -540 µV/K at 330 K and ZTs of 0.65 with power factors substantially higher than n-Bi2Te3. A range of microfabricated test structures have been developed to characterize the electrical and thermo properties of a range of SiGe heterostructures grown directly on silicon wafers using a 200 mm diameter chemical vapour deposition growth system with growth rates up to 6 nm/s. Quantum well and quantum mechanical tunnel barriers with dimensions down to 1 nm have been designed, grown and tested. Band structure and phonon engineering has been used to optimize the material whilst low specific contact resistivity Ohmic contacts (down to 1.2 x 10–8 Ω-cm2) have been developed for high output powers in modules. Complete microfabricated modules using bump-bonding of both p-type and n-type Ge/SiGe superlattices will be presented and the performance compared to commercial modules.

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Development of Pulse Transient Hot Strip Method to Measure Thermal Transport Properties of Thin Film Materials

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A transient method for measuring thermal conductivity and thermal diffusivity of thin film materials has recently been developed. The method is based on a procedure by which a train of square on-off current pulses over a series of pulse periods (varied from a few nanoseconds to around 100 microseconds), via an AC-coupled circuit, is applied to a vapor-deposited gold strip. The gold strip acts both as a heat source and as a sensor of the temperature increase of the thin film sample. By performing transient experiments over short periods of time, it is possible to limit the probing depth under the strip so that the thermal properties of the substrate do not influence the recorded thermal properties of the film. A series of experiments with probing depth ranging from ca. 8 to 30 ìm has shown that the thermal properties measured with this technique are in agreement with literature values. Using this method it is also feasible to study how the anisotropy of the thermal properties evolves with increasing probing depth. Three reference 2'' wafers, fused quartz, gallium arsenide and silicon, have been successfully tested so far. This novel technique will likely open up possibilities for studying more complex materials such as thin films or layered thermoelectric materials.

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The Role of Sodium Rich Pre-Treatments in the Enhanced Sintering of Sodium Cobalt Oxide Thermoelectric Ceramics

Jakubczyk, J.E.; Dorey, R.A.; Sansom, C.L.
Cranfield University, School of Applied Sciences, UNITED KINGDOM

Oxide based thermoelectric materials are of growing interest for high temperature operation and as route to eliminate materials, such as Te and Pb, that pose issues of safety, sustainability and security of supply. NaCo2O4 bulk ceramic materials were prepared from powders synthesized using a solid state reaction (SSR) process. The effects of different Na-enriching pre-treats were evaluated with respect to microstructural evolution and thermoelectric and electric behavior of the samples. Such modifications were found to be a critical factor affecting the microstructure of the bulk ceramic materials. Both premixing the powder and infiltrating with a Na rich precursor solution into the material prior to sintering were found to improve density by up to 10%, increase electrical conductivity and help to compensate for Na loss at high sintering temperatures. A Seebeck coefficient and resistivity of 17μV/K and 2.85mΩm, respectively, was recorded around room temperature.

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High Temperature Thermoelectric Properties of Y and Fe co-dopants in $Ca_3Co_4O_{9+\delta}$

Wu, N.Y.; Nong, N.V.; Pryds, N.; Linderoth, S.
Technical University of Denmark, DENMARK

A series of $Ca_{3-x}Y_xCo_{4-y}Fe_yO_{9+\delta}$ powders was synthesized by auto-combustion reaction and densified with spark plasma sintering (SPS) processing. The electrical resistivity and the Seebeck coefficient increase with the increasing yttrium content, while the electrical resistivity decreases with the iron content below 0.05. The reasons for the increase in both the electrical resistivity and the Seebeck coefficiet with the yttrium substitution are due to the carrier (Co^{4+}) number reduction in CdI_2 type CoO_2 layer. In contrary, iron substitution below certain content may only occur in rock-salt type Ca_2CoO_3 layer resulting in the increase of the carrier number. The Y and Fe co-dopants effect on the thermal conductivity is not significant even though the yttrium heavier atomic weight is expected as an effective phonon scattering site. At 800 °C, the improved power factor of 520 $\mu W/m \cdot K^2$ from x=0.2 and y=0.03 sample was obtained, compared with the power factor of 450 $\mu W/m \cdot K^2$ from pure $Ca_3Co_4O_{9+\delta}$, which demonstrates the improvement of $Ca_3Co_4O_{9+\delta}$ thermoelectric properties with co-dopants yttrium and iron.

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Growth of Epitaxial $Ca_3Co_4O_9$ Thin Films by Reactive RF-Magnetron Sputtering with Post Annealing Process

Paul, B.; Kerdsongpanya, S.; Eklund, P.
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The misfit layered calcium cobalt oxide $Ca_3Co_4O_9$ are good thermoelectrics with high thermal and chemical stability in air, important for applications in high temperature regime. In term of thermoelectric properties $Ca_3Co_4O_9$ has large Seebeck coefficient together with relatively high electrical conductivity. Due to its layered structure the physical properties of $Ca_3Co_4O_9$ are highly anisotropic so for thermoelectric performance, epitaxial films are favoured. Thin-film synthesis of $Ca_3Co_4O_9$ has been investigated only to limited extent. Nevertheless, there are few methods have been reported: reactive solid-phase epitaxy by topotactic-ion exchange [1], pulsed laser deposition (PLD) [2, 3], and rf-magnetron sputtering from compound target ($Ca_3Co_4O_9$ target) [4, 5]. Here, we report the growth of epitaxial misfit layered cobalt oxide $[Ca_2CoO_3]_x[CoO_2]$ on $Al_2O_3(0001)$ substrate by co-

sputtering from Ca and Co-target by reactive rf-magnetron sputtering in presence of 1.5 % O_2 followed by post.deposition annealing. As-deposited films are found to be a mixture of CaO and CoO_2; after heat treatment at 700 °C in O_2-atmosphere well crystallized highly c-axis-oriented $[Ca_2CoO_3]_x[CoO_2]$ films are obtained. X-ray diffraction theta-2theta scans and pole figures reveal the films are epitaxial having out of plane (001)-orientation. Further, annealing of the grown films is found to vary its O_2-content depending on the annealing temperature and surrounding atmosphere. As thermoelectric performance is expected to be influenced by the variation of relative concentration of Ca and Co in the film the structural variation of the film as well as the presence of spurious phases with the evaluation of Ca and Co concentration are also studied.

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Manufacturing Process for TiO_x Based Thermoelectric Modules – from Suboxide Synthesis to Module Testing

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The class of reduced (non-stoichiometric) titanium dioxide, often designated as titanium suboxides, comprises different TiO_x phases with different reduction degree and hence varying amount of oxygen, is a promising material for thermoelectric investigation due to the peculiarity of the crystal structure and physical properties. These phases have a high melting point (T_{melt} > 1900 K), low electrical resistivity, e.g. for Ti_4O_7 of 1 mΩ·cm and high Seebeck coefficient of approx. 500 µV/K for $TiO_{1.99}$.

An overview of different TiO_x synthesis methods with regard to enhancement of the thermoelectric properties and the transfer of the synthesis process to cost-efficient methods as well as joining techniques for module manufacture will be presented. Different synthesis routes were carried out and investigated: the synthesis of TiO_x via carbothermal reduction of TiO_2 by a carbon source, a process with lesser gas-building by mixing TiO_2 and TiO_x, the bottom up approach, the precursor route for synthesizing the TiO_x directly and the combination by coating TiO_2 with precursor. All approaches reveal an adjustable phase composition with different oxygen content and, therefore, tunable electrical properties as well as different microstructures to enhance the physical and thermoelectric properties. The electrical resistivity could be adjusted by the oxygen content of TiO_x from 1 to 1000 mΩ·cm. With the precursor approach the syntheses of single Magnéli phase Ti_4O_7 and Ti_8O_{15} were realized. However, the research work has to expand not only to the optimization of the thermoelectric properties but also investigations of cost-efficient production chains of the material and joining techniques to build up a complete thermoelectric module. Thus, under aspects of shaping, sintering and machining, methods were investigated.

To realize thermal and electrical connections, technologies for joining and packaging were developed. For a first demonstration of the feasibility of TiO_x-based thermoelectric modules for high temperatures a unileg n-type module with a footprint of 30 x 30 mm^2 was designed. The low volume fabrication yielded in more than 20 single modules. Finally, the modules were successfully tested under conditions close to the desired applications with a hot side temperature up to 600°C.

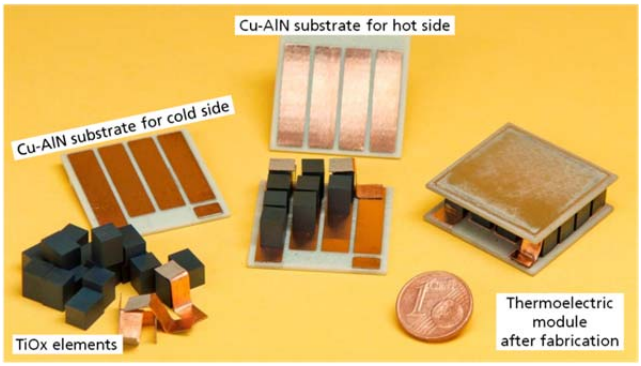

Image 1: Components for TiO_x based unileg modules

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Microstrucutre of Nb-$SrTiO_3$ Ceramics with SrO-excess and with Addition of $Sr_3Ti_2O_7$ Platelet Seeds

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Nb-doped $SrTiO_3$ is a promising candidate for n-type high-temperature thermoelectric material. Although its figure of merit ZT is one of the highest among high-temperature oxides[2] (ZT ~ 0,37), it still needs to be improved for practical use. The main drawback of this material is its relatively high thermal conductivity. However, in Nb-

doped $SrTiO_3$ the thermal conductivity can be lowered by incorporation of more or less ordered SrO planar faults with a rock salt-type structure into the perovskite structure and/or by processing textured microstructures. The latter can be achieved by addition of platelet seeds to powder mixture prior to sintering. It is expected that the presence of more or less ordered SrO planar faults in SrO-doped Nb-$SrTiO_3$ will increase phonon scattering and consequently lower the thermal conductivity of this material.

In view of this, our present work was focused on processing Nb-doped $SrTiO_3$ with either nonstoichiometric composition and/or with anisotropic microstructure. In Nb-doped $SrTiO_3$ the planar faults were introduced by small excess of SrO which was added in the form of carbonate prior to sintering. Furthermore, $Sr_3Ti_2O_7$ platelet seeds, obtained with molten salt synthesis, were also added to the Nb-$SrTiO_3$ solid state powder to increase the anisotropic growth of the grains. The samples were pressed and sintered in hydrogen atmosphere at 1450-1500°C for 2-3 hours. The microstructure analysis using SEM and TEM showed that the SrO-excess indeed caused planar faults formation within anisotropic grains in Nb-doped $SrTiO_3$ and that the $Sr_3Ti_2O_7$-type seeds additionally promoted the anisotropic growth of the grains. However, the XRD and EDXS results also revealed that the material was not exclusively Nb-doped $SrTiO_3$; excess strontium partly reacted with the dopant Nb_2O_5, forming strontium niobates.

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Band Structure Engineering in Geometry Modulated Nanostructures for Thermoelectric Efficiency Enhancement

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Several band structure engineering strategies have been adopted in the last two decades to achieve enhancement of the efficiency of thermoelectric materials. Characteristic examples are low-dimensional structures and heterostructures, where quantum confinement results in modification of the energy spectrum of charge and heat carriers favoring their thermoelectric properties. Resonant states introduced by impurities have also shown to modify the density of states of carriers and work in the same direction. Geometry modulated nanostructures are also structures where quantum confinement effects have dominant role and the energy spectrum of carriers can be engineered. We have shown that modulation of the confining dimension of a nanowire causes modification of the energy dependence of the transmission probability of electrons and phonons. On one hand, the overall transmission of phonons can be thereby reduced resulting in significant decrease of the thermal conductivity. On the other hand, the energy dependence of the electron transmission can have complex structure with sharp features, discontinuities and resonances that result in enhanced thermopower and power factor. Our recent calculations on the band structure of width-modulated nanowires show that their electron energy spectrum consists of minibands and resonances that are known to favor the thermoelectric transport properties. Here, we will present our results and we will discuss the relation between the geometry modulation and the formation of minibands and resonances in the electron energy spectrum for materials of interest.

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Influence of Nonlinearity of Phonon Spectrum on Thermal Conductivity in Nanostructured Material Based on Bi-Sb-Te

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A theoretical investigation of thermal conductivity in nanostructured material based on Bi-Sb-Te is presented. The real phonon spectrum from first-principles calculations based on density functional theory was taken into account. The phonon spectrum was calculated using both local density approximation (LDA) and generalized gradient approximations (GGA). It has appeared that influence of the anisotropy of relaxation time on the anisotropy of thermal conductivity exceeds the influence of the anisotropy of phonon spectrum. The decrease of thermal conductivity caused by nanostructuring was compared to a calculation in the linear Debye approach. The calculations have shown that phonon boundary scattering can lead to decrease of lattice thermal conductivity on 55% at the grain size ~ 20nm in Debye approach taking into account specified Debye boundary frequencies of acoustic phonons defined from the calculated spectrum. The nonlinearity of the acoustic phonon spectrum additionally predicts 20 % decrease in thermal conductivity connected with the phonon

boundary scattering. The reason is that consideration of the real phonon spectrum increases the relative contribution to thermal conductivity of acoustic phonons with low frequencies which scatter more strongly on nanograins boundaries. The similar situation takes place also for phonon scattering on nanoinclusions. Estimations in Debye approach show that thermal conductivity decrease on 15 %. And taking into account the real phonon spectrum gives additionally 8 % decrease of thermal conductivity. A role of optical phonons can increase at such considerable reduction of lattice thermal conductivity. Therefore a calculation of optical phonons contribution in thermal conductivity has been fulfilled. Estimations have shown that their contribution is insignificant and can reach 18 % in a pure material and 6 % in a solid solution. As a result the reduction of lattice thermal conductivity due to optical phonon scattering can decrease no more than for 10 %. Besides, estimations of minimum lattice thermal conductivity taking into account the calculated real phonon spectrum have been fulfilled. The contribution of acoustic phonons in minimum lattice thermal conductivity taking into account axes averaging is 0.07 W/m.K (or 0.09 W/m.K in Debye approach). Taking into consideration the contribution of optical modes the minimum lattice thermal conductivity reaches the value 0.14 W/m.K. The work was supported by the Russian Foundation for Basic Research, grant 1 12-08-00283-a.

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Effect of Spin-orbit Interaction on Electronic Structure and Electron Transport Properties of Mg_2X (X=Si, Ge, Sn)

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Mg2x (X= Si, Ge, Sn) compounds and their alloys belong nowadays to the most promising materials for thermoelectric applications, due to high abundance of relatively cheap elements and high figure of merit. The scope of this work is to study relativistic effects, including spin-orbit (SO) interaction, on electronic structure and electron transport properties of Mg2X. Based on the Korringa-Kohn-Rostoker method [1-2] with fully relativistic crystal potential, electronic dispersion relations were calculated. Hereafter, electron transport properties as electrical conductivity, thermopower and electronic thermal conductivity, were determined in the framework of the Boltzmann transport theory [3]. The large SO splitting of the valence bands at Gamma point are found for X= Sn, Ge,while for X= Si the effect is much weaker, with the SO splitting values in very good agreement with optical measurements [4]. Comparing computational results of transport coefficients within relativistic and non relativistic treatement, we show that the SO splitting of top valence bands has remarkable influence on overall transport properties, e.g. p-type thermopower decreases almost twice for $p<10^{20}$ cm-3 for Mg2Sn. Conversely, rather small effect of SO interaction on electron transport properties was computed in n-type Mg2X compounds.
The work was partly supported by the National Science Center (NCN) in Poland under grants (DEC-2011/02/A/ST3/00124 and UMO- 2011/03/N/ST3/02644)

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Coherence Appearance in Thermal Transport from a Thermodynamic Approach

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Understanding the behaviour of thermal conductivity in all kind of materials is one of the key points to definitely control thermoelectricity. Thermoelectric Figure of merit (Z) tells us that reduction of thermal conductivity is related with improvement of thermoelectric efficiency and that usually, a loss of performance is related with the inefficacy of a material to correctly block heat flux.

In the last years, reduction of thermal conductivity by reducing the size of the system has been the main choice to improve thermoelectricity. Theoretical predictions of the influence of boundary effects on thermal transport led the engineers to follow this tecnique. This has given new materials with significatively better values of efficiency than classic materials. But this size related improvement seems to be achieved a limit and new ways of improvement are needed. Some other techniques like modulating the concentrations in alloys are starting to replace miniaturization. Scalability of this kind of techniques is also important in order to bet on their practical expectations.

From the theoretical point of view, the influence of the different scattering mechanisms on this transport property is still under debate. Parallelly, observations in this new class of materials seem to indicate that coherence is important to undestand the data, introducing new phenomenology in the topic. A model able to describe and predict all this experiments are needed to help the engineers in their future designs.

We present a model to account for the physics behind thermal transport that is able to predict the influence of the size and the change in the relative abundances in pure and alloy materials. The resulting model is expressed as a smooth transition between ballistic regime and coherent regime. We apply the model to predict the thermal conductivity of Si, Ge and Diamond materials in bulk, thin films and nanowire geometries and an accurate fit is obtained.

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From Oxides to Sulfides and Selenides: Optimization of the Power Factor

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Among new materials for thermoelectricity, the oxides have been investigated in details due to the potential positive impact of electronic correlations on thermopower. Several structural families have been prepared, and in this talk I will first briefly summarize the results concerning the best oxides. The power factors are still too small, due to a large value of electrical resistivity, and the possibility to decrease this resistivity by going from oxides to selenides and sulfides is now considered. Following our work on oxides, I will present two different examples among these chalcogenides, of materials in which a large power factor can be obtained. I will first present results obtained in selenides pseudo - hollandites, in which large ZT values (0.5 at 800K) can be obtained due to the combination of a large Seebeck value, associated to a large scattering parameter in the standard Boltzmann transport equation, together with a very small thermal conductivity [1]. I will then show the results recently obtained in sulfides.

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Thermoelectric Properties and High-Temperature Stability of $Ca_3Co_4O_9$ Thin Films

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Oxide materials are good candidates for thermoelectric applications due to their chemical stability at elevated temperatures, with several layered cobaltites, such as $Ca_3Co_4O_9$, as the most promising p-type materials. Using thin films or superlattices, additional control over the structural properties of $Ca_3Co_4O_9$ can be achieved because of the structural coupling with the substrate. Here we present our results of the thermal stability and high-temperature thermoelectric properties of single-phase $Ca_3Co_4O_9$ thin films under different environmental conditions.

We show that single-phase epitaxial $Ca_3Co_4O_9$ thin films can be grown on hexagonal Al_2O_3 and cubic LSAT single crystal substrates by pulsed laser deposition. Additionally we demonstrate that for optimized deposition parameters and a thickness of at least 60nm, the Seebeck coefficient and electrical conductivity at room temperature are comparable to bulk samples, when deposited on an Al_2O_3 single crystal substrate. While the in-plane Seebeck coefficient remains nearly constant with film thickness, the in-plane resistivity shows a sharp increase when the film thickness is reduced below 60nm. Furthermore, for these optimized $Ca_3Co_4O_9$ thin films a significant suppression of the out-of-plane thermal conductivity, compared to bulk and single crystal samples, is observed at room temperature, demonstrating their thermoelectric potential.

Additionally we present the thermal stability of these $Ca_3Co_4O_9$ thin films by high-temperature X-Ray diffraction measurements and relate the structural stability to the high-temperature thermoelectric properties. We show that the background gas strongly influences the thermal stability of the $Ca_3Co_4O_9$ thin films. While thin films only remain stable up to 250°C in helium background gas, in an oxygen environment the thin films remain even stable up to 600°C demonstrating the importance of the environment on the stability of these thermoelectric oxide thin films. For these stable samples in an oxygen environment a significant enhancement of the Seebeck coefficient to 200µV/K is observed at a temperature of 600°C.

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The $(ZnO)_k$ In_2O_3 System and its Microstructural, Structural and Thermoelectric Evaluation

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The main goal of our work was to assess the influence of the amount of added In_2O_3 on the phase composition, microstructure and formation of structural defects in $(ZnO)_k$ In_2O_3 ceramics and correlations to their thermoelectric properties. We studied compositions for selected k values in range from 5 to 36. The samples were

prepared from oxide powders by standard ceramic procedure and conventionally sintered them in air atmosphere at temperatures in the range from 900 to 1500 °C for 2 h to 144 h on peak temperature. For comparison, we also prepared samples using PECS (Pulsed Electric Current Sintering) in temperature range from 900 to 1150 °C for 2-10 min holding time at peak temperature. For microstructure observations using SEM we thermally etched pre-polished pellets in cross-section. This revealed planar defects and indicated their control of grain growth with development of oblong shaped grains. Nevertheless, there is a profound difference in density connected to the composition between samples; for k = 5 is the lowest and is getting higher with increasing k values. The slow densification process is connected to the early $Zn_5In_2O_8$ phase formation around 1100 °C with oblong grains, creating large voids in between them. With increasing temperature, the grain growth is filling up the voids and enhancing density. We also investigated defect structure under HRTEM and found consistency with previous reports. The In ion incorporation is done through basal planes in ZnO and is creating a series of planar defects acting as inversion boundaries. All these microstructural and structural characteristics are contributing to the thermoelectric characteristics of the samples as shown by measurements of their thermoelectric parameters, which will be presented and discussed.

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Synthesis of $Nd_{1-x}Ca_xCoO_3$ Perovskites Nanowires for Thermoelectric Applications

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Recently, thermoelectric materials have attracted a big interest due to the possibility of developing devices to produce energy. The thermoelectric efficiency of these materials is measured by the dimensionless figure of merit $ZT=S^2T\sigma/\kappa$; σ and κ being the electrical and thermal conductivities, respectively, and S the Seebeck coefficient. Perovskite materials are great candidates for thermoelectric applications because they have a large Seebeck effect and good electrical conductivity at high temperatures. Nanostructuration, especially as nanowire type structures, can be the key to develop high efficient thermoelectric materials. In comparison with bulk, in nanostructured materials the density of electronic states usually has sharp peaks and theoretically a large Seebeck coefficient if the Fermi level is located around a maximum in the electronic density of states. Also, the phonon dynamics and heat transport in a nanostructured system can be tailored. Nanomaterials with one or more dimension smaller than the mean free path of phonons, but larger than that of electrons will noticeably reduce ê without affecting electrical transport. In this work, we have synthesized $Nd_{1-x}Ca_xCoO_3$ nanowires (diameter 25 nm) by hydrothermal method with different amount of calcium in order to evaluate the thermoelectric properties.

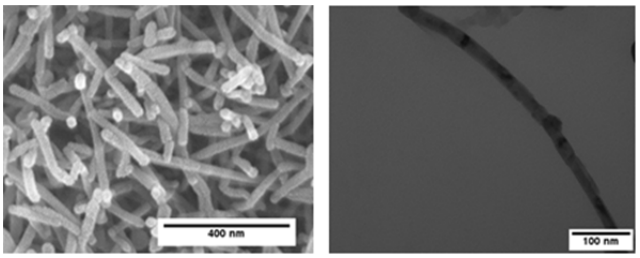

Figure 1: SEM and TEM images of perosvkite nanowires.

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Theoretical Study of Point Defects in Mg_2X (X = Si, Ge, Sn) Thermoelectric Materials

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The point defects as vacancies, interstitials and anti-site defects were investigated in the antifluorite-type structure Mg2X (X =Si, Ge or Sn) materials from the ab initio electronic structure calculations. The theoretical study included analysis of the influence of the point defects on the electronic structure, crystal stability and also thermoelectric properties. The electronic structure calculations of compounds containing defects were performed using the self-consistent Korringa-Kohn-Rostoker method within the Coherent Potential Approximation (KKR-CPA) [1,2]. The electron or hole type of electrical conductivity was determined from the Fermi level position with respect to the conduction or valence bands, respectively, but in the case of some defects neutral effect on electronic properties was detected. On the whole, it was concluded that the presence of these crystal imperfections may strongly affect electronic and then electron transport properties of real Mg2X compounds. In order to enlighten potential reasons of the defects' onset in these materials, their crystal stability was investigated in view of the formation energy as obtained from the total energy KKR-CPA calculations [3]. Moreover, in order to discuss crystal stability limits, an influence of variable chemical potentials, as referred to Mg and X solids, was considered. The point defects in Mg2(Si-Sn), extremely promising alloys for thermoelectric power

generation [4], were also studied. The work was partially supported by the EU Human Capital Operation Program, Polish Project No. POKL.04.0101-00-434/08-00 and the European Space Agency FP7-NMP-2010-SMALL-4 Collaborative Project ''THERMOMAG'' (No. 263207).

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Electronic Structure and Thermoelectric Properties of Pseudo-Quaternary $Mg_2(Si,Sn,Ge)$-Based Materials

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$Mg_2Si_{1-x}Ge_x$, $Mg_2Si_{1-x}Sn_x$, $Mg_2Ge_{1-x}Sn_x$ alloys have attracted much attention as they are composed of cheap (except germanium), abundant, and non toxic raw materials, have a high figure of merit and the lowest density amongst all efficient thermoelectrics. $Mg_2Si_{1-x}Sn_x$ has been found to be the most favorable in terms of thermoelectric energy conversion as it has the highest thermal resistivity due to the maximum mass difference between its components [1]. However, quasi-ternary solid solutions$Mg_2(Si,Sn,Ge)$ have attracted much less attention. Electronic structure of $Mg_2Si_{1-x-y}Sn_yGe_z$ system with complex disorder was calculated in the framework of the Korringa-Kohn-Rostoker method with the coherent potential approximation (KKR-CPA) [2] to treat chemical disorder. Electron transport coefficients as electrical conductivity, thermopower and electronic part of thermal conductivity were studied combining the KKR-CPA technique with Boltzmann transport theory [3]. The computed 2D plots (in function of electron carrier concentration and temperature) for power factor and Seebeck coefficient fairly support large thermoelectric efficiency detected experimentally in n-doped $Mg_2(Si,Sn,Ge)$ solid solutions [4]. Finally, employing experimental value of lattice thermal conductivity as adjustable parameter the computed figure of merit fairly explains very high ZT~1.4 measured in n-doped $Mg_2Si_{1-x-y}Sn_yGe_z$ system [4]. Furthermore, the question of X-site disorder, likely yielding conduction bands convergence and affecting electron transport properties, is addressed to detailed examination of complex Fermi surfaces in $Mg_2Si_{1-x-y}Sn_yGe_z$ with respect to those computed in ordered Mg_2X compounds [5].

The work was partially supported by the National Science Center in Poland (grant No. UMO-2011/02/A/ST3/00124) and the European Space Agency FP7-NMP-2010-SMALL-4 Collaborative Project THERMOMAG (No. 263207).

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Computational Investigation of the Electronic and Thermoelectric Properties of Strained Bulk Mg_2Si

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Mg2X (X=Si,Ge,Sn) alloys have been identified as promising advanced thermoelectric materials in the temperature range 500 to 800 K [1,2]. Compared to other thermoelectric materials operating in the same conversion temperature range, such as PbTe and CoSb3, Mg2X are environmental-friendly materials, their constituent elements are nontoxic and they are abundant in the Earth's crust [3]. With this type of materials, thermoelectricity usage will be possibly extended to large scale applications rather than being confined to technological niches. In the last decades, nanostructuring has proven to be a successful way to improve the figure of merit of the thermoelectric materials [4,5]. In layered heterostructures, the lattice mismatch leads to uniaxial and isotropic deformations at the interface that may change the fundamental properties of the film compared to that of the bulk material. The aim of this work is to investigate the influence of isotropic and anisotropic pressures on Mg2Si transport properties. This investigation is conducted by coupling density-functional theory with Boltzmann transport theory. A detailed study of electronic and thermoelectric properties has been performed by gradually varying compressive and tensile strain intensities. Various charge carrier concentrations and temperatures have been considered for each strain condition. A detailed analysis of the impact of these parameters on the evolution of the energy gap and on the thermoelectric properties of Mg2Si will be given in this paper. The gap evolution depends strongly on the type of stress applied to the structure. The Seebeck coefficient (S) and power factor (PF) are strongly modified; a gain of up to 40% can be obtained for S and up to 100% for PF under certain conditions of stress. The temperature corresponding to the maximum value of PF has been found to shift downward under the effect of stresses. References 1. Morris RG Redin RD and Danielson GC 1958 Phys. Rev. 109 1909–15 2. Akasaka M, Iida T, Matsumoto A, Yamanaka K, Takanashi Y, Imai T, Hamada N 2008 J.

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Phonon Drag Effect in $FeGa_3$

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The thermoelectric properties of a compound are not only influenced by the charge carrier concentration, but also essentially depend on the microstructure. In combination with the chemical composition, the knowledge about grain boundaries and size are keys to understand the structure-property relation.

In this study we investigated the intermetallic diamagnetic semiconductor $FeGa_3$ in single- and polycrystalline form. Large single crystals, oriented in [001] and [100] direction, were grown. Polycrystalline specimens were prepared with adjusted grain size from powdered single crystals and additional spark plasma sintering treatment. The chemical composition was investigated via X-ray powder diffraction and metallographic analysis before determining the thermoelectric properties of the single crystals (compound properties) and the polycrystalline samples (material properties) over the whole temperature range.

Remarkably huge peaks in the thermal conductivity up to 800 W K^{-1} m^{-1} with corresponding absolute maxima in the thermopower reaching 16000 µV K^{-1} (*n*-type) were found for the single crystals. Only a slight anisotropy is observed depending on the crystallographic orientation. In the polycrystalline specimens the phonon peak is drastically suppressed accompanied with a strong decrease in the thermopower. Additional investigations via electronic structure calculations were performed, which reproduce the high temperature part of the experimental transport properties. Based on heat capacity and susceptibility measurements, a magnetic or structural phase transition as a possible origin for the unusual thermopower behavior at low temperatures for the single crystals is rejected. A phonon drag mechanism is suggested and discussed, for explanation of the relationship between high thermal conductivity and thermopower values.

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A First-Principles Study of the Role of Lanthanum Substitution in Reducing Lattice Thermal Conductivity of the Thermoelectric Compound $AgSbTe_2$ (P4/mmm)

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Attempts to optimize the thermoelectric (TE) *figure of merit*, ZT, require reducing the lattice thermal conductivity of a TE material, while maintaining relatively high values of electrical conductivity. Solid-solution forming elements have the potential of reducing the lattice thermal conductivity of single-phase TE materials by suppressing lattice vibrations. Employing computational approaches has proved to be a very useful and cost-effective way for examining the effects of dopants on TE performance. Herein, we perform lattice dynamics first-principles calculations for the promising TE compound $AgSbTe_2$, and estimate the stability of its three polymorphs at a wide temperature range. We predict that the formation of substitution defects at the Ag-sublattice sites of the $AgSbTe_2$ (P4/mmm)-phase will manipulate its vibrational density of states and impede lattice vibrations, thereby reducing its lattice thermal conductivity. Calculations performed for a $La_{0.125}Ag_{0.875}SbTe_2$ compound indicate significant reduction of the average sound velocity from 1727 to 1046 $m{\cdot}s^{-1}$ due to La-doping. This corresponds to an estimated decrease of lattice thermal conductivity by a factor of 2.7, which is expected to yield a significant improvement to the ZT-value of $La_xAg_{1-x}SbTe_2$-based materials up to values larger than 3. This research is supported by the Grand Technion Energy Program (GTEP) and the Leona M. and Harry B. Helmsley Charitable Trust. [1] Y. Amouyal, Computational Materials Science. **78** (2013) 98.

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Current Status of Mg_2Si to Realize Practical Thermal-to-Electric Power Generation Device

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Magnesium silicide (Mg2Si) has emerged as the most promising thermoelectric (TE) material for automotive application, especially in European countries. This is mainly due to the light weight of Mg2Si, the abundance of its constituent elements associated with few national risk to material supply, and to good TE properties with sufficient durability at elevated operational temperatures. To align with automotive developers for the installation of the waste-heat recovery systems, the establishment of scalable and reproducible processes are required in order

to take Mg2Si TE generators (TEGs) into production. We have been engaging in the establishment of fundamental fabrication techniques for the manufacture of Mg2Si TEGs, including the use of all-molten polycrystalline source material, plasma activated sintering with tunable pulse wave current operation, sintering scalability, and monobloc sintering or modified plating method for metal electrode termination to Mg2Si. Regarding dopant incorporation in Mg2Si, an all-molten synthesis process allowed well-controlled incorporation of various types and concentrations of dopant, spatial homogeneity, and thermodynamic stability. To further elevate the TE capability of Mg2Si, it needs to be doped, and typical device operating temperatures require that any element used as an impurity be highly stable and electrically active at substitutional sites. Stable and substitutional impurity elements in Mg2Si are needed to ensure advancement of TE characteristics and long lifetime operation at elevated temperatures. In this report we describe some modifications to the fabrication process of single /double doped Mg2Si thermoelectric chips and subsequent improvements to the thermoelectric and mechanical properties, focusing on the doping characteristics, the sintering adaptability and scalability. The ensuing specimens were examined with regard to their power factor, thermal conductivity as a function of temperature, and durability as long as several hundred hours at operation temperature. The observed resistance of the ohmic-contact at the interface between the Ni electrode and the Mg2Si was sufficiently low for the realization of a practical thermoelectric generator. In addition, to ensure the structural reliability of the thermoelectric module, the mechanical properties of the Mg2Si were examined by bending tests, indentation fracture toughness tests, and ultrasonic tests. Through these experiments, the Young's modulus, bending strength and fracture toughness were measured. We also present a possible structure of a single n-type Mg2Si device, several proto-types of Mg2Si unileg TEGs have been evaluated with regard to practical power generation characteristics. To realize the stable thermal contact is an effective way to keep high performance of TE power generation. Since the use of thermal interface materials (TIM) is one of the effective approaches to stabilize a thermal conjugation, thus, we examined TIMs for mid-temperature operation to avoid the loss of heat flow from heat source. Regarding the thermal drain side, we also inquire TIMs from the point of view of thermal conjugation, electrical insulation, and fixability.

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Thermoelectric Property of N-Type Mg_2Si Synthesized by the Convenient Melt-Growth Method

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Magnesium half silicide, Mg2Si and related compounds are widely attracted attentions as the mass- product thermoelectric materials in the intermediate temperature range. Recently, n-type Mg2Si thermoelectric materials with high ZT and high stability were synthesized using pre-synthesized stoichiometric Mg2Si powder and plasma sintering methods [1, 2]. However, both processes of the presynthesis of stoichiometric Mg2Si powder and plasma sintering elevated the cost of Mg2Si thermolegs and also those devices. Melt growth is an alternative method to obtain a high quality Mg2Si thermoelectric bulk. In this paper, we report the synthesis of n-type Mg2Si thermoelectric bulk crystals using the convenient melt growth method, in which the stoichiometric Mg2Si crystals are synthesized under the atmospheric high temperature without any inert-gas and vacuum atmosphere, and also their thermoelectric property[3]. Synthesis of the Mg2Si bulk was carried out using a vertical furnace system. A certain amount of Si and Mg (Mg:Si=2:1) and Sb dopant were charged in a BN coated alumina crucible(ID=12mm) and the crucible was sealed by a ceramic fiber cap. After heating the crucible above 1085

Figure 1 shows the typical Mg2Si crystals synthesized in the air. The Mg2Si had a shiny surface with well-developed crystalline grains. Notable oxidation or nitridation and also voids and clacks were not observed in the crystals. Measured density of the ingot was 1.99g/cm3, was similar to the theoretical density of Mg2Si. Powdered XRD measurements confirmed the obtained Mg2Si were single phase without any unreacted Si and Mg and also MgO phase. The obtained Mg2Si bulk had high electrical conductivity compared with that of sintered Mg2Si due to the lower scattering of electrons. The power factor of the crystals with Sb dopant from 0.127 at% to 0.507 at% was between 21 *f*êWK-2 and 32 *f*êWK-2 at 300K.

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Mg and Mn Silicides : Material Development and Up Scaling, Thermoelectric Properties, Pre Contacting and Module Assembling

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We report on the synthesis, thermoelectric properties and production up-scaling of p-MnSix (1.75 ≤ x ≤ 1.85) and n-Mg2Si0.4Sn0.6. Beside the low price and environmental friendly characteristics, these materials show large ZT values (0.7 and 1.4, respectively) in a temperature range of 300 °C to 600 °C in laboratory scale samples and therefore they are very interesting for the energy harvesting in industrial processes or automobile industry. Simple and low-cost powder metallurgical method (High–energy ball–milling, HEBM) was used for the production of the starting powders. The powders are reacted in-situ and compacted by Spark Plasma Sintering (SPS), resulting in samples with densities over 95%. Powder X-ray diffraction and metallographic analysis indicate that MnSix samples (x = 1.75) contain a small amount of a MnSi secondary phase. The Seebeck coefficient (S) and the electrical conductivity (σ) were simultaneously measured in an ULVAC ZEM3 from 25 °C to 700 °C.
The Power Factor (PF) of MnSix increases from 0.7 x 10-3 W/mK2 for samples containing MnSi impurity to 1.5 x 10-3 W/mK2 for MnSi free specimens. Moreover, PF > 1.4 x 10-3 W/mK2 extends in a temperature range from 300 °C to 600 °C making these materials very interesting for the energy harvesting. ZT = 0.4 has been reached for non-doped and non-optimized MnSix. Clean preparation conditions and adequate pure reactants (non-oxidized) are crucial for the quality of the final samples. S and σ of Mg2Si0.4Sn0.6 are enhanced with the purity of the samples. The temperature dependence of the PF in single phase Mg2Si0.4Sn0.6 (non-doped) shows two maxima, at ~ 150 °C (5.3 x 10-4 W/mK2) and at ~ 580 °C (4 x 10-4 W/mK2). The temperature dependence of σ reveals the semiconducting character of the specimens. The PF of Bi-doped Mg2Si0.4Sn0.6 single phase samples (3.5 x10-3 W/mK2) shows a 10 fold enhancement at 300 °C in relation to the non doped state which results in ZT > 1. Such an enhancement in the PF arises from the large increment of σ due to the doping. The temperature dependence of σ displays the metallic character of the doped samples. The industrial application of these material
s requires scalable synthesis and processing methods. The amount of starting powders prepared by HEBM was up-scaled to produce 400 g per batch and the SPS parameter have been optimized to produce samples of 60 mm in diameter and 0.5 cm thickness. The measured thermal expansion coefficient of MnSix ranges from 10 to 12x10-6 /K-1 at 300 °C and 600 °C, respectively.
A technology to pre-contact the silicide sinter-bodies with metallic foil via SPS was developed. Pre-contacted thermoelectric legs were fabricated and a soldering process was implemented to fabricate thermoelectric modules. Aspects related to the oxidation of the silicides will be addressed.

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Thermoelectric Properties of P- and N-Type Mg_2Si Compounds Obtained by SHS

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Abstract:
The p- and n-type Mg2Si compounds were prepared using self-propagating high-temperature synthesis (SHS). Dopants were introduced in the form of pure metals (Ag, Bi) or compounds (Ag2C2O4, (BiO)2CO3), which easily decompose upon heating. Fine powders were consolidated by hot pressing supported by a dedicated induction heating system. Sintering conditions were adjusted to each specific composition of the sample. Characterization of bulk materials comprised microstructure, chemical composition and phase composition (XRD, SEM, EDS). Thermal properties of undoped and doped Mg2Si were evaluated on the basis of thermal expansion coefficient, heat capacity and thermal diffusivity measurements. Seebeck coefficient and electrical conductivity were measured in the temperature range of 300 K to 900 K.

Keywords: magnesium silicide; thermoelectrics; low density intermetallics

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Optimizing Thermoelectric Properties of Mg_2Si: Fabrication Parameters and the Influence of MgO

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Magnesium silicide is a very attractive medium-to-high-temperature thermoelectric material due to its excellent thermoelectric properties, the low density as well as the abundance and the non-toxicity of its constituents. Both n- and p-type materials have been reported while the best thermoelectric properties have been shown for Sb-doped n-Mg2Si. Apart from the chemical composition and the dopant concentration one critical parameter for the performance of the material is the fraction of the secondary phase MgO. While this has often been noted in the literature a thorough analysis of this aspect is still missing. Using Sb-doped Mg2Si powder from a single production batch we have fabricated Mg2Si pellets using a direct sinter press. Adjustment of the fabrication parameters allows for a systematic variation of the MgO content and thus a study of its effect on the thermoelectric transport properties and the overall performance. We found a clear decrease of the electrical conductivity with increasing MgO content while the Seebeck coefficient and the thermal conductivity are virtually unaffected. It is also noteworthy that the effect of MgO is strongest at lower temperatures and decreases significantly and relatively abrupt at higher temperatures, this indicates a temperature-(de)activated scattering mechanism. Electron microscopy indicates an oxygen accumulation at the grain boundaries, supporting the picture of small MgO particles as additional charge carrier scattering centers. Employing the temperature-dependent thermoelectric measurements as well as supplementary Hall measurements we will develop a model for the effect of MgO on the thermoelectric properties of Mg2Si. This will make the effect of MgO on the thermoelectric performance of Mg2Si easily quantifiable. Finally we will also discuss the effect of other fabrication parameters (particle size, sintering temperature/pressure) on the performance of the material. Using optimized fabrication parameters we were able to achieve a ZT of 0.8 at 820 K.

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Electrodeposition of Composition-Controlled $(Bi_{1-x}Sbx)_2Te_3$ Nanowires in Polycarbonate Membranes

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Among thermoelectric materials, Bismuth Antimony Telluride compounds exhibit high transport properties at room temperature. Their characteristics are highly dependent on their global composition, as proven by the lattice thermal conductivity which is minimum for a mixture of 25 mol. % Sb2Te3 + 75 mol. % Bi2Te3 [1]. Moreover R. Martin-Lopez et al. have shown that these ternary compounds, obtained by mechanical alloying, can present n-type conductivity or p-type conductivity for respectively a large excess of Bismuth or a large excess of Antimony [2]. Due to theoretical calculations predicting further enhancement of the adimensional figure of merit of nanowires [3], some recent reports in literature are focused on the electrodeposition of (Bi1-xSbx)2Te3 1D nanostructures [4-6]. It appears that large deviations from the targeted composition (Bi0.25Sb0.75)2Te3 (p-type) are observed depending on the experimental conditions (bath composition, electrochemical parameters).
In this work, efforts were made to fabricate (Bi1-xSbx)2Te3 nanowires with controllable composition based on an analytical approach. Bismuth antimony telluride nanowires were potentiostatically deposited within etched ion-track polycarbonate membranes covered with a platinum substrate. According to the experimentally determined diffusion coefficients of metallic precursors in the electrolyte and to the analysis of related voltammetric studies, various parameters (applied potential, concentrations of cations) were tested to deposit nanowires. After chemical dissolution of the polycarbonate template, individual characterizations (morphology, cristallinity and composition) were realized by TEM (Transmission Electronic Microscopy) with EDS (Electron Diffraction Spectrometry) analyses. Results show that a large excess of antimony is necessary to reach the global composition of (Bi0.25Sb0.75)2Te3. Transport properties of electroplated bismuth telluride nanowires were investigated as function of their composition. In particular electrical resistivity of released individual nanowires was studied through the fabrication of dedicated microstructured devices.

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Defect Engineering of Bi_2Te_3-Based Thermoelectric Nanowires and Topological Surface States

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Chalcogenide nanowires based on Bi_2Te_3 and related materials are of significant interest for two scientific fields: nanostructured thermoelectrics and topological insulators. In the presentation, we will describe two important chemical synthesis approaches for nanostructured thermoelectric materials on the way towards optimized physical model systems. We will present the thermoelectric properties of nanostructured objects which have been synthesized by the following two different approaches: Growth by the Vapour Liquid Solid (*VLS*) mode of single-crystalline and binary semiconductor nanowires and nanobelts is a widespread technique. The resulting Bi_2Te_3 nanowires exhibit reduced tellurium content at the nanowire surface. After annealing in a Te atmosphere, single-crystalline Bi_2Te_3 nanowires have been obtained, which show reproducible electronic transport properties (electrical conductivity and Seebeck coefficient) close to those of intrinsic bulk Bi_2Te_3. Millisecond-Pulsed Electrochemical Deposition is a quite flexible approach for achieving nanowires of ternary chalcogenide compounds, which have been grown in nanoscale confined spaces. After annealing in Te, enhanced transport properties close to those of bulk materials have been observed: Single $Bi_2(Te_{1-x}Se_x)_3$ and $(Bi_{x-1}Sb_x)_2Te_3$ nanowires exhibit power factors of 3100 mW/K^2m and 1600 mW/K^2m, respectively. Both combined approaches, each based on a chemical synthesis technique and subsequent balancing of the stoichiometry by annealing under Te atmosphere, have resulted in bulk-like power-factors for Bi_2Te_3- based nanowires, which are very promising for systematic investigations of the thermal conductivity as a function of the nanowire diameter and the determination of the figure of merit ZT. Furthermore, we report on low temperature magnetoresistance measurements on single crystalline Sb_2Te_3 volume ratios. The observation of Aharonov-Bohm oscillations and weak antilocalization indicates the presence of topological surface states. *The financial support by the German Priority Program DFG-SPP 1386 on Thermoelectric Nanostructures is gratefully acknowledged: www.spp1386thermoelectrics.de*

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Thermal Conductivity of Bi_2Te_3 Nanowires Arrays: Theory, Fabrication and Measurements

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The effects of quantum-confinement on the thermoelectric properties of Bi2Te3 has not yet a clear answer mainly because up to now nanowires of diameters down to 40 nm have not being measured with enough metrology. Quantum confinement can actually be expected in nanowires with diameters smaller than 15 nm. One reason for the lack of results in nanowires arrays down to 15 nm is that they have not being prepared until recently [1].

Bismuth telluride nanowires arrays of small diameters have being prepared and measured. For that purpose, porous alumina template with porous size of 200, 40, 25 and 15 nm in diameter and 60 microns in length have being synthetized followed by the electro-deposition of Bi2Te3.
Bismuth telluride is a layered binary compound crystallizing in the R-3m space group. It has 15 optical modes. Since the space group is centrosymmetric, the 12 optical phonons are divided into "gerade" and "ungerade" (even and odd symmetry) depending on the lack of inversion symmetry in the vibration. There are 6 Raman active modes (the other six are infrared active), two Eg modes (bidimensional) and two Ag modes (one-dimensional). The higher frequency Eg and Ag modes are clearly observed in the spectra, while the lower frequency modes are not so clearly seen. A resonance effect appears in the Raman spectra as soon as the laser frequency is changed. The effect of confinement [2]. on the Raman data on the smaller diameter nanowires has been analyzed.
The thermal conductivity of the whole nanowire arrays have also been measured by Raman spectroscopy. The thermal conductivity has actually being extracted from a model taking into account the existence of the alumina template. A lattice dynamics model (rigid ion model) has been developed for Bi2Te3 to properly include the phonon dynamics into a lattice conductivity model. A model to calculate the thermal conductivity as a function of nanowire diameter has been recently developed [3].

The experimental results agrees quite well with the experiment for the different nanowire diameters. [1] J. Martin, C.V. Manzano, O. Caballero-Calero, M.S. Martin Gonzalez ACS Applied Materials and Interfaces, 2013, 5, 72-79. [2] F. Comas, A. Cantarero, C. Trallero-Giner, J. Phys. Cond. Matt. 1995, 7, 1789. [3] C. de Tomás, A. Cantarero, A. F. Lopeandia, and F. X. Àlvarez, J. Thermoelctricity 2013, 4, 1-9.

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Investigation of Thermal Transport in InAs Nanowires for Thermoelectric Applications

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Lower dimensional structures can show a significant modification of transport properties due to quantization of the carrier energy in one or more directions. 20 years ago Hicks and Dresselhaus predicted that these effects could enhance the thermoelectric properties of 2D and 1D structures[1]. This has led to an increase in the research on thermal transport in nanowires, and a significant decrease of the thermal conductivity was found with respect to the bulk values in e.g. silicon nanowires[2,3]. In this work, we report on our investigations of the thermoelectric properties of InAs nanowires.
The nanowires are grown using the Vapor Liquid Solid (VLS) method in a Metal Organic Vapor Phase Epitaxy (MOVPE) reactor. This gives complete freedom over wire length, crystal symmetry, diameter, radial and axial composition etc[4]. In this way, the dependence of the phonon heat transfer on these parameters can be studied systematically.
The experimental study of the thermoelectric properties of the nanowires is done using suspended SiNx membranes with implemented heaters as previously used by Li Shi et. al.[5]. By placing a nanowire over the bridging gap between two membranes, the wire conducts the heat generated by joule heating on one membrane to the other side. With platinum thermometers on both platforms, heat conduction of the nanowire is investigated.
The microdevice fabricated for the measurements consists of 20x20micron freestanding SiNx pads suspended above a Si substrate by six 450micron long SiNx beams. The final SiNx layer is 450nm thick and supports a Pt heater and two Pt electrodes for thermal and electrical characterization. The nanowire is placed on the device using nanomanipulators to prevent short circuiting. A scanning electron microscope (SEM) image of the complete device is shown in Figure 1.

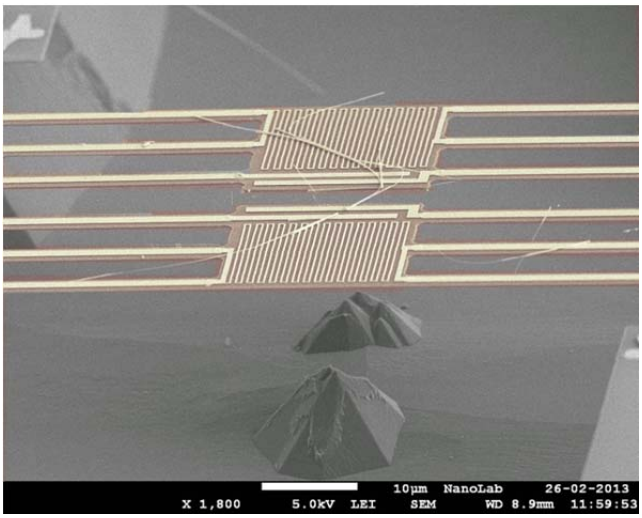

Figure 1: SEM picture of the final device showing the freestanding membranes (red) with the platinum contacts and the wire (yellow).

The thermal conduction of the InAs nanowires was measured as a function of temperature. We found a reduction of thermal conductivity by approximately a factor 7.5 compared to bulk as has also been found by Feng Zhou et. al[6] The conductance was found to be independent of the temperature within the range investigated (300-400K) as shown in Figure 2.

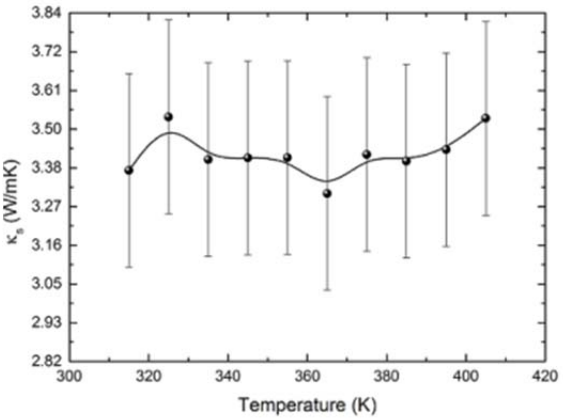

Figure 2: Thermal conductivity versus temperature for an InAs nanowire. The black line is a guide for the eye.

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Thermal Transport Across Ultrathin Silicon Membranes and Asymmetric Nanowires

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Suspended devices with integrated heaters/sensors and reduced thermal losses with the surroundings have emerged as potential structures to measure the thermal conductance of nanowires (NWs) and/or thin membranes. We have recently developed a methodology to fabricate, starting from silicon-on-insulator wafers, suspended structures bridged by a crystalline Si membrane. The thermal conductivity of the 17.5 nm thick membrane is reduced to 19 W/mK, a 8-fold reduction compared to bulk Si. The device provides enough flexibility for further nanostructuration of the membrane into arrays of NWs of different shapes and dimensions by means of focused ion beam (FIB). However, ion milling on these ultrathin membranes produces strong damaging of the structure, even at 200 nm far from the edges. After nanostructuration with FIB the thermal conductivity of the 500 nm wide beams is reduced to 1.7 W/mK, close to the amorphous limit for Si. Laser illumination recrystallizes the structure, increasing k to 9 W/mK. This value is largely affected by the presence of grain boundaries in the recrystallized Si membrane.

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Synthesis and Seebeck Measurements of Thermoelectric $Bi_{1-X}Sb_X$ Nanowire Array

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Thermoelectric Bi1-XSbX (0<X<1) of the with for Bi1-XSbX nanowires are then deposited using both potentiostatic [2] and pulsed electrochemical deposition in the pores of the template. The crystallographic orientation and composition of the nanowire arrays as a function of the deposition conditions are investigated by X-ray diffraction, while their morphology is studied by high-resolution scanning electron microscopy. We have developed a set up to measure the Seebeck coefficient and the electrical resistance of embedded nanowires array down to 20 K. We present first Seebeck coefficient measurements on nanowire arrays as a function of wire diameter, composition and temperature. Nanowire with diameter as small as 15-20 nm are excellent model systems to investigate the thermoelectrical properties of nanostructures [3,4].

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Relation between Crystallographic Structure and Thermoelectric Properties of Undoped and Ag-Doped $Mg_2Si_{1-x}Sn_x$

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Numerous investigations in the field of Mg_2Si-based thermoelectric materials development have revealed that Mg_2Si-Mg_2Sn is a very promising system for thermoelectric applications because of the high figure of merit (ZT>1) [1,2]. A part of this work consists on determining which composition has the better thermoelectric properties. A problem in this system is to find a p-type compound. In this purpose, Ag-doped materials have been studied.

In this work $Mg_2Si_{1-x}Sn_x$ samples are synthesized for x=0, 0.25, 0.4, 0.5, 0.6, 0.75 and 1 with and without Ag doping atom [3,4,5]. The crystallographic structure of the compounds is systematically studied by X-Ray diffraction. The cell parameters obtained from these studies are then used to determine the real composition of the samples and to check whether or not the doping elements are incorporated.

The determination of the better composition of undoped samples considering the thermoelectric properties is studied by measuring thermal and electrical resitivities, and Seebeck coefficient.

The above experimental studies determine that Ag doping atom is inserted into the lattice. However very few things are known about the doping atom position into the cell which in fine leads to n or p conduction. Ab initio calculations are performed to understand which model of disorder is appropriate to describe the electronic structure and understand the conduction mechanisms. Two extreme cases have been considered. CPA calculations are performed to describe a completely disordered material and supercell calculations to describe local order.

The results we obtain are consistent with transport properties measured on our samples and reveal that for

Ag doping, a small perturbation can change the type from p to n.

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Synchrotron Study of Ag doped Mg_2Si: Correlation Between Properties and Structure

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Mg2Si-based alloys belong to the most promising group of materials for developing thermoelectric devices operating at medium temperatures. In order to produce thermoelectric generators, high-performance p- and n-type materials must be balanced. It has been reported that figure of merit, ZT, reaches about 1.4 for n-type Mg2Si based material [1]. It is thus important to develop reliable p-type Mg2Si counterpart. Extensive theoretical and experimental work has been done to select suitable p-type dopants. Silver was identified as a promising one [2] but the observed strong variations of the properties of Ag-doped Mg2Si with temperature, characterized by the Seebeck coefficient drop between 470K and 700K, hinder the development of envisaged applications. To understand and optimize the effect of doping, knowledge of the dopant atom site occupancy is essential. We present and discuss the results of in-situ synchrotron powder diffraction measurements of Ag-doped magnesium silicide, carried out on ID31 beamline in ESRF. The analysis of high resolution in-situ powder diffraction patterns taken upon thermal cycling reveals anomalous behaviour of silver diluted in Mg2Si matrix, which can be correlated with the change in thermoelectric properties.

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Evaluation of the Performance of a Two-Leg Unicouple (Bi-Doped $Mg_2Si_{0.6}Ge_{0.4}$ / Ge-Doped $Mn_{1.75}Si$)

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As part of a European Space Agency R&D project led by AREVA TA, a thermoelectric converter made of 12 couples (N-P) was to be built. In the present work, we focus on the steps leading to the fabrication of one unicouple, describing the difficulties encountered and the associated solutions employed. A first evaluation of the unicouple performance is presented.

Each unicouple comprises two connected legs, one made of p-type material and the second of n-type material. In this case, the n-type leg is made of Bi-doped Mg2Si0.6Ge0.4 synthesized by solid state reaction, whereas the p-type leg is made of Ge-doped Mn1.75Si manufactured using a high frequency induction furnace. In order to allow the brazing of the legs the metallic interconnects, intermediate layers of various materials were incorporated at the end of the hot pressed ingots for both n- and p- type materials.

Thermoelectric properties measurements were performed on test benches, including measurements of material resistivity, thermal conductivity ad Seebeck effect as well as an assessment of performance in terms of electric power generation. These results allow a comparison between the electric power deduced from the measurement data with the one predicted by models established beforehand.

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In Situ and Ex Situ Doping of Mg_2Si - Thermodynamics of Selected Mg-Si-dopant Systems

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Abstract: In the manufacturing of p-type and n-type Mg2Si-based materials, dopants are mostly added to the initial powder mixture either in elemental form or as compounds which decompose on heating. During the synthesis, almost every dopant reacts either with magnesium or silicon, yielding intermetallic phases detectable by XRD in the as-received products. These intermetallics are often below the detection level in the hot pressed materials. However, dopant-rich dispersions, located along the grain boundaries of the matrix, are clearly visible in SEM/TEM/EDS analyses. As a result of dopant reactions with magnesium or silicon, only part of the dopant can be actually active in the matrix. One of

possible solutions of this problem is to add dopant after the synthesis (ex situ doping) and to promote its diffusion into the Mg2Si matrix upon consolidation. In some cases, however, this procedure may appear unsuccessful because of thermodynamic stability of foreign intermetallics. This work will demonstrate thermodynamic background of selected Mg-Si-dopant systems to better understand and optimize relevant manufacturing processes.

Keywords: magnesium silicide, thermodynamic stability of Mg-Si-dopant systems

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Macro-Micro-Nano Features in Magnesium Silicide/Stannide/Germanide Compounds

Polymeris, G. S.[1]; Vlachos, N.[2]; Khan, A.U.[2]; Lioutas, Ch. B.[1]; Pavlidou, E.[1]; Hatzikraniotis, E.[1]; Paraskevopoulos, K. M.[1]; Kyratsi, Th.[2]

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Recent reports of good thermoelectric properties with high thermoelectric figures of merit, (ZT), have added to the interest in $Mg_2(Si,Sn)$ and their doped compounds as promising thermoelectric materials. Nevertheless, the reports dealing with the morphology in-homogeneities of these materials are scarce over the published literature. In the present study, a comparative study is attempted, dealing with the in-homogeneities monitored in the cases of $Mg_2(Si,Sn)$ based ternary compounds as well as the quaternary system based on $Mg_2(Si,Sn,Ge)$. In-homogeneities may occur at different scale lengths; at atomic scale (as dopant and alloying), at nano-scale (as nano-inclusions and nano-crystals), at meso-scale (as grains of different composition) and at macro-scale (as dopant modulated structures and dopant grated materials). Structural in-homogeneities were monitored by using Transmission Electron Microscopy of moderate and high resolution (TEM&HRTEM), Scanning Electron Microscopy (SEM) equipped with EDS analyzer, X-Ray diffraction analysis as well as conventional Fourier transform infrared spectroscopy in the reflectivity mode. X-Ray diffraction indicates that all materials subjected to the present study exhibit two phases, one Sn-rich and another Si-rich. Compositional in-homogeneities extend from nano-scale to macro-scale, as observed with HRTEM (nano-scale), SEM studies and EDS (micro-scale) and IR Reflectivity mappings (macro-scale). The results are discussed in the framework of existing models about the constitution of the alloys for the Sn composition range $0.4 < x < 0.6$. Finally, the implications of these in-homogeneities to the thermoelectric properties of these compounds are also discussed, indicating that both phases are participating in the enhancement of ZT through the lowering of the thermal conductivity.

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Paradoxical Enhancement of the Power Factor in Polycrystalline Silicon Due to the Formation of Nanovoids

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Holey silicon has been considered a viable candidate as a thermoelectric material [1] in view of its low thermal conductivity. However, since voids are efficient scattering centers not just for phonons but also for the charge carriers, achievable power factors (PFs) are normally too low for its most common embodiment, namely porous silicon, to be of practical interest [2]. In this communication we show that the presence of nanopores themselves is not incompatible with thermoelectric efficiency in highly doped silicon. High power factors, up to a huge 22 mW $K^{-2}m^{-1}$ (more than 6 times higher than bulk values), were observed in heavily boron doped nanocrystalline silicon films where nanovoids (NVs) were generated by He^+ ion implantation. Differently than in single-crystalline silicon [3, 4], He^+ implantation followed by annealing at 1000 °C led to the formation of a homogeneous distribution of NVs with final diameters of about 2 nm and densities in the order of 10^{19} cm^{-3}. Its morphology shows silicon nanograins of ≈50 nm in diameter decorated by SiB_x 5-nm precipitates. The details of this remarkable PF enhancement are currently under investigation. We recently reported that PFs up to 15 mW $K^{-2}m^{-1}$ can be achieved in silicon-boron nanocomposites (without the NVs) [5, 6] due to a simultaneous increase of the electrical conductivity and Seebeck coefficient [7,8]. In that case, high Seebeck coefficient was achieved by potential barriers on the grain boundaries, and high

electrical conductivity by extremely high doping values. The additional increase in the PF observed in the case of the new structures with NVs (that also include SiB_x precipitates) might be attributed to several possible reasons, currently under investigation: i) a further increase of the mechanism described above, ii) increase of strain in the grains, iii) increase in active dopant density, iv) change in the electronic and phononic spectrum, v) reduction of carrier energy relaxing mechanisms. Experimental and computational evidence will be put forward to elucidate this paradoxical effect of NVs on silicon PF.

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Reduction of Thermal Conductivity in Compositionally-Graded $Si_{1-x}Ge_x$ Superlattices

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SiGe superlattices (SLs), in which phonon transport is dominated by a high density of interfaces, have been previously reported in an effort to reduce the thermal conductivity below the alloy limit. In this work, we explore the effect of compositionally-modulated Si1-xGex layers, grown in direct and reverse order. Several sets of samples have been prepared by molecular beam epitaxy at 450oC ; one consisting in a (Si1-xGex)/Si superlattice on Si(001) with a continuously increasing Ge content (x from 0 to 0.55 or 0.70) in the growth direction and the others with the compositional gradient in exact reversed order. The SLs consist of 4 periods of 40 nm of graded Si1-xGex alloy separated by 5 nm of Si. The growth starts and ends with Si layers of 60 nm and 5 nm thickness, respectively. We use the 3ù method to obtain ê in the T range 50-400 K. Under a temperature gradient from the top surface, heat will travel across different interfaces and different compositional gradients. We demonstrate this asymmetry has a remarkable effect in the heat flow. The compositionally-graded Si1-xGex SLs also show a significant reduction of phonon transport compared to traditional SLs superlattices or even quantum dot superlattices, with conductivity values below 2.5 W/mK at room temperature. We discuss our results in terms of the asymmetry of the compositional modulation and the thermal boundary resistance and about the possible influence of extended defects. We also use X-ray diffraction tools to map the strain in the superlattice.

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Effect of Pore Sizes on the Reduction in Lattice Thermal Conductivity of Nano to Micro Scale Porous Materials

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We study the effect of thermal phonon scattering on the reduction of lattice thermal conductivity (LTC) in porous semiconducting materials with nonconnected spherical hole pores of varying diameter from nano to micro scale sizes. We use a model based on the Gamma distributions of the nondimemsional pore diameters. The volume fraction (porosity) of each pore group is proportional to the second moment of the distribution. We have calculated effective cross-section area and phonon mean free paths at scattering on randomly distributed pore boundaries and obtained a general relationship for the LTC in porous materials for an arbitrary number of pore groups with various size scales. We have shown that the presence of the pores with all-scale hierarchical disorder leads to a considerable reduction in the LTC and have estimated that in the presence of nano and microscale pores. Particularly, we have shown a possibility for the reduction of the LTC more than in two orders in several specific cases, which can be very useful for a large enhancement in the thermoelectric figure of merit of porous semiconductors.

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Monte Carlo Simulations Of Thermal Conductivity Nanoporous Si Membranes

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Nanoporous membranes made of single-crystalline Si (otherwise referred to as 'holey' Si) are promising candidates for thermoelectric materials as they can provide extremely low thermal conductivities, relatively

high thermoelectric power factors, and the structure stability that other low-dimensional systems lack. In addition Si is an abundant, non-toxic material with well-established manufacturing processes that provide the feasibility of large-scale implementations. Recently, room temperature ZT values up to ZT~0.4 were demonstrated using such material, a large increase compared to bulk ZT_{bulk}~0.01 [1] .

In this work we calculate the thermal conductivity (κ) of nanoporous single crystalline Si membranes by solving the Boltzmann transport equation (BTE) for phonons using the Monte-Carlo method [2, 3]. We investigate the thermal conductivity as a function of: i) geometrical features such as the arrangement of the holes (i.e. rectangular, hexagonal, and random hole arrangements), ii) porosity, and iii) the specular/diffusive nature of the roughness of the pores and the membrane boundaries.

We find that the pore arrangement has some influence on the thermal conductivity. The hexagonal and the randomized arrangements provide somewhat lower thermal conductivities compared to the rectangular ones. As expected, the thermal conductivity decreases with increasing porosity but, interestingly, most of the reduction is observed up to a porosity of 35%. Increasing the porosity from 0% to 35% results in a factor of 4 reduction in the thermal conductivity. Further increase in the porosity results in smaller relative thermal conductivity reduction. In addition, we show that with increasing porosity the roughness strength becomes less effective in determining the thermal conductivity, indicating the relative importance of the porosity over the roughness. After extracting the statistics from a large number of sample devices with random hole arrangements and find that: i) Under the same porosity conditions, increasing the roughness strength by an order of magnitude, reduces the thermal conductivity by only ~40%. ii) Under the same roughness conditions, however, it takes only 10% increase in the porosity to reduce the thermal conductivity by the same amount (40%). Finally, we show that in the simulations the statistical randomness in the structures with randomly arranged holes becomes smaller with the increase of either the porosity or the roughness strength. This indicates that under the strong boundary scattering, the exact geometrical arrangement of the pores loses its importance.

Our results will be useful in the design of thermoelectric devices based on Si nanomeshes, but also nanocomposites that consist of different material phases as well.

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Enhancement of the Thermoelectric Performance of Semiconductors Utilizing Self-assembled Monolayers

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We investigate how self-assembled monolayers (SAMs) improve (or deteriorate) the thermoelectric (TE) performance of semiconductors. The concept of SAMs was proposed in 1946 [1], and was realized experimentally in the early 1980s [2]. To date, the SAMs have been widely applied in many branches of science such as biology, electrochemistry and electronics [3]. However, to our knowledge, no studies have ever tried to employ the SAMs to improve the TE performance. We expect the SAMs are promising for achieving high *ZT* due to two reasons. 1. The SAMs in semiconductors act as good thermal insulators and thermal filters because only the phonons which are resonant with the discrete modes of the SAMs can pass through the SAMs [4]. 2. The thickness of the SAMs can be smaller than one nanometer so that electrons could easily tunnel through the SAMs.

In the present study, we consider the case of GaAs-SAM-GaAs at room temperature. The conductivity and the Seebeck coefficient of the bulk GaAs as functions of carrier concentration are calculated through the Boltzmann equation. In order to describe the electronic transport through the SAMs, we treat the SAMs as a quantum barrier, whose parameters, i.e., the effective mass and the barrier height, are determined by experiments [5]. The thermal conductivity of the bulk GaAs and the boundary thermal conductance of the SAMs are also obtained from the previous experimental data [4]. We find the *ZT* of the GaAs-SAM-GaAs can be several times higher than that of the bulk GaAs. In addition, we find the Seebeck coefficient can be enhanced by the presence of the SAMs because the average energy of the electrons in the SAMs is higher than that in the GaAs.

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Optimizing Thermoelectric Properties of Germanium Antimony Tellurides in Different Temperature Ranges by Substitution

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Compounds on the pseudobinary line between GeTe and Sb2Te3 (GST materials) exhibit nanostructures that depend on the GeTe content and the thermal treatment. They are due to a diffusion-controlled phase transition from a cubic high-temperature (HT) phase to a trigonal layered phase at ~500 °C. Quenching the HT phase yields metastable materials with intersecting defect layers; thermoelectric figures of merit ZT up to 1.3 at 450 °C are obtained. Most of these nanostructures are not long-term stable at elevated temperatures as diffusion sets in at ~300°C and leads to the stable trigonal phase. The properties of such materials are influenced by substituting cations or anions with elements like Se, Sn, In, or transition metals as well as by varying the vacancy concentration in the (pseudo)cubic phase, e. g. by replacing Ge^{2+} by monovalent elements like Li, Na or Ag that act as further phonon scatterers. DFT calculations suggest various substitutions with 3d metals that may influence the properties [1].

Substituting Te by Se in (GeTe)nSb2Te3 yields compounds with less extended defect layers. This may enhance the ther¬mo¬electric properties in analogy to Se-doped AgSbTe2. Se substitution leads to an increased See-beck coefficient, which increases ZT of Ge12Sb2Te12Se3 to 1.4 at 400 °C, i.e. significantly higher than for Ge12Sb2Te15. The substitution of Ge by Sn leads to more complex parquet-like structures; intersecting defect layers occur at lower GeTe contents compared to GST itself. The electrical conductivity is increased e. g. for n = 4 and a slight increase of ZT at high temperatures results. There is a solid solution series between Ge12Sb2Te15 and Ge12In2Te15: substituting Sb3+ by In3+ has little influence on the nanostructure but affects the Seebeck coefficient for Ge12SbInTe15 over the whole temperature range which leads to an increased ZT value up to 300 °C compared to pure GST.

Introducing magnetic centers like Fe, Cr or Mn is another way to optimize GST materials; the possible degree of substitution can be increased by exchanging Te against Se. This allows one to synthesize magnetic materials which may exhibit the magneto-Seebeck effect.

The stability of the nanostructures at elevated temperatures is enhanced by substituting one Ge2+ by two monovalent cations. This changes the cation/anion ratio and thus the vacancy concentration in rocksalt-type compounds and impedes diffusion processes. (GeTe)11Li2Sb2Te4, exhibits a GeTe-type structure without vacancies and forms a rock-salt type HT phase above 250 °C with ZT = 1.0 at 450 °C which is almost unaffected by temperature. Various materials are accessible by partially "filling" the vacancies of GST compounds with Li, Na or Ag. This leads to ZT values of up to 1.8 at temperatures between 100 and 300 °C and above ~430 °C.

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Electrodeposition of Thick Bismuth Telluride Layers Assisted by Soluble Anode

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The integration of thermoelectric devices onto automotive heat exchanger could allow the conversion of lost heat into electrical energy contributing to improve the total output of the engine. For this purpose, the synthesis of thick bismuth telluride films (Bi2Te3) is needed. Films of this thermoelectric material were fabricated by an electrochemical method in nitric acid using a sacrificial bismuth telluride anode as a cationic source. The binary deposit is growing on the working electrode, Bi2Te3 is simultaneously oxidised in BiIII and TeIV at the counter-electrode made with a Bi2Te3 disk obtained by mechanical alloying and hot press sintering. This process leads to an auto-regeneration of the solution without modification of its composition. Deposition thickness using the Bi2Te3 anode was about 10 times larger than without. To demonstrate the utility of a soluble anode in Electrochemical Deposition (ECD), we present the composition and morphology characterizations of the obtained films according different experimental conditions. Perfectly dense and regular Bi2Te3 films (~400 µm) were prepared with low internal stress and uniform composition profile across the cross-section and their thermoelectric properties were determined.

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Influence of Sn on the Thermoelectric Properties of P-Type $Bi_{0.48}Sb_{1.52}Te_{3.1}$

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The ternary compound $Bi_{2-x}Sb_xTe_3$ is well known to be promising for cooling applications near room temperature. During the last decades most of the efforts for improving its efficiency were made in the direction of decreasing the lattice thermal conductivity by means of decreasing grain size and introducing local scattering centers.

Meanwhile it was mentioned in literature [1] another way to obtain high performance thermoelectric material by using resonant impurity levels. The introduction of dopants possessing energy level in the band of the host material may create resonant levels which can distort the density of states near the Fermi level and contribute to an enhanced thermopower. Tin was found to be a resonant impurity in the binary compound Bi_2Te_3 [1].

In this work we tried to modify the electrical properties of polycrystalline $Bi_{0.48}Sb_{1.52}Te_{3.1}$ by addition of a small amount of Tin. The samples were prepared by melt-spinning and the resulting ribbons were densified by Spark Plasma Sintering. Electrical and thermal properties were measured from 300 to 460 K. The influence of Sn on the transport properties of $Bi_{0.48}Sb_{1.52}Te_{3.1}$ is discussed.

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Promising Thermoelectric Properties of the $AgBiCh_2$ System with ZT>1

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p-type I-V-VI compounds have been known for long as promising lead-free thermoelectric materials, with large ZT values in the 500K-800K temperature range, mostly originating from their intrinsically very low lattice thermal conductivity. AgSbTe2 is one of the typical members of this family of materials. When alloyed with GeTe and PbTe, it constitutes the main building block of the TAGS and LAST compounds respectively, which exhibit among the largest thermoelectric figure of merit ever reported in the medium temperature range. However, their wide scale applications potential is limited due to the presence of expensive Ge, scarce Te or toxic Pb on the one side, and on the other side to the thermodynamic instability of their nanostructures which makes these alloys loose part of their excellent thermoelectric properties upon long term annealings. In the past few years, our group has focused part of its activities on the search for new lead and tellurium free thermoelectric materials, which could be used for wide scale applications in the medium temperature range. These studies resulted in evidencing the large ZT values of the p-type BiCuSeO-based oxychalcogenides, with ZT>1.4 at 900K. It also resulted in evidencing the promising thermoelectric properties of n-type I-V-VI materials with AgBiSe2 parent compound (ref 1,2). This material is a moderate band gap n-type semiconductor, which can be switched from n-type to p-type with appropriate doping. Although its thermoelectric power factor, which can be optimized by tuning the charge carriers concentration, is moderate (PF<5.10-4 W.m-1.K-1), it is more than compensated by the intrinsically very low values of its lattice thermal conductivity, which are lower than 0.5 W.m-1.K-2. Therefore, ZT=1 is reached at 800K with appropriate doping level. Although this figure of merit is very promising, AgBiSe2 exhibits two phase transitions at 470K and 570K, which could preclude the use of this material is thermoelectric devices. However, the high temperature phase can be stabilized by a partial substitution of Se by S to form AgBiSeS, while keeping the figure of merit unchanged. In this presentation, I will present the main properties of this family of materials, and discuss their potential for further improvements. 1. L. Pan et al., Journal of the American Chemical Society 135, 4914 (2013) 2. Y-L. Pei et al, Energy & Environmental Science 6, 1750 (2013)

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The Study of Topological Insulator in $Bi_{1.5}Sb_{0.5}Te_{1.7}Se_{1.3}$ Nanoflakes and their Thermoelectric Properties

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Topological insulator (TI) is a new quantum material. The surface states of TIs are protected by time-reversal symmetry which allows charge carrier to propagate on the edge of surface conducting channel without scattering. Bi1.5Sb0.5Te1.7Se1.3 (BSTS) is a well-known TI [1] and thermoelectric material because of its promising thermoelectric performances at room temperature. The conversion efficiency of thermoelectric material is characterized by the dimensionless figure of merit ZT. Decades of effort were devoted to ZT optimization either through composition alteration or nanostructure fabrication.

In this study, a series of BSTS flakes 80 nm to 140 £gm in

thickness was fabricated to investigate their metallic surface states. Up to 90% of the total conductance from the surface channel was estimated based on the thickness dependence of electrical conductance and the result of the Shubnikov-de Hass oscillations in a 200-nm BSTS nanoflake with two distinct frequencies of relativistic Landau levels were present in the top and bottom surfaces.
It is found that the thermopower in topological insulator BSTS nanoflake with 130 nm thick shows pronounced p-n transition at 150 K which resulted from the difference of Fermi level positions of two surfaces. The tunable Fermi level position in BSTS nanoflakes at a low temperature may open up a way for low temperature energy conversion applications with TI base devise. [1] Zhi Ren et al., Phys. Rev. B 84, 165311 (2011).

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Experimental Validation of a Multiphysic Model for Optimization of Thermoelectric Generators

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Energy harvesting from waste heat is an important goal. Exhaust gases and combustion gases are typical sources of waste heat that can be converted into electricity by the proper use of thermoelectric generators (TEG). A multiphysics computer model based on fluid mechanics, heat transfer and thermoelectric equations which simulates performances of the whole thermoelectric systems has been developed with Matlab®. By using a combined genetic/Newton Raphson algorithm applied to this model, we have been able to maximize the produced electrical power optimizing both the occupancy rate and the currents for different operating points of TEG (Hot gas temperature and airflow rate). To validate both the code and the optimization, an experimental loop including a hot gas source, a cold fluid sink and a TEG composed of a hot fin exchanger, tubular cold exchangers and a flexible number of thermoelectric modules has been designed. Two designs have been tested, one with the hot exchanger partially covered and the other with the hot exchanger completely covered. Open circuit voltage measurements on the TEG have been carried out first. Specifics MPPT (Maximum Power Point Tracker) DC/DC converters developed by the laboratory have also allowed us to complete the study of the TEG with a generator loading a battery. First comparison between experimental results and the model will be presented. They include the produced electrical power and the temperatures profile along the exchanger. We have mainly studied the influence of the occupancy rate, when both the airflow rate and the hot inlet gas temperature vary. Both of them show the interest of optimizing the occupancy rate to maximize the produced electrical power.

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Feasibility Study on Screen Printing as a Fabrication Technique for Low-Cost Thermoelectric Devices

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Conventional fabrication techniques for thermoelectric devices at present are expensive, time-consuming, have low yield of material and come with a high failure rate for the devices. The proposed fabrication technology, screen printing of thermoelectric devices, offers a low cost, flexible and quick manufacturing solution with a high yield of material which would help boost the market for miniature thin film thermoelectric devices of high voltage outputs, which can be utilised in numerous applications (e.g. energy harvesting, aerospace and automotive applications) but where current devices are too expensive to be commercially attractive.

The materials used for the prototype screen-printed devices within the project were: n-type Bi_2Te_3 and p-type Sb_2Te_3 thermoelectric materials, silver for the electrical contacts and glass and aluminium oxide as substrate materials.

Five discrete stages were described and well-defined as part of the ink formulation and screen-printing process: powder synthesis, the formulating stage, the milling, screen printing, and finally heat treatment. Trials defined the right composition for the inks, the screen-printing parameters, as well as the sintering process parameters.

A mathematical model developed for the estimation of the electrical performance of screen-printed devices. The model was 'calibrated' using simulation and test results.

A test rig for testing thin to thick thermoelectric devices was designed and developed. Tests of screen-printed single semiconductor pair samples using the test rig proved that the fabrication technique proposed is very promising, by demonstrating a power output of 16μW and a voltage output of 2.1mV for the single p-n junction at a AT of 20°C across it, which compares well to existing systems in terms of voltage (power output needs to be improved).

The feasibility study has not only helped to define a promising fabrication method for thermoelectric devices,

but also to identify the main challenges associated with it and realise that in many energy harvesting application the ZT of a thermoelectric device may not be as important as the thermal stability and longevity of it.

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Characterization of High-Temperature Thermoelectric Modules

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The development of high-temperature thermoelectric generators will enable the conversion from waste heat into electricity in a wide range of applications. For example, in the automotive production, high performance thermoelectric generators are vital for reducing energy consumption and emissions. Considerable effort is needed in order to implement the existing range of materials with high ZT into efficient and reliable generators. In addition to a high power output, a high performance module is characterized by the robustness against a multitude of temperature changes.

Fraunhofer IPM is focusing on assembly and characterization of thermoelectric modules with operating temperatures up to 600°C. Measurement instruments have been developed in order to determine the power output as a function of temperature. A number of temperature cycles is applied in order to test the stability of the modules.

Modules based on filled cobalt antimonite skutterudites as well as on half Heusler compounds have been developed [1,2]. An update on module performance and stability tests is given for high temperature modules. Simulation results are presented and compared to the experimentally determined module data.

[1] K. Bartholomé et al., ICT 2013 Proceedings, to be published
[2] J. Heuer et al., EMRS 2013 Proceedings, to be published

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The Effect of Temperature Mismatch on Interconnected TEG Arrays

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The use of thermoelectric generators (TEG's) to recover waste heat energy has increased rapidly in recent years with applications in fields such as remote sensing, automotive and space systems, and industrial power plants. The power requirements depend strongly on the application, but span the range from microwatts to kilowatts. In systems where more than a few Watts are needed, several thermoelectric modules are deployed in arrays with series and/or parallel interconnections in order to provide the required power level. The method of interconnection of the TEGs is usually determined by the voltage and/or current required.

Maximum power point tracking (MPPT) electronic converters are typically employed to maximise the power extracted from each TEG array. This leads to the formation of what is called a distributed MPPT subsystem in which each TEG array's electrical operating point is controlled independently. The primary motivation for this approach is that in most TEG systems the individual thermoelectric modules are subject to temperature mismatch. Examples of situations where this mismatch occurs directly include thermal variability as found in exhaust gas systems or where the thermal conductivity of the mechanical system is poorly controlled. Variability of the electro-thermal performance of individual TEG modules is also sufficient to cause a significant mismatch. The mechanical clamping force the TEG is subjected to indirectly contributes to similar variation in electrical operating point, due to changes associated with the thermal contact resistance which is partially pressure dependent. Consequently, when in operation each TEG in the array will have a different maximum power point. This maximum power point is the electrical operating point at which maximum energy can be extracted from the TEG. Ideally each TEG should be independently electronically controlled but this would greatly increase the number and complexity of the MPPT power electronic converters needed and adversely affect the cost of implementing the system.

As the application of TEGs extends into progressively lower cost applications the overall system economics dictate that a compromise must be found between the number of MPPT converters and the number of TEG modules connected to each converter. Problems of decreased thermal efficiency (due to parasitic Peltier effects) or decreased power output arise if the TEGs connected in the same array are subject to temperature mismatch because the MPPT converter sets the same suboptimal electrical operating point for each module in the array. This work analyses the impact of thermal and mechanical mismatches on the power produced at module and system level in a TEG array connected to a single MPPT converter. Experimental results clearly illustrate the issue and a theoretical model is presented to quantify the impact.

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Waste Heat Recovery in Steel Works Using Thermoelectric Generator

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In Japan the integrated steel works has largely lowered its energy use for the past several decades throughout the investment of energy efficient processes and facilities, and has kept the highest energy efficiency in the world. However, in view of energy security, the steelmaking industry is strongly required to develop new technologies for further energy saving. Waste heat recovery can be one of the key technologies to meet the requirement. To recover the waste heat, particularly radiant heat from steel products which had not been used yet efficiently, a thermoelectric generation is one of the most effective technologies to recover it, because thermoelectric generation can convert heat directly into electric power. A thermoelectric generation system was installed in the butt welded pipe mill at East Japan Works (Keihin District) of JFE Steel Corporation in the May of 2011. In this system, a thermoelectric generation unit consists of 16 Bismuth-Telluride thermoelectric generation modules, each module can generate 24 W when the hot-side temperature is 553K and the cold-side temperature is 303K. These thermoelectric generation modules are separated into 4 groups and four thermoelectric generation modules were connected in series, and the other were connected in parallel. A maximum power point tracking (MPPT) control unit which is commercial battery charger for off-grid photovoltaic system was used, and the output of sixteen thermoelectric generation modules is used to charge storage batteries and supply power to LED lamps through MPPT controller. This paper describes the performance and durability of the thermoelectric generation system which had been investigated under some operating conditions in butt welded pipe mill.

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Scalable, Non-equilibrium Processing of Thermoelectric Materials and Their Properties

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We present a review of recent progress on bulk thermoelectric materials synthesized via non-equilibrium routes at Brookhaven National Laboratory and others. Melt-spin and thermal spray are two well-established non-equilibrium manufacturing processes. We have experienced both. A family of high performance thermoelectric materials has been developed by converting rapid solidified precursor into crystalline bulks. This family includes tellurides, silicides, half-Heuslers, and filled skutterudites. We have studied basic relationships between nanostructures and the macroscopic properties of these materials by a coordinated characterization approach, including direct transport measurement, neutron scattering, and electron microscopy to provide both basic understanding and understanding of materials aspects for practical energy conversion. The rapid conversion process reduces grain growth, suppresses second phase formation/segregation, and enhances grain boundary coupling. The range of gain size spans from a few nanometers to a few micrometers that is very effective in scattering a broad spectrum of heat carrying phonons at various wavelength. In case of the filled skutterudites, percentage of cage-filling elements can be substantially increased during non-equilibrium processing, extending the range of chemical tuning, or position of the Fermi-level. Reduction of lattice thermal conductivity and increase of power factor can be achieved simultaneously. Measurements of the phonon density of states by inelastic neutron time-of-flight scattering and specific-heat measurements along with first-principles calculations, not only provide compelling evidence for the existence of Einstein oscillators (rattler) motion at low energy (for instance, at 5 meV in the filled skutterudite Yb0.2Co4Sb12), but also revealed multiple dispersionless modes in the measured density of states (such as in Yb0.2Co4Sb12) at intermediate transfer energies which suggests these modes are owed to a complementary mechanism for the scattering of heat-carrying phonons in addition to the low energy mode, and hence offers a plausible explanation for the significantly higher dimensionless figures of merit of filled skutterudites, *The work at Brookhaven National Laboratory was supported by US Department of Energy (DOE) Office of Science, DOE Office of EERE, DOE/NSF Partnership, and Brookhaven Technology Maturation Fund.

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Thermoelectric Transport in Cylindrical Ni and NiCo-Alloyed Nanowires

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The anisotropic magneto-thermal resistance (*AMTR*) effect is the thermal analogue of the anisotropic magneto-resistance (*AMR*) effect observed in ferromagnetic conductors. We have investigated the AMTR effect in Ni nanowires [1]. We present measurements of electrical and thermal transport properties of cylindrical Ni nanowires in the temperature range between 78 K and 380 K. The determined AMTR ratios lie below the AMR ratios, resulting in an anisotropic Lorenz number. To explain this observation, we apply a

simple model that considers spin mixing due to electron-magnon scattering. In comparison, we will present measurements of the magneto-thermal resistance (AMTR) on GMR Co/Ni multi-layer multilayers under thermal transport in-plane [2], where a Field-independent Lorenz number over the entire temperature range is observed.

The magneto-thermopower (Seebeck coefficient) is measured and correlated to the anisotropic magneto-resistance of Co-Ni alloyed nanowires [3]. By a micrometer setup, three magneto-thermoelectric quantities are determined along the nanowire in magnetic fields applied perpendicularly to the nanowire axis: temperature difference, thermovoltage and electrical conductivity. The highest absolute and relative variation of the Seebeck coefficient are determined to be 1.5 µV/K at RT for $Co_{0.24}Ni_{0.76}$ nanowires and 10.9 % at 100 K for Ni nanowires. Power factors of 3.7 mW/mK^2 have been achieved, which is competitive with common thermoelectric materials like TiS_2 and Bi_2Te_3. For Co-Ni nanowires containing up to 40 % Co a linear relationship between the magnetic field dependent change of the Seebeck coefficient and the electrical conductivity is found following the Mott relation.

Acknowledgements:
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Preparation, Nano Processing and Thermoelectric Properties of Boron Carbide

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Ceramic thermoelectric (TE) Materials are receiving increased attention for energy conversion from waste heat because they are cost-efficient, environmentally friendly and thermally stable at high temperature. Among them boron carbides with large Seebeck coefficient, moderate electrical conductivity and low thermal conductivity are promising candidates as high temperature thermoelectric materials [1]. Recent studies indicate that nanostructuring can be an effective method for increasing the dimensionless thermoelectric figure of merit (ZT) in materials [2].

In the first part of this work boron-rich carbides were prepared by spark plasma sintering (SPS) of B_4C with addition of boron powder. The composition and the microstructure of the dense ceramics are characterized by means of XRD, SEM and EDX. In addition, the correlation between the composition and the thermoelectric properties was investigated. The electrical conductivity of the samples increases with increasing addition of boron and the thermal conductivity decreases with boron addition. In the measuring temperature range from 50 to 600 °C high Seebeck coefficient >200 µV/K has been achieved. Accordingly the dimensionless Figure of Merit ZT of the samples was improved compared with that of the boron carbide without boron addition.

In the second part nanostructuring experiments of boron carbide were performed using amorphous boron and carbon powders. The effect of nanostructure on the thermoelectric properties was investigated.

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High-Temperature Thermoelectric Properties of Tetrahedrites $Cu_{12}Sb_{4-x}Te_xS_{13}$

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Over the last years, an increasing number of studies were devoted to the identification of new efficient thermoelectric materials based on non-toxic and abundant elements. Sulfur-containing natural minerals such as sulfosalts, or tetrahedrites of general formula (Ag,Cu,Fe)12(Sb,As)4S13 belong to this class of materials. The latters were recently shown to exhibit very interesting thermoelectric properties. The rather complex cubic lattice that contains 58 atoms results in very low thermal conductivity values (0.4 - 0.3 W/m.K at 300K). Combined with high thermopower values, promising ZT

values were reached in Cu12-xZnxSb4S13 (1.0 at 673 K). These good thermal and electrical properties together with the numerous possibilities of substitutions make this family of compounds a worthwhile area of research to achieve higher ZT values. In this study, we tried to influence and optimize the thermoelectric properties of Cu12Sb4S13, substituting Sb by Te. The tetrahedrites Cu12Sb4-xTexS13 (0<X<2) class=breakhere of the with for and between at in by The

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Adaptive Thermal Conjugation at the Proximity of TEG Contacting Surface for Mid-Temperature Operation

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For the practical application of thermoelectric power generation (TEG) system, it must be needed not only the development of TEG device but also its of the system integration. In particular, to realize the stable thermal contact is an effective way to keep high performance of TE power generation. The use of thermal interface materials (TIM) is one of the effective approach to stabilize a thermal conjugation. These are used to fill the air gaps on the thermal contact interfaces and reduce a thermal contact resistance. Generally, silicone based TIMs are applied for low temperature devices such as Bi-Te TEG and CPU cooler. However, these are difficult to use long time at the mid-temperature and uncertain about the electrical insulation and a fixing of TEG in the system because of these liquidity. Thus, we examined TIMs for mid-temperature operation to avoid the loss of heat flow from heat source. Regarding the thermal drain side, we also inquire TIMs from the point of view of thermal conjugation, electrical insulation, and fixability. Here the important characters of TIMs are its of the thermal conductivity and the thickness of the material, and its ability to fill the contact surfaces. Above mentioned points of view, we chose a Boron-Nitride (BN) paste for the middle-high temperature TIM. It seemed to fill the air gap because it is composed by 0.5~0.7 µm grains. Regarding the thermal drain side, i.e. the low temperature (~473 K) side, 60 *f*êm poly-urethane sheet and 500 µm silicone rubber were chosen. These sheet type TIMs are able to realize an certain electrical insulation and fixing on the heat sink. The performance of TIMs were evaluated by comparison of the each thermal contact resistivity on the thermal interface between two of oxygen-free Cu blocks. These were calculated using measured heat flow, temperature decreasing on the interface, and the cross-sectional area of the interface. The main parameters are the effect of surface roughness characteristics, applied contact pressures, and the interface temperatures. The results of high temperature range, the thermal contact resistivity of BN paste-filled interface was constantly shown the value of 0.5×10^{-4} m^2K/W, which of the interface temperature dependence and the surface roughness dependence are smaller than that of the non TIM-used interface. Especially, at the case of rough interface (Rz = 100 *f*êm), the thermal interface resistivity of BN paste-filled interface is smaller than its of non TIM-used ($\geq 0.7 \times 10^{-4}$ m^2K/W). Regarding the low temperature side, poly-urethane sheet reduce the thermal contact resistivity for all temperature range (383~473 K) and various roughness compared with the case of non-TIM-used. These results lead to the conclusion that the use of BN paste and poly-urethane sheet seems to be effective way to stabilize and increase the TEG performance for the mid-temperature operation.

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Improving Thermoelectric Cooling by Light Emission

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Conventional approach to improve the cooling performance of a thermoelectric refrigerator is to increase its coefficient-of-performance (COP), which in turn requires to improve the thermoelectric figure-of-merit of thermoelectric materials. However, it has been recognised that improving the heat dissipation from the hot side of a thermoelectric refrigerator can indirectly improve the cooling performance of the thermoelectric refrigerator. In this paper, a new approach is proposed that explores the possibility of reducing heat dissipation from a thermoelectric refrigerator through a combined thermoelectric-photoemission effect. The desirable device structures and the conditions required for observing the improved heat dissipation through combined thermoelectric-photoemission effect will be discussed.

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Heat Sinks for Miniature Thermoelectric Coolers: Selection and Characterization

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Finned heat sinks (HS), separate or assembled with fans, are widely used for removing heat from miniature electronic and optoelectronic components such as miniature thermoelectric coolers, microprocessors, semiconductor lasers, LEDs and other small-sized electronics. As a rule, dimensions of these components are considerably smaller than those of a heat sink base while their heat flux can exceed 100 W/cm2.

The state-of-the-art heat sinks available at the market are supplied with full set of dimensional and thermal characteristics including measured value of thermal resistance R_d. It must be noted that the specified R_d value corresponds to the concrete dummy element used as a heater in manufacturer's experiment. In practice, the footprint of the cooled electronic device can differ greatly from that of the dummy element. As a result, the HS actual thermal resistance R_{hs} in real application can vary greatly from its certified R_d value due to significant change in the heat spreading resistance of the heat sink base. In this paper the following problem is formulated and solved: given is the heat sink with its experimentally defined thermal resistance R_d which corresponds uniquely to the concrete dummy heater used in the manufacturer's test; it is necessary to define its thermal resistance for any other heating element using R_d value as a sole reference point. To solve this problem, the HS thermal model with 3-dimensional heat spread in its base is developed and analytical method of transition from certified R_d value to the actual thermal resistance R_{hs} for the heat source with arbitrary dimensions is proposed. The method is applied for characterization heat sinks of the Alpha Company, Ltd. [1], the leading HS manufacturer which gives detailed description of their experiments including dummy heater dimensions. Considered are heat sinks of LPD series in the conditions of natural and forced convection. It is shown that their thermal resistance, being dependent on heat source dimensions, can significantly differ from its certified value. Particularly, this concerns the case of forced convection when HS base spreading resistance becomes predominant. Developed theoretical approach is generalized on the case of heat rejection from thermoelectric cooler with localized heat source at its cold substrate.

1. Alpha Company Low Pressure Drop Heat Sinks, LPD series, www.micforg.co.jp

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Development of Enhanced Bi_2Te_3-Based Thermoelectric Materials and Modules for an RTG for Space Exploration Missions

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Radioisotope Thermoelectric Generators (RTGs) are useful for producing sustainable energy used for powering spacecraft, especially for deep space missions where solar arrays are not feasible. Thermoelectric efficiency is one of the most important parameters for such systems and this work describes the process of developing optimised thermoelectric (TE) materials and devices for maximum efficiency.

High aspect ratios (thickness/cross-sectional area) of the pellets within thermoelectric modules (TEMs) lead to an increased module efficiency, but at the cost of reduced structural strength and more challenging manufacturing processes. The improvement of the inherent mechanical properties of the thermoelectric material and the development of an optimum fabrication method for both the materials and the devices were investigated in order to tackle the aforementioned two problems.

Two approaches were followed while assessing ways to improve the thermoelectric materials: different fabrication methods and different material compositions. As part of the first approach, sample pellets fabricated via the Vertical Bridgman method and pellets fabricated via Spark Plasma Sintering (SPS) were tested according to the Single-edge V-notch beam (SEVNB) method. Pellets made via SPS had two different compositions (no B4C nano-inclusions and 0.2 vol% B4C). Vickers hardness measurements were also performed for both vertical Bridgman and SPS samples.

Since the limiting material for the overall module manufacturability and properties is the p-type TE material, the composition studies only focused on that. $Bi_{0.5}Sb_{1.5}Te_3$ was found to be the most advantageous in terms of TE properties among the 3 proposed compositions. The nano-inclusion of B4C was assessed in 4 different concentrations: (0, 0.1, 0.2 and 0.5 vol%) via simple TE properties measurements, XRD analysis for grain sizes and the SEVNB method.

Compressive strength tests were conducted for 3 TEMs with pellets 4mm, 6mm and 8mm high, made via the Vertical Bridgman method. The aim was to identify the ultimate clamping strength for the TEMs, to demonstrate that it is higher than the clamping pressure required for good thermal contact to the radioisotope heat source. Assessment of failure modes for each TEM was carried out using SEM and a binocular optical microscope.

The study helped in defining all SPS and ball milling parameters, developing a pelletising strategy for taller pellets and deciding on a clear TEM assembly route.

The study concluded that the SPS process adds greatly to the mechanical strength and fracture toughness of the TE materials without affecting significantly their

performance. 0.2 vol% B4C has little effect on TE properties, increases the material hardness and has negligible effect on fracture toughness. The compressive strength of the TEMs was found to be in excess of their optimum clamping pressure.

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Standardisation of Thermoelectric Material Characterization

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Measurement and comparison of physical quantities is an essential background for research and business. Therefore the availability of standards and precise metrology is necessary in every field. Herein we report about the status of thermoelectric standardization and metrology which gets more and more important to verify path breaking results of high values for the dimensionless figure of merit (ZT) as well as for acceptance of thermo¬electricity in industry. The measuring instrumentation itself and the way samples are measured are important issues. Therefore a central point is the development of simultaneous measurements of the thermoelectric properties in order to avoid annealing effects disturbing the validity of a ZT calculation from sequential property measurements and thus to reduce measurement uncertainties. Several measurement setups were developed and different affecting factors on the accuracy of the measurements were investigated. SiGe and FeSi2 are synthesized and qualified as reference materials for the interlaboratory round robin test which has already been started. The status of the development of these materials as high temperature measurement standards will be presented and an overview of the measurement setups including the reference measurement setup SRX-PTB will be given. The intermediate status of the international interlaboratory round-robin test organized by the German project TESt (Thermoelectric Standardization) will be reviewed.

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Uses and Description of a 3-Layer Model for the 3Omega Method in Cartesian and Cylindrical Coordinate Systems with or without Buried Heater and for Various Boundary Conditions

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The 3Omega method is a well-established method for the measurement of the thermal conductivity and heat capacity of liquids and solids. A heater is used to generate a thermal wave. The temperature amplitude measured on the heater is a function of the thermal properties of the materials in its vicinity. The 3Omega method is highly versatile and useful for characterizing functional materials in all physical states at various temperature and pressure. The shape of the heater depends on the properties that must be measured. Narrow heaters are used for the measurement of the thermal conductivity while much wider heaters are used to access to the heat capacity. The heater material can be the material under investigation as well. The heater may be deposited on top of films, immerged in liquid, or fabricated on a substrate of known properties and buried below the film to be characterized. For simple measurement configurations, analytical formula exists but the most advance measurement configurations rely on finite element or volume methods. In this article all measurement configurations known to date are reviewed. A 3 layers model in Cartesian and cylindrical coordinate systems with or without a buried heater is presented. The uses of the model are identified and illustrated. It is found that the model is relevant for extracting in-plane and cross-plane thermal properties of printed thermoelectric materials or any thick enough films. The model removed biases in the ac hot wire method and in the heat capacity measurement. It enables to take into account the finite size of the sample better, but also buffer and diffusion barrier when needed.

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Measurement of the Temperature Dependent Thermal Properties of TE Materials by a Simple Methodology Using Photothermally Generated Seebeck Effect

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Accurate knowledge of material's thermo-physical properties are necessary for the optimization of TE generators[1]. In these transport properties, thermal conductivity measurements are often conducted by

methods which involves a separate temperature sensor. Recently, we have introduced an accurate and direct method, so called photothermoelectric technique (PTE) [2], for measuring dynamic thermal parameters of TE samples by measuring their thermoelectric signal in harmonic regime, generated by an intensity modulated laser induced temperature gradient in the TE sample under investigation. The PTE procedure usually needs a continuous scan of thermoelectric signals in a specified frequency range generated by the periodical laser excitations on the TE sample. The selection of the frequency range depends on the sample's thermal properties as well as its thickness. Here, a simple experimental procedure for investigating the temperature dependent thermal transport properties of TE samples using PTE signal is described from a single and properly selected laser excitation frequency instead of doing time consuming frequency scans for each temperature steps. The theory for analyzing the experimental signals and some of our experimental results will be presented. [1] G Jeffrey Snyder and Eric S Toberer. Complex thermoelectric materials. Nature mate- rials, 7(2):105{14, February 2008. [2] Maju Kuriakose, Michael Depriester, Roch Chan Yu King, Frdrick Roussel, and Abdelhak Hadj Sahraoui. Photothermoelectric effect as a means for thermal characterization of nanocomposites based on intrinsically conducting polymers and carbon nanotubes. Journal of Applied Physics, 113(4):044502, 2013.

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On Improvement of the Accuracy and Speed in the Process of Measuring Characteristics of Thermoelectric Materials

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Analysis of known methods and equipment for measurement of thermoelectric material properties has shown that the errors in determination of thermoelectric figure of merit Z reach 10-15%. The largest values of errors are specific to figure of merit determination by measuring the electric conductivity, thermoEMF and thermal conductivity on different samples. Such errors become an obstacle for solving the tasks of material figure of merit improvement, as long as measurement accuracy may prove to be lower than a change in material properties with a variation of affecting factors. In so doing, the absolute method and the Harman method can yield the most reliable results. Research cycle performed at the Institute of Thermoelectricity has shown that the errors in figure of merit determination by the Harman method can be on the level of 5-6% only in some cases, namely when a plurality of additional parameters is known, such as sample and thermostat radiative properties, thermal conductivity of current leads and thermocouples, etc. The absolute method which permits instrumental minimization of the majority of error sources seems to be more efficient.
The results of creation of new error reduction methods obtained by studying the real physical models of the absolute method by object-oriented computer simulation are given. The influence on measurement accuracy of radiation, heat losses in electrodes and structural elements of measuring setup, non-point probes and sensors, imperfection of thermal and electrical contacts has been established. Methods for reduction of this influence have been developed. Automated measuring equipment for comprehensive study of thermoelectric material properties has been created whose accuracy in the determination of thermoelectric figure of merit exceeds several times the accuracy of known analogues. The errors achieved when measuring in the range of temperatures 30-500°ñ on Bi-Te based materials are as follows: electric conductivity ~ 0.5%, thermoEMF ~ 0.7%, thermal conductivity ~ 3%, figure of merit Z ~ 4.7%. Dynamic processes when reaching steady-state measurement conditions and possible errors due to deviations from these conditions have been also investigated. Functions of current through the sample, reference heater and radiation shield heater have been determined whereby measurement speed is increased by a factor of more than 1.5, which is particularly important when studying large size samples, such as parts of thermoelectric material ingots.

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Testing Bench for the Thermoelectric Modules and Materials

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We present the complex measuring facility which enables characterize the power generating thermoelectric modules under a wide range of temperatures (Tcold = 20-80^{o}C ,Thot < 500 ^{o}C) and mechanical loading conditions (P = 0 - 20 MPa). In addition to the simultaneous temperature and electrical monitoring of the thermoelectric module, the actual heat flow through the module, heat rate and mechanical load are also monitored. The key components of the testing bench represent the thermally shielded heating block with mechanical loading system, water cooled copper cold-plate, electrical load system, K-type thermocouple array, data acquisition computer controlled apparatus and

interconnecting cables. Our testing bench is thus a useful tool enabling to asses e.g. the thermoelectric parameters of newly developed thermoelectric modules and/or to extract the thermoelectric parameters of commercially available modules and confront these values with parameters declared by manufacturer.

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Effect of Open Die Pressing on Chemical-Physical Properties of Zn_4Sb_3 Compound

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Recently, semiconducting intermetallic compounds, belonging to the Zintl's Phases, have attracted much attention due to their unexpectedly low thermal conductivity, which leads to improved thermoelectric properties. The glass-like thermal conductivity of Zn_4Sb_3, originated in the framework Zn position of its structure, make this compound one of the most studied phases in the thermoelectric field. The reduction of grain size obtained by the melt spinning process can lead to an improvement of Figure of Merit-ZT but, unluckily, is associated with an increase of material brittleness. As prosecution of a previous work, Zn_4Sb_3 and $Zn_{3.96}Al_{0.04}Sb_3$ melt spun samples and powders obtained by a solid-phase synthesis were sintered by Open Die Pressing (ODP) process: with this technique, already used to sinter chalcogenides nanopowders, bulk samples with high density and compactness were produced. Chemical physical properties and the stability of the pure and doped â-phase Zn_4Sb_3 are investigated after ODP process. All samples were studied in terms of crystal structure (PXRD), phases composition (SEM_EDXS), thermal stability (DSC) and thermoelectric properties. Preliminary results show the formation of ZnSb phase into the â-Zn_4Sb_3 matrix after both, melt spinning and ODP processes: the effects of time and temperature parameters of ODP process on ZnSb phase formation has been investigated. Thermoelectric properties have been compared for the different conditions.

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Multiphase Behaviour in $Ti_{1-x}Zr_xNiSn$

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Half-Heuslers show great promise as thermoelectric materials due to their naturally high Seebeck coefficients (S) and low resistivity values (ñ). Amongst the most successful half-Heusler compounds are those based on XNiSn, where X = Ti, Zr or Hf. Substitution on the X-site has been used very effectively to reduce the thermal conductivity (ê). However, there are discrepancies in the reported thermoelectric parameters for nominally identical samples. This suggests that structural and compositional variations may exist, but detailed structural analysis of these compounds is often not given in the literature.

To address this we have prepared a series of Ti1-xZrxNiSn (x = 0, 0.25, 0.5, 0.75, 1) samples by standard solid state reactions, and undertaken a detailed structural characterisation involving X-ray and neutron powder diffraction, and electron microscopy [1]. Ti and Zr were chosen as these elements afford both size and mass fluctuation effects which are effective at reducing ê. The diffraction data were fitted using multiple half-Heusler phases, demonstrating that a semi-continuous distribution of Ti1-xZrxNiSn half-Heusler compositions is present in the prepared samples. Analysis of the phases present suggests that this compositional inhomogeneity is caused by sluggish reaction kinetics and is not a thermodynamic effect. We will use this contribution to present our current understanding of the formation of these important thermoelectric materials, and the impact of the multiphase behaviour on the thermoelectric properties.

[1] R. A. Downie, D. A. MacLaren, R. I. Smith and J. W. G. Bos, in preparation.

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Controlling the Thermoelectric Properties by Interstitial Doping in TiNiSn

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Half-Heuslers are of much interest in the field of thermoelectrics due to their naturally high Seebeck coefficients and low resistivity values. Unfortunately, their overall performance is hindered by a relatively large thermal conductivity (κ).

We prepared TiNiSn-based half-Heusler samples by arc-melting, and found that these have an unusually low κ = 4 mW m^{-1} K^{-1}[1]. This leads to ZT = 0.5 at 700 K for nominal $TiNiSn_{0.95}$ and ZT = 0.6 at 700 K for nominal TiNiSn. Rietveld analysis of neutron powder diffraction data revealed the presence of 3-6% excess Ni, located on a vacant interstitial site. Similar reductions in κ have been observed by other groups and have been attributed to either nano- or micro-inclusions of a full-Heusler phase [2-3]. No link to non-stoichiometry within the half-Heusler phase has been made, and it is therefore not yet clear what is causing the large reduction in κ.

We have subsequently prepared TiNiSn samples containing a deliberate excess of transition metal. These were prepared using conventional solid state reactions in order to more tightly control the final composition. We used neutron powder diffraction and electron microscopy to investigate the composition and structure and will discuss how this doping technique affords a novel route to systematically control the electronic properties of these half-Heusler phases.

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Durability Testing of Multiple Coated and Uncoated $CoSb_3$ Unilegs

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Thermoelectric material based on skutterudite, CoSb3, have got a lot of interest the last decade becuase of its high figure of merit at temperatures applicable for heat recoery in automotive and process industry. One challenge is the durability of the material on the hot side where both severe oxidation and sublimation can result. To prevent this some sort of protection is needed to avoid sublimation of Sb and also prevent oxygen to reach the material surface. Also the quality of the interconnects can degrade over time.

In this work we present a fast and reliable method to test the extent of degradation at the surface of the thermoelectric material on multiple legs simultaionusly. This method can be used to evaluate the protective ability of leg-level coatings. Also the metallization layers can be evalutaed mesureing in-situ changes in electrical properties over time. Measurements of the thermoelectric properties before and after thermal cycling on both coated and uncoated material where done and showed that selected leg-level coatings based on Al2O3 offered increase in the durability of the CoSb3 material.

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Nanostructured Thermoelectrics with $CoSb_3$ Precipitates in Ge-Sb-Te Materials

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Quenching high-temperature phases of Ge-Sb-Te (GST) materials yields a metastable modification with layer-like short-range defect ordering that leads to a pronounced intrinsic parquet-like nanostructure. The ZT values of these samples reach values higher than 1.3 at 450 °C [1]. Skutterudite-type $CoSb_3$, which itself as well as substituted or filled variants [2,3] is an important thermoelectric material, can be doped with Ge and Te. Quenching melts with a nominal composition that corresponds to mixtures of GST materials and $CoSb_3$, affords heterogeneous nanostructures with additional phase boundaries. In contrast to top-down fabricated nanostructures, endotactic intergrowth may occur as the lattice parameters of both compounds fit together. This is expected to reduce the phononic part of the thermal conductivity with little impact on the electrical conductivities. In such materials, skutterudite-type precipitates are homogeneously distributed in single-crystals of the matrix. The partial substitution of Sb by Ge and Te in the precipitates has an impact on the composition of the matrix and its microstructure. The substitution degree and the size of the precipitates are stongly influenced by various annealing procedures. Structure analyses of both the matrix and the precipitates using a microfocused synchrotron beam combined with EDX and X-ray fluorescence prove the composition of the material as well as the substitution effects.

The Seebeck coefficient, the electrical and the thermal conductivities in such materials are significantly influenced by the GeTe contents of the GST phase and the amount of $CoSb_3$ present. For example, a 1:1 ratio of both components yields a Seebeck coefficient of 202 µV/K at 450 °C, which is almost twice that of samples with a 2:1 ratio. In the existence range of the metastable GST modification, the ZT value could be notably increased compared to pure GST materials. Ball-milling of annealed material followed by hot-pressing or spark plasma sintering is another intriguing approach to modify and further optimize the thermoelectric characteristics.

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Effect of High Pressure Torsion in Texture, Microstructure and Raman Spectroscopy Study of the Fe and Te Substituted Co_4Sb_{12}

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The double elements substituted skutterudite (Fe0.2Co3.8Sb11.5Te0.5) has been prepared by induction melting, annealing and hot pressing (HP) process. Later on the hot pressed sample was exposed to high pressure torsion (HPT) process with 4 GPa at 673 K. X-ray diffraction was performed on before and after HPT processing samples and it was confirmed that polycrystalline nature of samples with skutterudite phase as the main phase and a small amount of (CoSb2) as a secondary phase in HPT sample. The surface morphology was carried out by high resolution Scanning Electron Microscope (SEM). In the HP sample, coarse grains with grain size approximately 100 to 300 nm ranges were obtained and they changed to fine grains with reduction in the average grain size of 100 nm by HPT process due to the severe plastic deformation. Crystallographic texture, as measured by X-ray diffraction technique, indicated the strengthening of (001) pole and weakening of (123) pole on HPT. Raman vibrational active modes have been investigated which showed that the peak position shifted towards lower energy side (softening the modes) after HPT process. The distortion of the structure of Sb-Sb rings leads to broadening of Sb-Sb vibrational modes which is due to local strain fluctuation. In the HPT process, significant effect on the shorter Sb-Sb bond of Sb was observed as compared to the longer Sb-Sb bond.

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A Flexible Measurement System for Characterization of Thermoelectric Materials

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The figure of merit needs to be determined to rate the quality of thermoelectric materials. Therefore, it is necessary to measure all involved parameters –the Seebeck coefficient (S), the thermal conductivity (λ) and the electrical conductivity (σ). Currently there is no commercial measurement system available which is able to measure all three parameters on a single device. Hence, a measurement system was developed to perform a quick and global characterization of thermoelectric materials. Thereby a movable platform can be lifted up by a pneumatic system. This platform represents the base for two different devices which are used to characterize all thermoelectric parameters. The first device is used to determine electrical conductivity by a four-point-measurement. The used measurement needles are realized by spring mounted pogo-pins to ensure good reproducibility. Due to a pneumatic cylinder the contact pressure can be controlled and thereby caused effects can be studied. The other device includes a water cooler to establish a fix cold side temperature. Two buffer blocks above and below the sample with two thermocouples each are integrated to measure the thermal flow through the sample. Two more thermocouples are pressed against the sample by springs to measure the temperature difference across the material and the voltage between these points to determine the Seebeck coefficient. The simultaneous measuring of λ and S is an additional advantage regarding accurateness and measurement time. A data logger records all parameters and sends them to a computer. A heat insulation around the system reduces the parasitic heat loss to a minimum. Thereby the system is capable to measure the performance of completed thermoelectric generators in a temperature range from 273 K to 873 K. Due to the flexibility of the measurement system it is possible to save time during the measurement, and simultaneously gain higher accurateness because all measurements are performed at the same sample partly at the same time.

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Microfluidic Low Cost Calorimeters for Biological and Chemical Applications

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Thermal analysis or calorimetry is a widely used technique for obtaining both qualitative and quantitative information about thermal transitions associated with a particular material or process. However, the range of

potential applications for calorimetry is far wider as every chemical and physical process is characterised by the change of its energetic state. Calorimetry is therefore a universal analytical method for investigating thermal effects resulting from chemical or biochemical reactions and/or changes in physical states.
Moreover calorimetry does not require any labelling or immobilization of the reactants and is therefore also an attractive methodical approach of detecting biochemical interactions without employing fluorescent markers. However, commercially available classical calorimeters require an unfavourable large test volume and thus a relatively huge amount of test substance. Hence, these calorimeters are not suitable for biochemical or screening applications. These problems can be overcome by applying miniaturised calorimeters containing micro fabricated thermopile chips. Such devices have many significant advantages when applied to biochemical and screening applications including low cost, small sample consumption and fast response times.
Here, we present the development of a low cost thermopile chip. Low cost thermopile chips capable of analyzing small quantities of samples that are easy to use, have fast response times, and good operational stability are needed in many biochemical, chemical and clinical diagnostic applications. To fit a wide range of applications the thermopile chip and the microfluidic device is developed modularly. The device structure can be adapted easily to enable a wide variety of other standard calorimeter operations. DSC, DTA, reaction calorimeters, and "lab on a chip" concepts are possible for single measurements as well as for high throughput characterization. First results will be shown for selected chip layouts.

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A Comparison of Thermoelectric Devices Evaluation Results Obtained with a Harman Method Based and a Porcupine Method Based zT meters

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A comparison is presented of results obtained for the series resistance R and a the dimensionless figure of merit zT of a number of different thermoelectric devices with two instruments based on alternative approaches. One is a commercial zT meter (DX 3065) manufactured by RMT and based on the Harman method, and the other one is a prototype realized at the Politecnico di Torino and based on the porcupine method1, which was introduced at the ITC-2012 in Aalborg2.

All devices were evaluated with both instruments at three different temperatures (20°C, 25°C and 30°C) in a climatic chamber, and results were compared.

As expected from the theoretical analysis1 the porcupine method consistently returned lower R values and higher zT values than the raw data obtained by the Harman approach. A discussion of such results is offered, with some considerations on the corrections of raw data proposed by the manufacturer in the Harman approach.

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Issues, Solutions and Instrument Design Features for Testing and Characterization of Unconventional Thermoelectric Devices

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Thermoelectric materials may play a role in the large scale energy industry with the possibility to effectively exploit waste heat recovery. Well established traditional thermoelectric material, thermoelements and device configuration have been considered and eveluated in the past under this perspective, but their success was limited to special applications due to their limits in conversion efficiency, high cost and low availability of raw material, and low specific electrical output. New thermoelectric devices (TEDs) based upon novel thermoelectric materials, thermooelement's new configurations and device's new architectures are often proposed for their potential in overcoming these limits thanks to improved conversion efficiency, improved specific electrical output, extended material availability and reduced material cost. The characterization of the performance of such TEDs often requires to update and adapt the established methods, facilities and instruments, as well as to rediscuss the modeling of the measure itself. Present work will discuss the issues faced for realization of a novel characterization facility for properties and performance testing of new type of TEDs.

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Finite Elements Modeling of Transient Harman Method Applied to Nanostructures to Elucidate Experimental Requirements

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Modified Harman method is a tool with great potential for rapidly scanning the figure-of-merit (ZT) of emerging

nanostructured thermoelectric materials [1, 2]. ZT is determined based on the voltage developed across a thermoelectric material subjected to an AC current flow at high and low frequencies. The low frequency voltage incorporates both ohmic and Peltier responses, while at high frequencies the Peltier component vanishes. For an accurate determination of the figure of merit is critical to select the correct limit for the higher frequency measurement. An objective of this work is to determine theoretically the lower bound for this high frequency requirement, which was found to depend on nanostructures' geometry (i.e. thin film thickness or nanowire diameter), thermal properties, as well as heat insulation conditions. To study the effect of these parameters, finite element modeling was carried out to resolve the transient thermoelectric transport equations in Bi2Te3 thin films and nanowires. The temperature and voltage response to an applied alternating current was monitored as function of time. It is shown that reducing the thickness of the films or the diameter of the nanowires increases the lower bound for the high frequency, often imposing challenging conditions for the measurement. In addition, the figure of merit calculated under atmospheric conditions is significantly smaller than the expected value, whereas vacuum insulation produces accurate results. However, the electrical contact resistance between the thermoelectric material and the contact electrodes was found to be the most important source of error when determining ZT. These aspects are of high importance to be taken into account in experimental efforts to characterize thermoelectric performance using the modified Harman method. ERC Starting Grant 240497 is acknowledged as a financial support. **References:** 1. R. Venkatasubramanian, E. Siivola, T. Colpitts and B. O'Quinn, Nature, 2001, 413, 597-602. 2. R. Singh, Z. Bian, A. Shakouri, G. Zeng and J.-H. Bahk, Applied physics letters, 2009, 94, 212508.

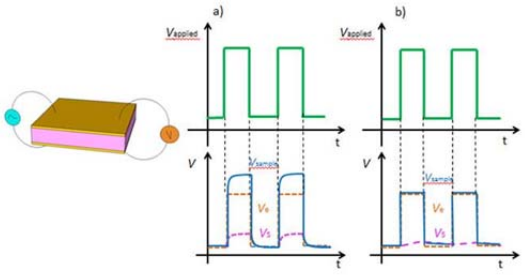

Figure 1. a) Low frequency regime. b) High frequency regime.

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Thermoelectric Properties of TiS_2-Based Compounds

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The particular interest of the TiS2 compounds (and most of layered TX2 chalcogenides) is the possibility to intercalate foreign atoms or molecules into the van-der-Waals gap between the host layers. This method of modifying the physical properties and in particular the electronic structure was widely studied and discussed in the past for practical applications (batteries). It is for instance possible to achieve semiconductor to metal behavior (or vice versa). The occurring changes are ascribed to a charge transfer from the introduced species to the host lattice. In the context of searching for efficient thermoelectric compounds, the Seebeck coefficient and the electrical conductivity of the TiS2 layered compounds can be then optimized through intercalation. Due to change in carrier concentration, the power factor can be then optimized in a specified temperature range. Moreover, if the CdI2 layers form a high-mobility semiconductor, the intercalated layer can create disorder and phonon scattering, decreasing the lattice thermal conductivity. This effect has been recently shown in misfit based sulphide, (MS)1+x(TiS2)2 (M = Pb, Bi, Sn) [1] and copper [2] or silver intercalated TiS2. Another way to reduce the lattice thermal conductivity is to add some disorder on the anionic and cationic sites; this is possible for instance by substituting sulfur by selenium [3] or Ti by heavier cations (Tantalum [4] or Niobium [5]) for example) in TiS2 slabs. Another approach stands in the change in the sulfur stoichiometry which induces some structural disorder and modification of the carrier concentration. The resulting ZT are then improved significantly.

Based on these different approaches, we have proven that the ZT values of TiS2 can be improved. We propose here a short overview of the different results obtained in the last 2 years.

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Thermoelectric Properties of $CuCr_{1-x}V_xS_2$ ($0 \le x \le 0.2$)

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In search of cost-efficient and environmentally-friendly thermoelectric materials, transition-metal sulphides have attracted considerable attention. This class of compounds frequently adopts a structure in which MS_2 slabs of edge-sharing MS_6 are separated by a van der Waals gap, within which there is a network of vacant interlayer sites. Occupation of a fraction of these sites by a second cation yields phases in which cations and vacancies may order, generating a variety of two-dimensional superstructures [1]. $CuCrS_2$ was recently reported to reach a very high figure of merit, ZT = 2, at room temperature [2], although subsequent work has cast doubt on the reproducibility of this level of performance [3]. It has been suggested that a further increase of the thermoelectric efficiency may be achieved through cationic doping that tunes the charge carrier concentration [4]. In the present study, we report the structural characterisation and thermoelectric properties of $CuCr_{1-x}V_xS_2$ ($0 \le x \le 0.2$), in which chromium is progressively replaced by vanadium. The synthesis was carried out by fusing stoichiometric amounts of the elements in evacuated silica tubes at high temperatures. Rietveld refinement using X-ray powder diffraction data shows ordering of the Cu atoms in the tetrahedral sites. The samples were subsequently consolidated by hot pressing in graphite dies and the density of the pellets exceeds 90% of the corresponding crystallographic values. Thermoelectric measurements were performed over the temperature range 30 - 300 ^oC for all samples. The results indicate a marked increase in the power factor for the V-doped compounds compared to $CuCrS_2$. The overall effect of the V substitution in the crystal structure and the thermoelectric properties is discussed. [1] A.V. Powell, P. Vaqueiro and A.D. McDowall, Solid State Ionics, 172, 469, (2004). [2] G.C. Tewari, T.S. Tripathi and A.K. Rastogi, J. Elec. Mat., 39, 1133 (2010). [3] Y.-X. Chen, B.-P. Zhang, Z.-H. Ge and P.-P. Shang, J. Solid State Chem., 186, 109 (2012). [4] N. Tsujii, H. Kitazawa and G. Kido Phys. Stat. Sol. (c), 3, 2775 (2006).

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Thermoelectric and Structural Properties of Co_xTiS_2

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There has been significant recent interest in TiS_2-based materials as potential low-cost thermoelectrics.[1,2] The parent TiS_2 structure consists of two-dimensional MS_2 blocks of edge-sharing MS_6 octahedra, separated by a van der Waals gap. Introduction of a guest species, A, into the van der Waals gap results in phases of general formula, A_xTiS_2 and is accompanied by a transfer of electrons to the TiS_2 block. This produces marked changes in electron-transport properties. Control of the extent of guest incorporation therefore provides a means of systematically modifying the electron transport properties and hence thermoelectric power factor.

Here, we report the results of a systematic investigation of materials Co_xTiS_2 ($0 \le x \le 0.75$) prepared by high-temperature reaction. Whilst the integrity of the TiS_2 block is preserved on cobalt incorporation, structural changes are observed, involving ordering of cobalt ions over the available sites in the interlayer space. Powder X-ray diffraction leads to the identification of a range of two-dimensional superstructures, some of which are stable over an extended range of composition.

Samples for thermoelectric measurements were prepared by hot pressing, which leads to densities that are 80 - 93 % that of the crystallographic value. The metallic behaviour of TiS_2 is preserved on cobalt incorporation. However, with increasing cobalt content, a systematic decrease in resistivity is observed leading to an increase in ZT at temperatures above 423K. All compositions are n-type conductors, with an S(T) dependence characteristic of metallic behaviour, whilst the absolute value, |S|, is reduced with increasing cobalt content.

At 320K, a maximum power factor of 1.18×10^{-5} W cm^{-1} K^{-2} and a ZT value of 0.2 are observed for TiS_2. At 573K, the highest power factor is obtained for $Co_{0.04}TiS_2$, which reaches 1.16×10^{-5} W cm^{-1} K^{-2} and a ZT value of 0.45.

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Structure and Thermoelectric Properties of Ag_xTiS_2 Compounds

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Transition metal dichalcogenides belong to the layered compounds of the type TX2, where T symbolizes an early transition metal of group IV (Ti, Zr, Hf), V (V, Nb, Ta), or VI (Cr, Mo, or W) of the periodic table and X is one of the chalcogenides S, Se, or Te. They are built up by three atomic sandwich layers, which are stacked on top of each

other. Each sandwich consists of a hexagonally ordered sheet of transition metals that is surrounded by two hexagonal layer planes of chalcogen atoms. Although all transition metal dichalcogenides are built up in a similar way, they still differ in their crystallographic description. The transition metal can be coordinated by the nearest chalcogen atoms in two different ways: in the 1T structure (symmorphic space group P-3m1), the chalcogen atoms form a regular octahedron forming a CdI2 type layer. The unit cell contains one sandwich layer in the c direction. The unit cell of the 2H structure is extended over two sandwich layers. In one layer the chalcogen atoms are situated above each other. It is rotated by 60° with respect to the neighboring layers.

The bonds within one sandwich are of strong covalent and ionic character, while the interaction between different sandwich layers is rather weak and van der Waals like. Due to their electronic structure and the degree of filling of d bands, each transition metal group induces different electrical, magnetic and optical character to the material. For example, the transition metals of IVb group are in a d0 configuration, so the dz2 band stays unoccupied and the respective materials are generally semiconductors. This electronic structure offers particularly interesting thermoelectric properties in TiS2-based compounds with high thermopower and relatively low electrical resistivity. The transport and thermoelectric properties are also governed by the possibility to intercalate cations between the layers which generally bring new electron carriers in the 3d conduction band of Ti.

As one of the severe limitation of such 2D materials lies in their difficult densification, the possibility to use spark plasma sintering (SPS) to densify and make silver cation diffuse in an open structure has motivated the present study of AgxTiS2. We demonstrate that dense and performing thermoelectric materials with ZT=0.52 at 700K can be obtained by the beneficial effect of the silver intercalation controlling the charge carriers concentration and creating local structural disorder which makes decreasing significantly the lattice thermal conductivity. Thanks to a detailed crystallographic structure analysis (X-ray diffraction and transmission electron microscopy), we clearly emphasize the effect of silver intercalation on the electronic and phononic properties of TiS2 based compounds.

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Physical Properties of the Clathrate - I Phase $Ba_8Ir_xGe_{43}$ ($x < 0.4$)

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Clathrates are considered to be phonon glass-electron crystal (PGEC) materials, where the electronic properties are similar to good semiconductor/metal single crystals and the thermal conductivity exhibits low values due to the interaction of acoustic phonons with rattling modes of the guest atoms. Therefore, clathrates have high potential as thermoelectric materials. Hall effect, magnetoresistance, Seebeck coefficient and specific heat measurements were performed on polycrystalline samples with nominal compositions $Ba_8Ir_xGe_{43}$ ($0.1 < x < 0.6$). Single phase samples were obtained for $x < 0.4$, crystallizing with a 2 x 2 x 2 supercell of the type-I clathrate structure. Electrical transport measurement revealed a transition from a low-temperature metal-like state to a semiconductor-like state at $220\ K < T < 350\ K$. The Hall resistivity $\tilde{n}_H$ behaves linearly with magnetic field at all temperatures. This behaviour together with the fact that Kohler's plot of magnetoresistance data deviates from a single curve suggest that the electrical conduction has multiband nature. The positive slope of $\tilde{n}_H$ points on the dominance of holes in this material, with a crossover to n-type behaviour above ~ 280 K, detected as well by Seebeck coefficient measurements. The Hall coefficient R_H shows pronounced temperature dependence. The evaluation of μ_H using a single-band picture shows that acoustic phonon scattering plays an important role at high temperatures ($\mu_H \sim T^{-3/2}$) while, at low temperatures, $i_H \sim T^0$. $Ba_8Ir_xGe_{43}$ shows a small and positive magnetoresistance, with a maximum value of ~ 1.12 % for $x = 0.1$ at 10 K and 9 T. The values of the DOS at the Fermi energy, $N(E_F)$ evaluated from the specific heat, are ~ 9.4, 0.1, 5.6 and 12.6 states.eV^{-1}.$(f.u.)^{-1}$ for $x = 0.1$, 0.2, 0.3 and 0.6, respectively.

We acknowledge financial support from the European Integrated Center for the Development of New Metallic Alloys and Compounds (C-MAC).

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Development of a thermoelectric Generator for a 1.4l gasoline Engine: Results, and Future Needs

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To increase vehicle efficiency and reduce consumption and emission maintaining drive performances and passengers safety has been a challenge for cars manufacturers ever since. In very recent years a further push in this direction has come from EU legislation: new CO2 emission performance standards for passengers cars are officially published in the form of Regulation (EC) No 443/2009 of European Parliament and Council (April 23th 2009). Emission target for passengers cars over homologation cycle has been fixed to 130g/km for 2012 while CO2 emission target is drastically reduced to 95g/km for 2020. Near term targets can be achieved through "last generation" engines with Energy Saving measures (e.g. Stop & Start), but car manufacturers must look at new technologies to satisfy long term (2020) requirements and the recovery of waste heat through thermoelectric (TE) elements is a promising candidate. FIAT Research Centre has developed for Magneti Marelli Exhaust Systems a TE generator for Alfa Mito 1.4 Multiair, the testing results and advantages of this device will be presented. Despite the significant power output and valuable benefits in terms of fuel consumption and CO2 emission reduction the generator cannot enter a market that potentially could be million products per year. The reason for this will be analysed and the weak points of present thermoelectric converters (materials and modules) will be examined from automotive manufacturers' point of view. These assessments will be the basis and the starting point to draw a roadmap and enlighten the needs for the very near term in order to definitely transform a promise into a product.

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Challenges in Dimensioning of an Optimized Thermoelectric Generator for Waste Heat Recovery in Cars

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An exhaust system in a car has to face and withstand a lot of different operating conditions and so does a thermoelectric generator (TEG) integrated in the exhaust system. In addition, the TEG has to transform heat into electricity at the highest possible efficiency in order to save fuel. This results in several challenges with regards to the design and the dimensioning of the TEG. One lever to improve the efficiency of a TEG is the optimization of the thermal resistance of the thermoelectric material. This paper shows performance data of TE-modules made of identical material and active area but of different thickness. Measured under thermostatic conditions, i.e. fixed surface temperatures. Subsequently the different TE-modules have been tested in a hot air test bench. Here the consequences of the different thermal resistances can be shown. Furthermore the measurements highlight the influence of the electric load on the thermal resistance of the module entailing different surface temperatures of the modules and different heat transfer rates.

Beyond the experimental results numeric optimization for the optimal thermal resistance of a thermoelectric module for the maximum power generation has been made. The optimum for a single module differs significantly from the optimum of the thermoelectric generator as a whole.

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Modular Modeling, Simulation and Verification of Car Thermoelectric Generation System

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In this paper, modular modeling idea of Advisor software is adopted to package thermoelectric power generation system into a system, using Matlab / Simulink software platform. The inputs are the speed, power of engine, output is the power generation of the system. Battery theory is used to evaluate its efficiency. The system is divided into two subsystems. One is computing subsystem of temperature at the entrance of the system, the other is computing subsystem of power generation of the system. The inputs of the first subsystem are the speed, power of engine, the output is temperature at the entrance of the system. The input of the second subsystem is temperature at the entrance of the system, the output is power generation of the system. For other secondary factors that affect the system, appropriate correction factors are selected to improve the accuracy of the system. Ultimately the effectiveness of the system will be tested through the bench. The system can be used as a new power system - thermoelectric battery system for vehicle use, laying a solid foundation for subsequent simulation of the power, economy, emission performances of low hybrid vehicles based on thermoelectric power generation system.

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Study on the Conversion Efficiency of Thermoelectric Modules Related to the Cooling Unit in the Automotive Exhaust-Based Thermoelectric Generator

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Abstract:The conversion efficiency of thermoelectric modules applied in the automotive exhaust-based thermoelectric generator is greatly influenced by the cooling performance of the cooling unit under different conditions. Wherein the effect brought by the change of cooling flow rate, flow and temperature is particularly prominent. The orthogonal experiment is carried out to analyze these influence factors. First the working process of the thermoelectric generator is simulated in the software CFX and then results are validated by doing bench test . Finally the principle about the influence that the cooling unit has on the modules is concluded according to the simulation and experiment results. The study can provide theoretical foundation for the optimization for the cooling unit to improve conversion efficiency of thermoelectric modules. Key words:the Cooling Unit ,the Thermoelectric Generator,Efficiency

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Thermal Conductivity Reduction in P3HT Nanowires Because of Diameter Confinement Effects

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Although the field of thermoelectric polymers is still in its infancy, the increasingly interest in this topic has resulted in several high index publications recently, such as PEDOT:ToS spin-coated thin films partially reduced either chemically [1] or electrochemically [2], PEDOT:PSS films [3] or P3HT with carbon nanotubes [4], which have evidenced very competitive ZT values with respect to classical Bi2Te3 materials.

This works deals with the study of the variation of the thermal conductivity of nanowires when reducing their diameter size due to confinement effects. This will involve an improvement in the performance of these thermoelectric materials. For that purpose, we have chosen poly(3-hexylthiophene) (P3HT) nanowires, an organic semiconductor polymer, which have been proven to have good thermoelectric properties [4]. In order to obtain these nanowires, we melted and infiltrated P3HT bulk material in three different porous alumina templates. Each one of these templates differs on the size of pore, whose mean average pore, i.e. NW diameters, are 350nm, 220nm and 120nm.

Measuring the thermal conductivity of individual nanowires embedded in matrix is still challenging and nowadays there aren't still many techniques able do it [5]. Nevertheless, there is a technique called the Scanning Thermal Microscopy (SThM) working in 3ù-configuration with which were measured successfully the thermal conductivity of Bi2Te3 and Si nanowires embedded in a matrix [6, 7]. We used this technique to measure P3HT nanowires with 350nm, 220nm and 120nm diameter sizes, whose thermal conductivities were determined to be: 2.22±0.07 W/mK, 0.59±0.04 W/mK, 0.50±0.04 W/mK, respectively. We observed a reduction in its thermal conductivity as a consequence of size confinement effects, which produces an alteration of the ordering of the polymer chains leading to changes of the thermal properties of the nanowire.

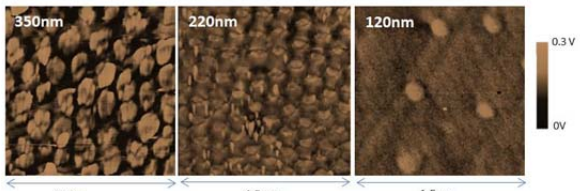

Figure 1. Thermal images of P3HT NWs.

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Development of Flexible Micro Thermo-Electrochemical Generators Based on Ionic Liquids

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Research on thermoelectrics has extended beyond conventional areas to include fields such as microtechnology and thermo-electrochemical technologies. Advances have been made to study physical properties such as the Seebeck Coefficient, electrical and thermal conductivity of ionic liquids (IL)[1]. This work presents a new design for micro thermoelectric generators based on a micro-machined electrode structure, ionic liquids as electrolytes with redox couple and a parylene sealing (SOLID technology [2]). The benefits of low temperature difference energy conversion are expected to have an important impact especially for biomedical and consumer electronic devices. The base material of the device consists of a double-sided Cu coated polyimide sheet. The copper layers are patterned with laser machining and the polyimide sheet is then etched isotropically in order to create reservoirs. The patterning allows series connection between the two sides of the sheet. The holes on one side are filled with p-type ionic liquid, while the other side contains n-type ionic liquid. The whole device is then sealed with parylene, by SOLID technology.

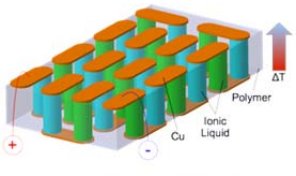

Figure 1 – Principle of monolithic serial connected thermoelectric generators [3]

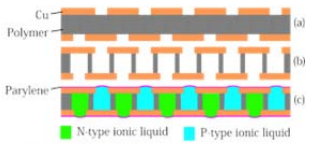

Figure 2 – Manufacturing of generators using liquids as thermoelectrical substances : (a) Cu/Polymer/Cu substrate is laser-patterned ; (b) caverns for the liquid are etched ; (c) after liquid loading, SOLID technology is applied for sealing.

In this paper the correlation between coefficient (α), thermal- (λ) and electrical- conductivity (σ) are studied for a large variety of ionic liquids. Using a single junction test cell (electrode / IL / electrode), the electrode distance, the redox couple concentration in the IL, and the temperature difference across the junction were varied. This set up allows determining the figure of merit ZT= α^2 σ/λ [4] as well as the conversion efficiencies of the generators. It was found in agreement with other authors that the Seebeck coefficient for e.g. 1-Butyl-3-methylimidazolium / tetrafluoroborate (BMIM / BF4) drops from 850 µV· K-1 without redox couple to 324 µV· K-1 with increasing redox concentrations (0.2 M) for LiI/I2 as redox couple. Looking at the single junction cell, surprisingly, it appears that the increase of the redox concentration tends to increase the power output despite the decrease of both conductivity and Seebeck coefficient. This is in strong contradiction to the link between the conventional figure of merit and efficiency of the thermoelectric generator. On the other side, a significant decrease in viscosity is observed for all studied IL's; for instance BMIM / BF4 has at 25°C a viscosity of 75 kg· s-1· m-1 and at 70°C of 18 kg· s-1· m-1. It is assumed that the carrier transport across the cell might be influenced by mechanical properties such as viscosity.

In a very simple model the origin of the Seebeck effect in a liquid is due to the mobility of cations and anions that create at constant heat-flow a steady state potential between hot and cold electrode. This model fits well looking at BMIM / BF4, but not at all for 1-Hexyl-3-methylimidazolium / iodide where the Seebeck potential changes sign in polarity. Apart from the experimental results, the paper aims to explain these phenomena.

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Enhanced Power Factor of PANI/GNP Nanocomposites

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Nowadays, the inorganic compounds (like Bi_2Te_3) are the best thermoelectric materials due to their suitable thermoelectric properties [1] for room temperature applications. Nevertheless, organic materials, like conjugated polymers, are becoming more important recently due to their increasing Figure of Merit (0.25-0.42)[2, 3]. Polymers generally have low thermal conductivity (©§≈ 0.1-0.5 W/m·K), flexibility, environmental stability, easily doping and de-doping, non-toxicity, potential processing advantages (e.g. printing) and straightforward preparation in comparison with inorganic semiconductors. The increase in the Power Factor of this materials, which is given by S^2¥ò, is being achieved by two mechanisms: doping the polymers [4] or blending them with different kinds of filling materials, such as carbon nanotubes, graphene nanosheets (GN) or graphene nanoplatelets [5].

Exfoliated graphene nanoplateles (GNPs)/Polyaniline (PANI) nanocomposites have been prepared by sequential processing comprising: (i) a first aniline oxidative polymerization step under acidic conditions; (ii) a mechanical blending with GNPs at different percentages. Finally, the pellets with different GNP contents have been obtained by cold pressing. The structural, morphological and thermoelectric properties have been characterized by means of elemental analysis, FTIR, SEM, electrical conductivity, Seebeck coefficient and thermal conductivity at room temperature measurements. On the one hand, a drastic increase in both the electrical conductivity and the Seebeck coefficient took place with the addition of the GNPs. The highest power factor value, 14 µW/m·K^2, is reached for a 50 wt% GNPs content which evidence a

1000-fold enhancement with respect to raw PANI polymer. On the other hand, the thermal conductivity has been measured as a function of the GNPs content so that the values range from 0.5 for pure PANI to 3.3 W/m·K for 50 wt.% GNPs content, which matches the thermal parallel resistor model for this nanocomposite.

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Organic Based Thermoelectric Materials for the Development of Flexible Heat Flux Sensors or Thermoelectric Generators

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Currently, the most efficient thermoelectric materials at room temperature are bismuth telluride-based alloys. Beside the fact that they are incompatible with the industrial scale, their scarcity and toxicity limit the range of applications. Recently, important research efforts have been focused on the development of alternative materials. Among them, organic materials based on conductive polymers are the most promising.

We synthesized fully organic and hybrid thermoelectric materials based on poly(3,4 ethylene dioxythiophene) (PEDOT). This polymer combines a high conductivity (from 100 to 3000 S/cm), a low thermal conductivity and moderate thermoelectric power (in the range 15-20 µV/K), while remaining highly versatile in terms of deposition methods, flexible and semi-transparent at low thicknesses.

We developed new routes to process PEDOT thick layers into thermoelectric devices, opening brand new possibilities. Our deposition technique consists in transferring pre-deposited polymer films through a solvation step. It is compatible with a wide range of geometries that are unreachable by usual techniques.

The thermoelectric power of the polymer was enhanced by modifying the oxidation level of the PEDOT:PSS, up to 160 µV/K. The oxidation level controls the characteristics of ionic charge carriers generated on the chains, leading to changes of the polymer properties. To this end, several reducing agents were used and their action was investigated. Thermoelectric and chemical characterizations were performed on the polymer layers. Several doping species were also tested on the PEDOT and their effects on the thermoelectric properties were discussed.

Based on these results, we fabricated a 100 % organic heat flux sensor, with a good flexibility and enhanced thermoelectric properties compared to pristine PEDOT:PSS.

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Thermoelectric Properties of Tetrathiotetracene Iodide Crystals: Modeling and Experiment

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The aim of the paper is to present a more complete physical model than has been applied so far for highly conducting organic nanostructured crystals of tetrathiotetracene iodide, TTT2I3, as a thermoelectric material. Earlier we have demonstrated that these crystals are very promising for thermoelectric applications. But the predictions were made in a simplified one-dimensional (1D) approximation. From experimental data it is known that the electrical conductivity along the molecular chains is almost by three orders of magnitude higher than in the transverse direction. Although from this fact it follows that the interchain interaction is weak, it is necessary to estimate the restrictions on the thermoelectric figure of merit ZT that this interaction will involve. We show that the elaborated more complete crystal model describes very well the temperature dependencies of electrical conductivity σ in the temperature interval between 150 K and 300 K and of Seebeck coefficient S even in a larger temperature interval from 20 K up to 300K, the highest temperature for which the measurements were made. 1D model can explain experimental dependencies only in a narrower temperature interval near 300 K.
A short review of publications about the thermoelectric properties of organic materials during the last two years is also presented. Modeling in a more complete model has shown that the predictions made in 1D approximation are valid only, if the crystal purity is not very high and σ is limited up to ~ 2.5×10^6 $\Omega^{-1}m^{-1}$ and ZT ~ 4. In this case the scattering on impurities already limits the carriers' mobility. If the crystal purity is higher and, respectively, σ achieves higher values, it is necessary to take into account the interaction between the chains, because this interaction begins to limit the carriers' mobility. Reported measured values of σ, S and thermal conductivity κ at

room temperature in stoichiometric TTT2I3 crystals grown from solution are: $1.8x10^5$ $\Omega^{-1}m^{-1}$, 43 μV/K and 1.0 W/Km, respectively, that gives ZT = 0.1. More perfect crystals with $\sigma = 10^6$ $\Omega^{-1}m^{-1}$ grown from gaseous phase were also reported, however *S* and *κ* were not measured in them. The modeling shows that when *σ* increases, the electronic part of thermal conductivity increases too, so that ZT remains small. But TTT2I3 crystals allow nonstoichiometric composition with surplus or deficiency of iodine which is an acceptor and in such a way determines the carriers' concentration. The modeling shows that if in the latest earlier synthesized crystals the carriers' concentration is decreased by two times, ZT increases up to 1.3 - 1.4, very promising result.

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Reliable Thermoelectric Generators for Space Missions

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Thermoelectric generators are almost the only devices which can work in deep space. At present time, a lot of various solar elements are used in space researches, but they can not efficiently supply space vehicles far from the Sun because of low intensity of solar radiation. The thermoelectric power is determined by physico-chemical properties of thermoelectric material and temperature gradient.
The Voyager 1 and Voyager 2 spacecrafts were launched by NASA in 1977 and still success work. They are the farthest man-made objects from the Earth. The power supply devices for these spacecrafts were based on thermoelectric technology and were the radioisotope thermoelectric generators (RTGs). Mars Science Laboratory Curiosity was launched in 2011 and also has RTGs on its board.

Ioffe Physical-Technical Institute RAS is very experienced in thermoelectric area. RTG "Life" for electrical and thermal life support, RTG "Visit" emergency power supply for Mars mission were developed, constructed and tested. At present time, high efficiently, long-life and reliable thermoelectric generators are worked out in Ioffe Physical-Technical Institute of RAS. The high reliability is greatly important in space applications and requires special attention to stability of thermoelectric materials. Nowadays, the most efficient thermoelectric average temperature materials are based on PbTe and GeTe composites, in temperature range 420 - 870K. Lifetime of such devices depends essentially on hot junction temperature during the work. It's important to notice that FeSi2, MnSi1.7, Mg-Si-Sn and another gaining popularity composites are also studied.
Efficiency of n-PbTe composites can be enhanced at low temperature by changing the charge carriers concentration, so that cold working temperature can be reduced.
High efficiently and reliable thermoelements were developed, constructed and tested in present work. Such thermoelements can really used in the thermoelectric generators for space exploitation. The thermoelements were tested during 9200 hours in temperature gradient 470 - 720K and were subjected to thermocycling. Electric power kept nearly the same value after the life tests. Intermediate resistances of switching junctions were absent after 1584, 3240 and 6000 hours at 720K. Representative properties of the single thermoelement are 130 mW and efficiency 6.5 % (cross-section of a thermoelement legs 5x5 mm, length 20 mm and temperature gradient 470 – 720K).
In addition, designed thermoelectric technology makes possible to construct the multistage thermoelements based on mean temperature (GeTe, PbTe) and low temperature (Bi-Te-Se-Sb) materials.

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Small-Scale Radioisotope Thermoelectric Generator Development Based on Am-241

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Space nuclear power systems are under development in the UK in collaboration with European partners as part of a European Space Agency (ESA) programme. Radioisotope thermoelectric generators (RTG) and heater units (RHUs) are important elements of this new European capability. A constant supply of electrical and thermal energy derived from radiogenic decay heat can benefit and enable a range of mission scenarios, providing more science return through increased longevity and the opportunity to carry out science in remote locations where solar power is not feasible. Given that the focus in Europe has been the cost effective production of americium-241, the development of small scale RTG systems (10 W to 50 W in electrical power output) and RHUs in the 1 W to 4 W thermal power range has been the focus of the work to-date. These technologies could enable a range of smaller or lower cost planetary missions. In addition, systems that harvest heat from RHUs to generate less than 1 W of electrical power have also been considered and could offer a range of

small-scale electrical power and thermal power solutions for future low cost or small planetary missions. A review of likely mission requirements and concept studies of small electrical generating units from <1 W to 50 W reveals a potential opportunity to also supply some heat to the spacecraft to aid thermal control. Thermoelectric conversion can be achieved using cost effective bismuth telluride modules produced using well-established industry methods and which have been tested in a small-scale RTG configuration in the UK as part of an ESA funded programme. This paper describes the most recent updates in system design and provides further insight into recent laboratory prototype test campaigns.

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Development of High-Efficiency Segmented Thermoelectric Couples for Radioisotope Thermoelectric Generators

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Radioisotope Thermoelectric Generators have been successfully used to power spacecrafts for deep space missions as well as for terrestrial applications where unattended operation in remote locations is required. They have consistently demonstrated their extraordinary reliability and longevity (more than 30 years of life). NASA's Radioisotope Power Systems Technology Advancement Program is pursuing the development of more efficient thermoelectric technologies that can increase performance by a factor of 2 to 4X over state-of-practice systems that are limited to device-level efficiencies of 7.5% or less, and system-level specific power of 2.8 to 5 W/kg. Over the last few years, under the Advanced Thermoelectric Couples (ATEC) task, several advanced high-temperature thermoelectric materials, including n-type La3-xTe4, p-type Yb14MnSb11, and n- and p-type filled skutterudites, have been developed for integration into advanced power generation devices at the Jet Propulsion Laboratory (JPL). The stability of their thermoelectric properties has been demonstrated for over 18,000 hours up to 1323K. Stable metallization and sublimation suppression barriers/coatings have been successfully developed. JPL is now focusing on developing segmented and skutterudite only couples based on these high-temperature materials to achieve high conversion efficiencies. Recent performance tests have demonstrated 11 to 15% conversion efficiencies with cold and hot-junction temperatures in the 423-473K and 973–1273K range, respectively. An overview of the progress in the development of the couples is provided and options for integration into advanced RTGs are described.

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Opportunities for Infusion of Advanced Thermoelectric Materials into Next Generation Space Power Systems

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NASA has successfully relied upon plutonium-based radioisotope power systems (RPS) for decades to support a number of space science and exploration missions. Fission Power System (FPS) technology has long been considered an attractive option for power levels that might not be either practical or achievable with RPS. While over 27 NASA space missions have used Radioisotope Thermoelectric Generators (RTGs from a few watts up to 300 W each), only one mission using FPS (a 500 W class SNAP-10A) was flown back in 1965 by the United States. All of these systems have relied on thermoelectric materials known since the late 1950s and high temperature device technologies developed in the 1960s and early 1970s. Recent discoveries of higher performance, practical bulk thermoelectric materials and the subsequent maturation of high temperature couple and module technologies may enable for the first time in over 40 years the develoment of more capable next generation power systems that could enhance or even enable future space missions. The NASA RPS Program is currently supporting advancement of the technology readiness of these new thermoelectrics together with concurrent detailed system trade studies to establish the most effective infusion paths. A recent joint NASA and Department of Energy feasibility study for a small 1-kW FPS also concluded that new technologies, including modular thermoelectric converters based on the high performance materials, were now available to pursue a revolutionary approach to reducing the size and weight of space reactors. We provide an overview of these advances and describe in more details the new opportunities for infusion into next generation power systems. The potential of these technologies for applicatio to terrestrial waste heat recovery and auxiliary power systems is also discussed.

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First-Principles Investigation on the Structural, Elastic, Electronic and Properties of the Filled Skutterudite $CeOs_4Sb_{12}$

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Using the full-potential linear muffin–tin orbital (FP-LMTO) method within the local density approximation (LDA) in the frame of density functional theory (DFT), we

have investigated the crystal structures, elastic, electronic and thermodynamic properties for CeOs4Sb12 filled skutterudite compound. The structural properties such as the equilibrium lattice parameter, bulk modulus and the pressure derivatives of the bulk modulus were computed. Using the total energy variation as function of strain technique we have determined the independent elastic constants and their pressure dependence. Through the quasi-harmonic Debye model, in which the phononic effects are considered, the effect of pressure P and temperature T on the lattice parameter, bulk modulus, thermal expansion coefficient, Debye temperature and the heat capacity for CeOs4Sb12 compound are investigated for the first time.

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Influence of the Exchange-Correlation Functional on the Electronic Properties of ZnSb: a Promising Thermoelectric Material

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In the quest of finding alternative energy resources, thermoelectric devices are undoubtedly very promising. Among the appropriate materials that can be used for thermoelectric purposes ZnSb draw the attention of scientists [1, 2] for several reasons. For commercial production and application, the thermoelectric compounds need to be cheap, abundant and non-toxic. That puts Zn and Sb in the forefront of the suitable elements. Moreover ZnSb is one of the best thermoelectric compounds in the important temperature range between 400 and 600K. Orthorhombic zinc antimonide has been investigated by means of first-principles calculations. This compound is a slightly anisotropic semiconductor with an energy gap of about
0.5 eV, but as many other semiconductors, suffers from an inadequate ab-initio description of its electronic properties (especially the width of the band gap). This mistake has an impact on the calculations of the band structure dependent quantities such as the transport properties; therefore as a result, they are also miscalculated. In order to avoid the disagreement between the experimental and the theoretical data, the hybrid functional (HSE06[3]) has been applied. Hybrid functionals, especially the screened versions, mixed with the Kohn-Sham[4] equations are a proficient method to clear out this well-known band gap problem. This communication presents thus the comparison of structural, electronic and transport properties of thermoelectric zinc antimonide, calculated using standard Density Functional Theory - DFT as well as using the HSE06 screened hybrid functional. By adding a certain amount of exact Hartree-Fock exchange interaction to the DFT description, it was possible to improve the accuracy of the results. We prove that the HSE06 method provides a good compromise between accuracy and computational cost, and leads to a better description of the electronic and transport properties.

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First Principles Studies of Thermoelectric GeTe, $AgSbTe_2$, and TAGS

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In this study, we computationally design practical materials based on GeTe toward a highly efficient thermoelectric material that should be alternative PbTe that is toxic and environmental unfriendly material.

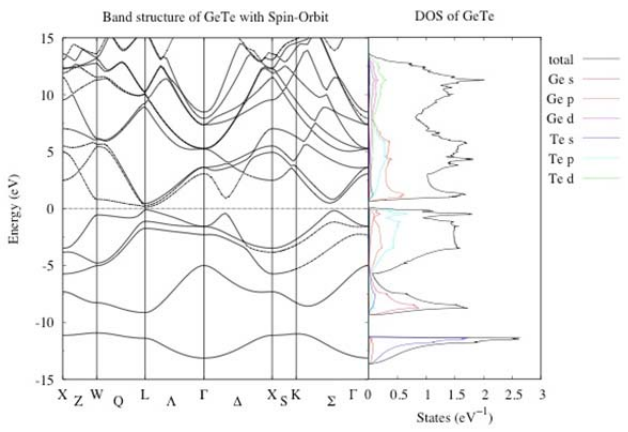
PbTe is an existing thermoelectric material with high efficiency. It has been believed from the following three advantages. One is a large electric conductivity, because PbTe is a narrow gap semiconductor. Another is a large Seebeck coefficient due to the band structure with high degeneracy at the band extrema near the Fermi level. The last one is the low thermal conductivity, because PbTe has heavy electrons.

However, Pb is toxic and environmental unfriendly material; therefore, Pb should be substituted with other candidates, which are comfortable for the environment. Here, we propose that GeTe can be the alternative material of PbTe. The figure shows the band structure and DOS of GeTe. The electronic structure of GeTe has two advantages that this figure suggests. GeTe has a large Seebeck coefficient due to the band structure with high degeneracy at the band extrema. Additionally, the large electric conductivity is expected due to the small effective mass near the Fermi level. Basically, the thermoelectric efficiency of GeTe is low because Ge is lighter than Pb. To improve thermoelectric efficiency of GeTe, we will suggest the way based on the first principles calculations in this talk.

Here, we research the behavior under an assumption that phonon scattering due to defects in GeTe causes the high thermoelectric efficiency. We have introduced defects in

GeTe and estimated the formation energies of defects in GeTe from the first principles. As the results, we found that the vacancies of Ge are introduced easily in GeTe. Besides, they will not be harmful carrier trap. Accordingly, there is the possibility that the vacancies of Ge reduce the high thermal conductivity in GeTe. Moreover, we have researched impurity-effects for the high efficiency from the Bloch-Boltzmann equation with the first principle calculation results.

We would like to refer to the solid solution $(GeTe)_x(AgSbTe2)_{1-x}$ called TAGS, where forms straightforward a layered structure since GeTe and $AgSbTe_2$ have the same crystal structures. This is because TAGS shows the high thermoelectric efficiency in the experiments, although GeTe and $AgSbTe_2$ low and slightly better thermoelectric efficiency, respectively. The origin of this high efficiency has yet to be understood theoretically and is under discussion. In this talk, our purpose is to clarify the mechanism of the high efficiency by the first principles calculations. We used the Bloch-Boltzmann equation in order to analyze this mechanism.



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The Influence of High-pressure, Magnetic Field and Inhomogeneity on the Properties of Thermoelectric Materials

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In the present work the ways of the improvement of thermoelectric (TE) parameters are considered basing on the exploring of both physical impacts including high-pressure and high magnetic field as well as configuration of inclusions. The experimental results on the influence of pressure and magnetic field on TE properties for a wide circle of materials are analyzed [1]. The data have been received at the pressure range 0-30 GPa using automated set up with the sintered diamond anvils [1], and the measurements of the thermo-magnetic (TM) Nernst-Ettingshausen effects have been carried out using the autonomous version of the diamond anvils cell [1]. The influence of pressure on TE parameters is reached by changing of the energy gap and the charge carrier's concentration, effective mass and mobility. The improve TE properties under pressure are observed for both direct and indirect narrow-gap semiconductors with the high density of states in the vicinity of Fermi level, while the best TM properties are achieved for direct-gap semiconductors (PbTe, PbSe, Te) with the low effective mass and very high mobility of carriers in the vicinity of the pressure-caused gapless state. The approach has been developed for the calculations of the above transport properties for non-uniform TE materials with variable configuration and concentration of inclusions [2]. The results of calculations are found to be in well agreement with the experimental ones for a lot of materials [1, 2]. Thus, it is shown that both physical impacts (high-pressure and magnetic field) and configuration of inclusions are able to improve the power factor of materials. The problems of both the conservation of advanced thermoelectric states at ambient conditions and of the exploring of high-pressure TE and TM properties of materials are discussed.

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QSPR Approach for Estimating Viscosity of Ionic Liquids

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Ionic liquids (ILs) is an exciting group of new chemical substances that have the greatest potential to improve the development of organic chemistry and chemical technology. These compounds may be used in many research fields, in various chemical processes including the synthesis, catalysis and separation techniques. Ionic liquids could be also used as new thermo-electric materials, in batteries, fuel cells and solar cells.

Since variations in cations and anions can produce a large number of ionic liquids the experimental measurements

of thermo-electric properties for all ILs become impossible. One of the promising group of methods that could be used to avoid time consuming and expensive experiments are Quantitative Structure-Property Relationship approaches (QSPR). This approach is based on defining mathematical dependencies between the variance in molecular structures, encoded by so-called molecular descriptors, and the variance in a given physicochemical property in a set of compounds.

Since viscosity corresponds to thermal properties such as Seebeck coefficient, thermal conductivity and ionic conductivity, the main purpose of this study was to develop the QSPR model for estimating the viscosity for ILs (such as imidazolium, sulfonium, pyridinium, pirrolidinium). We have calculated a set of WHIM (Weighted Holistic Invariant Molecular) descriptors for each ion separately. In order to develop the QSPR model we applied Partial Least Squared method combined with Genetic Algorithm (GA-PLS). Obtained model was characterized by satisfactory goodness-of-fit, robustness and the external predictive performance (R2=0.81, Q2CV=0.71, Q2Ext=0.73, RMSEC=0.26, RMSECV=0.32, RMSEP=0.33). The model has been carefully validated (including external validation) according to the OECD QSAR validation recommendations. Presented theoretical study allowed us to develop a QSPR model that reliably predicts the viscosity for different groups of ILs not only investigated in the current work, but also to unexplored related species, if they are located within the applicability domain.

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Molecular Simulations of Ionic-Liquid Based Thermoelectric Converters

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Research on converting thermal to electrical energy has, until recently, predominantly been focused on solid-state devices utilizing semiconductor materials. Liquid-based thermoelectrochemical technologies offer an alternative, potentially cheaper and more scalable route for direct thermal-to-electric energy conversion. Proposed device relies on recent advances in nanotechnology with the patented SOLID (Solid On LIquid Deposition) process, which offers the possibility to grow a stable solid layer of parylene polymer directly onto a liquids, such that the polymer uniformly replicates and encapsulates the liquid template. Ionic-liquid based thermo-electric converters utilize a redox couple within an ionic liquid electrolyte. These devices can be limited by both the diffusion and concentration of the redox species. Optimization of both the transport (diffusion) and the thermodynamics (Seebeck coefficient) of the system is important.

Ionic liquids are molten salts with melting points below 100 â°C, usually composed of relatively large organic cations and smaller organic or inorganic anions. In the last years there has been rapidly growing interest in ionic liquids because of their unique properties. However, despite the experimental and theoretical efforts, a detailed understanding between the structure and properties of the ionic liquids has not yet been achieved. Therefore, the computer simulations are valuable tools to gain additional knowledge on ionic liquids.

The charge transport in the electrolyte, typically iodide/tri-iodide ionic liquid, depends mainly on the molecular diffusion mechanism, which partly limits the thermo-electric converter performance. The molecular dynamics technique was employed to assess the ionic conductivity and diffusion coefficient of the charge transfer. The ionic conductivity was compared with a published experimental result. The goal of the study presented here was to systematically compare the dynamics and transport properties of iodide/tri-iodide in selected ionic liquids and their dependence on the conditions of simulation.

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Reduction and Oxidation Reactions in Thermo-electric Generators based on Ionic Liquids.

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Recent research show a very good relative efficiency of ionic-liquid (IL) based thermal harvesting. Cobalt(II/III) tris(bipyridyl) redox couple has been soluted in ionic liquids, thus generating the electrolytes with high Seebeck coefficients, S_e = 1.52.2 mVK^{-1} (T. J. Abraham, D. R. MacFarlane, J. M. Pringleb, Energy & Environmental Science, DOI: 10.1039/c3ee41608a). It is also known that pure ILs can generate good Seebeck coefficient too. While the standard solid-based thermoelectric generators give at best S_e < 0.2 mVK^{-1}. The so-called figure of merit for Bi_2Te_3 approaches 1 which is a large value in comparison with pure elements or even to other semiconductors.

Moreover, due to the fact that the ionic liquids constitute a large family of possible materials with negligible volatility and good thermal stability it became clear that this type of materials could be effectively utilized in thermoelectrochemical devices with even high temperature heat sources. The ILs basically work as electrolytes, and with soluted redox couple(s) generate a powerfull medium where liquid work as solvents while the ions of the redox couple conduct the current.

There are many factors influencing the overall efficiency and among them the electrochemical reactions occurring at the electrodes as well as the chemical equilibrium, especially close to the electrodes' surrounding.

The ionic surrounding plays role and the electronic-structure properties of all the species present in cells seem to be crucial in the final efficiency. The quantum-chemical methods were employed to determine and characterize the electronic structures of all the species in redox reactions. Moreover, electronic-structure properties influencing the reactivity or inertness were taken into account. Yet the electrochemical observables were found and compared to finally describe the most important scenarios involving reduction and oxidation accurring in the pool of ILs and additional redox couples in the heat-into-electricity converters.

Acknowledgements: The investigations were supported by grant no PSPB-051/2010 from Switzerland through the Swiss Contribution to the enlarged European Union.

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Theoretical Study of Lanthanum Oxides as Thermoelectric Materials

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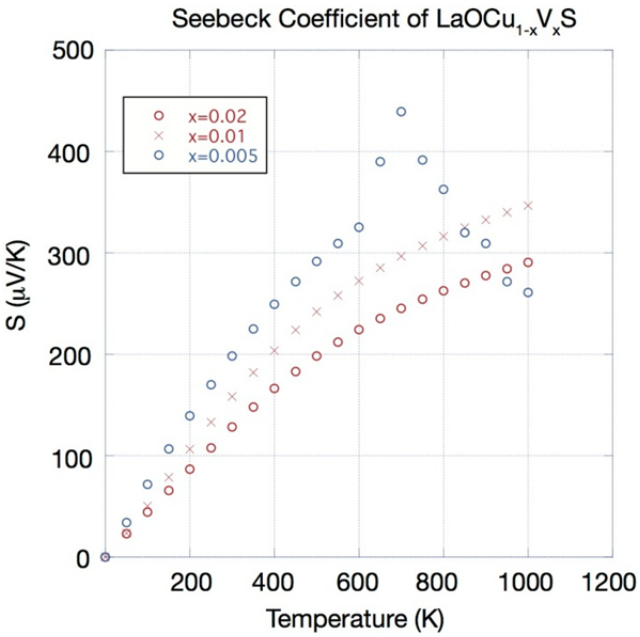
$(LaO(Cu_{(1-x)}V_x)_yM_z$(M=S,Se,Te) are known as transparent narrow gap p-type semiconductors, which give an excitonic absorption/emission near the band edge even at room temperature. These compounds have P4/nmm structure and are natural superlattice semiconductor.

In our talk we first calculated the band structure for these compounds, using the Full Potential Augmented Planewave (FLAPW) method based on LDA/DFT. Our results show that these compounds have large anisotropy in the k_z direction. On λ, V, and W axes, dispersion curves are very flat. We analyzed the electronic structure using group theory.

Secondly, we calculated the conductivity tensors, electronic conductivity and Seebeck coefficient using semi-classical Bloch-Boltzmann equations. The Bloch-Boltzmann equations show that materials that have small dispersion, so-called ''flat'', band structure, have a large Seebeck-coefficient. As mentioned, we showed that $(LaO(Cu_{(1-x)}V_x)_yM_z$ also have flat-band structure in the k_z direction, these large Seebeck coefficient are large. In addition, these compounds have a small hole-pocket in valence band, thus they have large electric conductivity and large Seebeck coefficient.

We performed first principles band calculations and then used the Bloch-Boltzmann equations to estimate the electric conductivity and the Seebeck coefficient for $LaO(Cu_{(1-x)}V_x)_yM_z$(y,z=2,3,4) We semi-quantitatively discuss temperature dependence and carrier concentration dependence of thermoelectric.

In LaOCuS case, its electronic structure has anisotropy in k_z the direction. To analyze electronic structure, we calculate the 'Herring sum' on λ, V and W axes. Along these axes, ''doubling'' and ''pairing'' occurs, as result of the crystal symmetry and time-reversal symmetry of LaOCuS. In addition, on these axes, dispersion curves are flat and have two-fold degeneracy. This electronic structure assumes an important role of large Seebeck coefficient Material. Because dispersion curves are flat on these axes, LaOCuS is expected to be p-type high-efficiency thermoelectric material. We have introduced defects in LaOCuS and estimated the formation energies of defects in LaOCuS from first-principles. As the results, we found that the vacancies of Cu are introduced easily in LaOCuS.



In our calculation, LaOCuS has a large Seebeck coefficient 441.23(μ V/K) in the case of x=0.005, it is expected to be a

good p-type thermoelectric material. We found how to fabricate p-type LaOCuS to calculate the formation energy and estimate the stability. As a result, we found that to control of pressure.

In our session, we will discuss about other ($LaO(Cu_{(1-x)}V_x)_yM_z$ case.

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Thermoelectric Properties of Layered Oxyselenides

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Recently, the use of "natural superlattices" has been proposed as a promising approach to improve thermoelectric performance. A "natural superlattice" is defined as a material that possesses excellent conductive/covalent layers alternating with insulating/ionic layers. A family of materials that could be considered as "natural superlattices" are the layered oxychalcogenides [AO][BCh] (where A = Bi, rare-earth element; B = Cu, Ag; Ch = S, Se and Te). In these materials, oxide layers, $[AO]^+$, and chalcogenide layers, $[BCh]^-$, are stacked along the c-axis in an alternating fashion, and act as charge reservoir and carrier transport channels, respectively. This results in interesting electrical and thermal properties, and makes these oxychalcogenides, and in particular the oxyselenide BiOCuSe, potential materials for mid-range temperature (500≤T/K≤900K) waste heat recovery. To date, the electrical transport properties of BiOCuSe have been controlled through doping at the Bi^{3+} site with divalent cations, and this leads to p-type semiconducting behaviour. Here, we present our results on the effect of doping BiOCuSe with Cd^{2+} and Zn^{2+} ions at Cu^+ site, on the structure and thermoelectric properties of this material. In addition, the effect of the layer thickness on the thermal and electrical transport properties of oxychalcogenides was also explored, through the synthesis and characterization of $Bi_2YO_4Cu_2Se_2$, which contains thicker $[Bi_2YO_4]^+$ oxide layers.

A series of samples with composition $BiOCu_{1-x}M_xSe$ (M= Cd, Zn and x= 0.05; 0.10) and $Bi_2YO_4Cu_2Se_2$ (prepared using 5% yttrium excess) were synthesized successfully by solid-state reactions at temperatures over the range 623≤T/K≤1023 for 15-36 hours and structurally characterized using powder X-ray diffraction and Rietveld refinements. The electrical and thermal properties were measured over the temperature range 100≤T/K≤673. Results show that substitution at the Cu site leads to an increase in the magnitude of the electrical resistivity and the Seebeck coefficient. The initial results on the synthesis of $Bi_2YO_4Cu_2Se_2$ indicate that this material is unstable at elevated temperatures, and can only be prepared using short reaction times. $Bi_2YO_4Cu_2Se_2$ exhibits p-type conduction, with relatively low values of the Seebeck coefficient.

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Thermoelectric Properties of Hydrothermal-Processed $Ca_{1-x-y}La_xSm_yMnO_3$

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[1]Sejong University, REPUBLIC OF KOREA; [2]Korea Institute of Industrial Technology, REPUBLIC OF KOREA

Recently, thermoelectric devices have been studied for recovering the waste heats from power plants, automobiles, incinerators, and factories. In this study, the microstructure and high-temperature thermoelectric properties of Ca1-x-yLaxSmyMnO3 were studied, depending on La and Sm contents. Ca1-x-yLaxSmyMnO3 powders were fabricated by the hydrothermal method. The microstructure of the sintered samples was investigated with a field-emission scanning electron microscope. The density of the sintered samples was measured by the Archimedes method. To obtain the power factor of the Ca1-x-yLaxSmyMnO3 samples as a function of temperature, we simultaneously measured the electrical conductivity and the Seebeck coefficient over the temperature range of 500 to 800 iE. The sintered Ca1-x-yLaxSmyMnO3 had the perovskite structure with orthorhombic symmetry, belonging to the Pnma space group. The values of the Seebeck coefficients were all negative, indicating n-type conduction. The hydrothermal process was desirable to obtain Ca1-x-yLaxSmyMnO3 powders with high purity and various shapes at lower temperature. The addition of La and Sm significantly improved thermoelectric properties. We will discuss the effect of La and Sm on the high-temperature thermoelectric properties.

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Thermoelectric Properties of $(Ca_{3-x}Fe_x)Co_4O_9$ Ceramics

Delorme, F.[1]; Diaz-Chao, P.[2]; Guilmeau, E.[2]; Giovannelli, F.[3]
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In order to improve the thermoelectric properties of Ca3Co4O9 ceramics, the substitution of calcium by iron has been studied. (Ca1-xFex)3Co4O9 polycrystalline samples (x = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1 and 0.2) have been prepared by solid state reaction and sintered by spark plasma sintering. All the sintered samples present a high bulk density with an apparent density value larger than 95 % of the theoretical density. XRD and SEM

observations have been used to determine the solubility limit and characterize the secondary phases. The thermoelectric properties of the synthesized ceramics have been studied between 323 and 1000 K. The substitution of calcium by iron leads to decreasing the Seebeck coefficient. On the other hand, the electrical conductivity increases up to circa 3 % Fe and then decreases. Therefore, power factor presents an optimum value for 3 % substitution. Such an increase is about 10 %. Moreover, thermal diffusivity is also decreased by about 10 % at 1000 K leading to an increased ZT value at 1000 K of about 20 % compared to the unsubstituted sample.

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An Alternate Approach for High Level Mg Substitution in Lamella Cobaltites, A(CoMg)O_2;(A=Li, Na) for Thermoelectric Applications

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The lamellar cobaltites ACoO2 are the well interested compounds to study due to their anisotropic structure as well as their electronic properties. ACoO2 compounds are used for several applications like cathode materials for ionic batteries, transparent semiconductors and thermoelectrics. In ACoO2, Cobalt is in (3+) low spin states, thus results zero entropy. In case of Cobalt with 4+, the t2g state has 6 fold degeneracy that causes large entropy thus thermopower in the compounds. The Co4+ in ACoO2 can cause much larger entropy than a hole in degenerate semiconductors, that leads us design for new thermoelectric materials. The mixed valance of cobalt (3+/4+) in ACoO2 can be realized in two ways; either by creating the vacancies at A-site (ex: A=Na or Li) or by substituting the di-valent cation at B-site; delafossite compounds. A wide range of substitutions were previously synthesized with di-valent ions at Co-site, and the changes in transport properties are observed. The substitution of di-valent ion at Co-site is limited in traditional synthesis approaches; using individual precursors for B-cation and the substitute. We used a new solid state chemical approach; solid solution between B-cationic element and the di-valent substitution as the precursor. The final compounds are obtained by solid state method for poly-crystalline samples. Investigation of structural, Magnetic and transport properties of highly substituted A(CoMg)O2 compounds; poly-crystalline is the main objective of present work.

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Effects of Particle Size on Thermoelectric Properties of $CuCrO_2$

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CuCrO2 has attracted attention as a promising thermoelectric material because its electrical conductivity can be greatly increased by doping. Here we study the effect of crystallite size on the thermal conductivity, another important factor for thermoelectric properties. We have synthesized polycrystalline CuCrO2 by three routes (solid state reaction, sol-gel method and hydrothermal synthesis) and characterized the crystallite size by X-ray diffraction and scanning electron microscopy. The smallest crystallites have a quasi-hexagonal shape of dimensions ~20nm. The thermal conductivity as well as the electrical resistivity and Seebeck coefficient of the particles have been measured and will be discussed as a function of particle size.

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Structural and Thermoelectric Characterization of a $La_{0,95}Sr_{0,05}CoO_3$-Silica Composite

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Perovskite type transition metal oxides are considered as promising thermoelectric materials. One of the main disadvantages is the high thermal conductivity. Methods to reduce thermal conductivity include reduction of grain size within bulk materials and nanocomposite fabrication by adding a second phase. The approach of both methods is to increase boundary phonon scattering by increasing interfaces.
We produced a Strontium-substituted LaCoO3 (La0,95Sr0,05CoO3) powder with small particle size by soft chemistry method. Different amounts of monodisperse amorphous Stober Silica were added during synthesis resulting in a composite material with lowered thermal conductivity.

After sintering the pellets the perovskite phase LaCoO3 was confirmed as major phase by powder XRD. REM pictures show domains of SiO2-rich and perovskite-rich areas. Electric conductivity and Seebeck coefficient were measured in a temperature range from RT to 1000 K. As expected electric conductivity was decreased in samples with Silica. All samples still showed semiconducting behavior. The Seebeck coefficient was increased from 200 µV/K to 250 µV/K at RT and indicates p-type conduction over the entire temperature range measured. Thermal diffusity and heat capacity measurements were carried out in a temperature range from RT to 573 K. Thermal

conductivity was calculated and it is lower for samples with added Silica compared to pure La0,95Sr0,05CoO3.

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Microstructure and Thermoelectric Properties of Si-Added $SrMnO_{3-\delta}$ for Power Generation

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[1]Sejong University, REPUBLIC OF KOREA; [2]KITECH, REPUBLIC OF KOREA

Thermoelectric energy conversion is widely recognized as a promising technology for both electric power generation and cooling of various electronic devices. A series of the Sr1-xSixMnO3 with x=0.05, 0.1, 0.15, 0.2, and 0.3 was prepared by the solid-state reaction technique. The starting powders used were SrCO3, SiO2, and Mn3O4. Appropriate amounts of the starting materials were mixed and pressed at 80 MPa to obtain green pellets. The green pellets were sintered at 1673 K for 10 h in air. The Sr1-xSixMnO3 samples with a small amount of Si (x=0.05, 0.1) were a single phase with a hexagonal structure. Secondary phase, such as Mn3O4, Mn2O3, SiO2, and Sr2SiO4, were detected for high Si contents (x=0.15, 0.2, and 0.3). The grain size and density of the Sr1-xSixMnO3 samples were decreased with an increase in Si content. The electrical conductivity was increased with Si content up to x=0.15, and then decreased with further increasing Si content. The Seebeck coefficients were found to be negative over the measured temperature range, suggesting that the electron carriers dominate the thermoelectric transport. The absolute value of the Seebeck coefficient was increased with Si content up to x=0.2, and then decreased with further increasing Si content.

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Crystallization and Transport Properties of Amorphous $CrSi_2$ Thin Film Thermoelectrics

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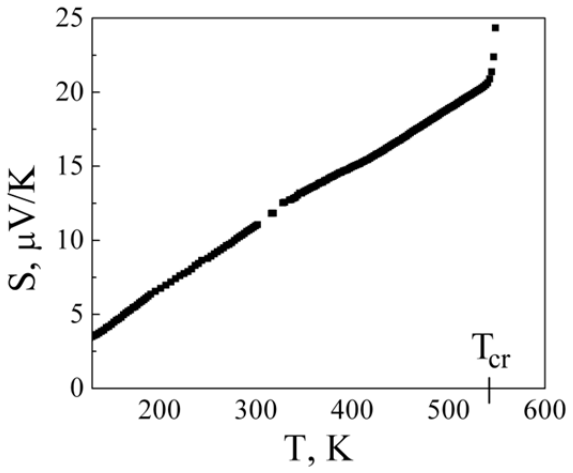
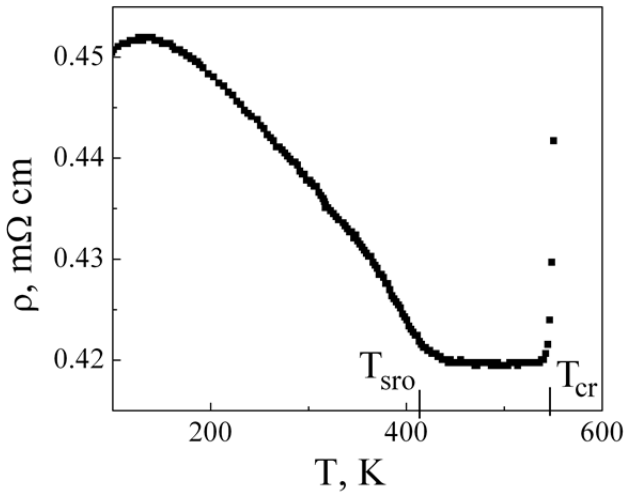
Ioffe Physical-Technical Institute of the Russian Academy of Sciences, RUSSIAN FEDERATION

Nanostructuring is considered as a promising way to a new generation of efficient thermoelectric materials. Among the variety of nanostructuring methods the crystallization from amorphous state represents a procedure to produce a most "clean" nanocrystalline material. The nanocrystalline materials are nanostructured materials which are very important from the view point of practical applications. Polycrystalline composites with average grain size less than about 100 nm are generally regarded as the nanocrystalline materials. Absence of the long-range order and large number of dangling bonds are the most characteristic features of amorphous state. Due to high degree of the structural disorder long tails of localized states appear in the band gap of electronic structure of amorphous semiconductors. While charge carriers mean free path can be comparable to de Broglie wavelength. There are two possible conduction mechanisms depending on Fermi level position. 1. hopping conduction via localized states; 2. diffusion conductance via extended states. In the first case resistivity temperature dependence has activation type, thermopower has nonlinear temperature dependence and is of the order of k/e , where k - Boltzmann constant and e electron charge. In the second case the resistivity temperature dependence follows power law, and has low values and is linear in the temperature. Fig.1. shows the resistivity and thermopower temperature dependences of a thin (164 nm) CrSi2 amorphous film. The resistivity increases with temperature up to 150 K while it slowly decreases at higher temperatures, having a maximum at 150 K. This unusual for amorphous materials behavior requires additional investigation. *p*(T) at higher temperatures is typical to amorphous metal. Accordingly, thermopower has low value and is linear in the temperature. This indicates that conduction in amorphous CrSi2 films is via extended states. Abrupt change of *p*(T) slope at about 440K relates to a change of short-range order in amorphous state (structural relaxation). This relaxation is not detected by X-ray diffraction. The structural relaxation during isothermal annealing is accompanied by increase of resistance. The rate of this increase depends on annealing temperature. Probably, short-range order changes results in annihilation of dangling bonds that leads to a variation of carrier concentration. Dangling bonds create additional levels in the band gap and so that they produce additional charge carriers. Charge carriers concentration decrease because reduced amount of dangling bonds resulting in resistivity increase. Temperature of structural relaxation doesn't depend on Si/Cr ratio and film thickness in the range 50-500 nm.





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Electrodeposition of Co-Sb Thick Films and their Thermoelectric Properties in DMSO.

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In the last decade there has been an increasingly interest in the Skutterudites in the field of thermoelectricity 1. This interest is based on the fact that the highest performance of this material happens at 400°C, which makes it ideal for multiple applications as energy harvesting devices. Generally, most of the actual compounds working under these conditions are unstable or presents a low figure of merit 2. However, Skutterudites have usually good values of the power factor, but also they offer the possibility of an enhancement of their efficiency due to the reduction of the thermal conductivity via doping the structure 3 or filling of the voids 3 of the structure with heavy atoms. Nevertheless, to obtain the right phase by electrodeposition is still not a solve question. 4 This work deals the electrodeposition of Skutterudite (CoSb3). We have been able to grow CoSb3 films via electrochemical deposition in an organic solvent (DMSO). After studying different parameters such as temperature, stirring, time of deposition or potential, we have been able to obtain quite homogeneously films with 1:3 ratio. For the first time, thermoelectric properties have been measured in different labs, to measure the Seebeck coefficient and electrical conductivity of the films in plane, and using a Seebeck microprobe system, to measure and make a map of the Seebeck coefficient in cross-plane. We determine the Seebeck coefficient to be -12 µV/K in plane and -37 µV/K out of plane, and an electrical conductivity of around 9 S/cm in plane.

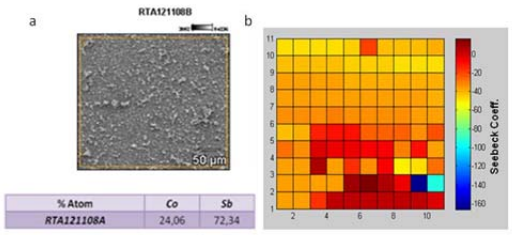

Figure 1.a Scanning Electron Microscopy and Energy Dispersive X-Ray Analysis of a $CoSb_3$ film. 1.b. Seebeck microprobe map

ACKNOWLEDGMENTS

The research work is supported by the European Commission under FP7-NEXTEC project, Grant # 263167 [FP7/2011-2013].

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Size Effects in Bi_2Te_3 Thin Films

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The recent intensive development of nanophysics and nanotechnology stimulates theoretical and experimental studies of the specific properties of systems whose behavior can be described only in terms of quantum mechanics. It is known that electron confinement in a quantum well results in the quantization of the energy spectrum and leads to the quantum size effects (QSEs) when quantum well width d and the de-Broglie wavelength λ_D of charge carriers are of the same order of magnitude. One of the possible manifestations of the QSEs in 2D-structures is an oscillatory behavior of the d-dependences of the transport properties. Metallic films are not very convenient objects for studying QSEs through

measuring the transport properties because the oscillation period Δ*d* is comparable to interatomic distances, which requires growing very thin films with a high degree of structural perfection. Semiconductors, which have significantly larger Δ*d*, represent more convenient systems for such studies; however, up to now the number of such investigations has been very limited. Earlier, we observed oscillatory character of the thickness dependences of the thermoelectric properties in thin IV-VI films (see, for example, [1-3]. The objects of the study were thin Bi_2Te_3 films with thicknesses in the range of *d*=20-500 nm, grown by thermal evaporation in vacuum of stoichiometric *p*-Bi_2Te_3 crystals on glass substrates at 500 Ê and annealed at 500 K for 1 hour. The condensation rate was 0.1 – 0.3 nm/s. The room-temperature d-dependences of the Seebeck coefficient, Hall coefficient, electrical conductivity, charge carrier mobility, thermoelectric power factor, and the temperature (80-300 K) dependences of the kinetic coefficients for the *p*-Bi_2Te_3 films with different *d* were obtained. The quantum oscillations of the thermoelectric properties were observed and the oscillation period Δ*d* for hole gas was determined. The experimental value of Δ*d* is in good agreement with the results of the theoretical calculations using the effective mass approximation and a model of a rectangular potential well with infinitely high walls. For thin film applications in thermoelectricity, it is necessary to take into account the QSEs, which can drastically change thermoelectric properties under thickness change.
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Development of Powder Metallurgy Based PbTe-PbS Materials for Thermoelectric Applications

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Thermoelectricity is concerned with the interaction between thermal and electrical phenomena. The most common application is the conversion of thermal energy (or heat) into electrical power for waste heat application. The dimensionless thermoelectric figure of merit, expressed as $ZT=T\alpha^2\sigma/\kappa$ is widely used as a measure of the thermoelectric efficiency with respect to the material's properties. Increasing ZT can be achieved by either increasing the numerator of ZT, or decreasing the thermal conductivity, κ which is sum of the lattice thermal conductivity, κ_L, and the electronic thermal conductivity. Therefore, choosing the appropriate carrier doping and lattice structure can have a significant impact in optimizing ZT values. It is already well established that nano-structures in materials allow significant reduction of the lattice thermal conductivity . A powerful method for reducing the lattice thermal conductivity is by generating of phase separation on the nano-scale, as was found at the p-type 3mol% Bi_2Te_3-doped PbTe-GeTe and the n-type 0.055mol% PbI_2-doped PbTe-PbS systems. In the current research the PbTe-PbS system was further electronically optimized by altering the PbI_2. The work was supported by the United States-Israel Binational Science Foundation (BSF), Grant No. 2008114.

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Structural Chemistry and Dimensionality of Chalcogenides Materials for Thermoelectric Applications

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In the last decade the search for thermoelectric materials with high ZT has attracted much interest for a wide range of systems. Recently several promising chalcogenides have been reported. For example the BiOCuSe oxyselenide has been found to exhibit a remarkable figure of merit ZT>0.8 around 900K which is much larger than oxide materials.

Chalcogenides materials for thermoelectric applications exhibit a variety of structural type with different dimensionalities, going from the one-dimensional material like TiS3 to the 3D structure materials such as pyrite-like CoS2. In our ongoing research to study compounds for thermoelectric properties, we have been investigating several chalcogenides with 1D, 2D or 3D structures.
The study of the quasi-one dimensioned TiS3 material by HR-TEM shows the existence of acicular microcrystals with the width/length ratio of at least 50 and with dislocations along the (b, c) plane for SPS prepared sample. The latter create some breaks along the conducting TiS chains which could explain the rather low conductivity (σ300K=1Ω.cm). This material exhibits a large Seebeck coefficient. Furthermore a metal insulator transition is observed in the σ(T) curve and a change of shape in the S(T) curve. Data about the thermal conductivity will be given and the potentiality of such a compound will be discussed.
Interesting 2D structures are AE2MO3(Ag/Cu)X (where AE = alkaline earth, M= 3d metal and X=S,Se) which are made of intergrowth of oxide with chalcogenides Cu2X2 layers. They exhibit common structural feature with the above cited BiOCuSe, which belongs to the larger family of ZrSiCuAs-structure type 1111 compounds, consisting of a conducting Cu2Se2 layer. While in a ZrSiCuAs-structure the oxide layer which act as charge reservoir is isostructural to the conducting layer, i.e. rock salt-type, in the AE2MO3 (Ag/Cu)X compounds the Cu2Se2 or Ag2Se2

layers are separated by perovskite-like layers. We will discuss here our results concerning thermoelectric properties in relation with the doping.

As for the 3D materials, the properties of the pyrite-like CoS2 compounds, densified by SPS, have been investigated. A clear relation between the magnetic ordering and S in this itinerant ferromagnet is evidenced showing strong analogy with the measurements reported for SrRuO3 another spin polarized material.

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Elaboration and Characterization of Thermoelectric Composites

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[1]CRISMAT / LCMT, FRANCE; [2]CRISMAT, FRANCE; [3]LCMT, FRANCE

Nowadays thermoelectric materials and devices are becoming more and more attractive. However, they still present major drawbacks. They are usually expensive, relatively heavy and their elaboration is often difficult. Incorporating thermoelectric fillers into an insulating polymer matrix might represent a solution to these issues.

To produce such composites, bismuth telluride has been used as a filler since it is the best current thermoelectric material at room temperature. The polymer matrix chosen is polyethylene because of its low cost and its easy processing.

The first part of this study consists in characterizing composites containing micro-sized bismuth telluride particles synthesized by mechanical alloying. The processing of the composites has been carried out using a micro-extrusion / injection process. The electrical conductivity of the composites has then been measured with a megohmmeter. The results show an enhancement of the polyethylene's conductivity by seven orders of magnitude. Additionally, a percolation phenomenon has been observed.

The second part of this work involves the synthesis of selenium doped bismuth telluride nanoparticles. Using this type of fillers with high specific areas would enhance the physical properties of the composites. To achieve the syntheses, a low temperature aqueous process has been employed. The synthesized compounds have been analyzed by X-ray diffraction. The morphology of the synthesized particles has been characterized by SEM and TEM observations.

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Physical Properties of Thermoelectric La_3X_4 (X=S, Se, Te) Compounds Using First Principles Calculations

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ICGM - Université Montpellier 2, FRANCE

Chalcogenide rare-earth compounds have been studied[1] for a long time due to their interesting physical properties such as superconductivity, mixed valences, strong electron correlations or good thermoelectric properties at high temperature[2]. The stoichiometric La_3X_4 compounds are bad metals with an electron concentration of about 4-6

10^{20} electrons per cm^3, but the insertion of large amount of vacancies leads to a metal-semiconductor transition. At the composition of $La_{2.67}X_4$ the compounds become very heavily doped semiconductors. In consequence their thermoelectric properties are improved significantly, since the vacancies in the structure scatter the acoustic phonons and therefore strongly reduce the thermal conductivity. The most promising is the compound based on lanthanum La_3Te_4 (ZT ~ 1.2 at 1300K[3]), but environmental problems and the cost of materials encourage to replace tellurium by elements of the same column, including sulfur. For this purpose "ab initio" calculations can be very useful for understanding the origin of the good thermoelectric properties of tellurides and for comparing them to selenides and sulfides. Therefore we present in this communication the results of "ab initio" calculations of the stability, vibrational properties, electronic structure and thermoelectric properties of the three related compounds La_3X_4 (X = S, Se, Te). The aim is to analyze their thermoelectric potential applications especially in the case of the sulfide which does not suffer from problems of abundance and toxicity like the telluride. We show the close similarity of vibrational and electronic properties of these materials, which explains the similarity of their thermoelectric properties. Therefore these materials are very promising for both n-type and p-type especially if the stability problems of the sulfide can be solved in the near future.

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A "Natural Superlattice" Oxytelluride as a Promising Thermoelectric Material for Waste Heat Recovery

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Doped bismuth telluride currently dominates the market of thermoelectric materials a figure-of-merit ZT around 1. "Natural superlattices", composed of alternating conductive and insulating layers, may be promising thermoelectric materials. Here we present an investigation of the properties of a potential "natural superlattice" material, BiOCuTe. The crystal structure of BiOCuTe consists of PbO-type chalcogenide layers alternating with anti-PbO oxide layers (Figure 1).We have prepared a series of $Bi_{1-x}Pb_xOCuTe$ ($0 \leq x \leq 0.08$) samples by conventional solid state reactions and investigated their structure using powder X-ray diffraction and Rietveld refinements.

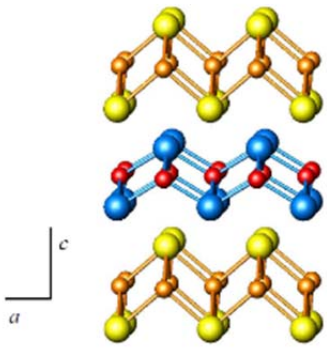

Fig. 1. Crystal structure of BiOCuTe along the [010] direction.

As-prepared BiOCuTe has a power factor, $S^2\sigma$, of 8.7 μW cm^{-1} K^{-2} at room temperature, comparable to those of other thermoelectric materials. This material also has an extremely low lattice thermal conductivity of ≈ 0.5 W m^{-1} K^{-1}, which may arise from the two-dimensional nature of its structure, and in particular from the scattering of phonons at the interfaces between the insulating $[Bi_2O_2]^{2+}$ layers and the conducting $[Cu_2Te_2]^{2-}$ layers. Because of its low thermal conductivity, BiOCuTe exhibits a remarkable thermoelectric performance at temperatures suitable for waste heat recovery, with a ZT of 0.42 at 373 K, which increases to 0.66 at the maximum temperature investigated, 673 K.[1] The electrical and thermal transport properties of the lead-doped samples will be also presented.

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Enhancing the Figure of Merit of GeTe-Based Thermoelectric Materials

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Abstract: Bulk thermoelectric materials are of interest for the generation of electricity from waste heat. However, for widespread commercial use, materials with better thermoelectric performance are required. The alloys (GeTe)X(AgSbTe2)1-X (commonly known as TAGS) are among the best known high-temperature thermoelectrics, largely due to their low thermal conductivity. This is thought to be due to a dense network of twin domain boundaries formed by a phase transition from cubic to rhombohedral on cooling. Here we report on the structural properties of TAGS as a function of temperature and how this depends on processing conditions and thermal cycling. Furthermore, the effect of doping TAGS with magnetic rare-earth and transition metals will be discussed with respect to the electrical conductivity and Seebeck coefficient.

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Thermoelectric Properties of Doped PbSe

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Bulk thermoelectric materials are of interest in the field of energy conversion technology due to their potential in the conversion of waste heat to electrical power[1]. Lead chalcogenide compounds show high performance at room temperature and above, especially in the range 600-850 K. As narrow gap semiconducting compounds, they exhibit outstanding electrical transport properties, and they also exhibit low thermal conductivities at high temperature, which is unusual for materials with simple structures (PbSe adopts the rock-salt structure)[2]. Doping with 4f electrons can introduce resonant states just below the Fermi level and shows promise for enhancing the thermopower and hence the thermoelectric figure of merit. Here we investigate the influence of Ce-doping on the thermoelectric properties of PbSe.
We have synthesized Pb1-xCexSe (x=0.00, 0.01, 0.03 and 0.05) alloys and examined the structural, magnetic and thermoelectric properties.

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Bismuth-Doped, PbTe-Based Thermoelectrics with Nanostructuring

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At this work, different synthesis-methods for assembling bismuth-doped PbTe-based thermoelectric alloys have been examined. During preparation, the starting materials were mechanical ball milled with a ball-to-powder ratio of 7.5:1 for 5 hours in a planetary ball mill. The starting materials were varied while the synthesis, either the pure elements were given in, or Lead and Tellurium were pretreated and given in as a PbTe-alloy. The characterization of these alloys showed, that planetary ball milling is an adequate method to get nanostructured PbTe-compounds. Furthermore, the effects of a pretreatment of the starting material on the size of the crystallite and the effect on the thermoelectric properties have been investigated, and as a result, a correlation between the crystallite-size and the thermal conductivity has been found.

The compounds, synthesized by different methods were doped by different percentages of Bismuth up to 6 percent to determine its influence on the thermoelectric properties of the alloys. While the characterizations, Bismuth was found to be a proper material for getting an n type species integrated into the substrate. Because of the done variations in the synthesis-method, the thermal conductivity was greatly reduced and the Seebeck-coefficient indicates enhanced values, even at room temperature.

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Texturing of N-Type Chalcogenides Nanopowders by Open Die Pressing

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Open Die Pressing (ODP) has been employed as a straightforward forming process for sintering and texturing *n-type* $Bi_{1.9}Sb_{0.1}Te_{2.85}Se_{0.15}$ nanopowders. The alloy nanopowders were compacted inside a metallic round tube, at room temperature under Ar atmosphere. The cylindrical composite, with its axis horizontally oriented, was inserted between two heated plates of a press and subjected to compression loading, at a temperature ranging from 370 to 400 °C. Thickness reductions from 60% to 70% were tested. After deformation, the composite was kept under load at the same temperature for a few minutes, in order to achieve the complete consolidation of the nanopowders. X-ray diffraction pattern showed that ODP samples were strongly textured, with the basal (*00l*) planes of the hexagonal crystal cell oriented parallel to the plates. The degree of texturing, evaluated as orientation factor, *f*, by the Lotgering method, resulted to reach values up to *f* = 64% for 10 mm thick samples. Thermoelectric performance of the samples were measured by Harman method in the range of 20 to 170 °C.

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Concentration Anomalies of the Thermal Conductivity in PbTe-PbSe Semiconductor Solid Solutions

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One of the most popular methods of increasing thermoelectric (TE) figure of merit ZT is the solid solution formation, as due the difference in the Fermi electron and phonon wavelengths under the formation of a solid solution TE figure of merit ZT increases. It is usually assumed that with increasing impurity concentration λ decreases monotonically. When predicting and interpreting TE properties of semiconductor compounds under doping them with electrically active impurities, it is usually believed that the action of impurity consists just in a change in carrier concentration, whereas properties determined by the lattice subsystem, for example, phonon thermal conductivity, do not practically change. At the same time in a number of solid solutions in the range of small impurity concentrations (~ 0.5 - 1 at.%) we observed anomalies of properties, whose presence was attributed to critical phenomena accompanying a percolation-type transition from diluted to concentrated solid solutions [1-3]. Taking into consideration that most of TE materials represent solid solutions, heavily doped semiconductors, or, in most cases, doped solid solutions, the importance of the observed effect for TE materials science calls for more detailed study of this phenomenon. The goal of the present study is to investigate isotherms of lattice thermal conductivity λ_p of the PbTe-PbSe solid solutions in the range of small concentration of impurity (0 - 3 mol.% PbSe) and in the temperature range of 170 - 670 K. PbTe semiconductor compound and PbTe-based solid solutions are among the best TE materials for the

temperature interval 450 - 900 ê. No detailed studies of the dependences of λ_p on composition in the range of the small PbSe content have been conducted. It is established that the dependences of the lattice thermal conductivity exhibit a non-monotonic behavior: in the λ_p isotherms in the range of 0.75 - 1.25 mol.% PbSe, an anomalous growth in λ_p occurs under increasing PbSe concentration. The observed effect is attributed to the critical phenomena of percolation type and the self-organization processes accompanying the transition from diluted solid solutions to impurity continuum.

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Anomalies in the Isotherms of Heat Capacity of the Bi-Sb Solid Solutions

Rogacheva, E.I.[1]; Doroshenko, A.[1]; Nashchekina, O.N.[1]; Dresselhaus, M.S.[2]
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Bi1-xSbx solid solutions attract attention of researchers as promising low-temperature thermoelectric materials, on the one hand, and as convenient models for studying a number of physical phenomena, on the other hand. Earlier [1-3], we revealed nonmonotonous character of the concentration dependences of the thermoelectric properties in the Bi1-xSbx solid solutions which is an evidence of the existence of the phase transitions in the range of solid solutions. These peculiarities we attributed to critical phenomena accompanying the transition from a dilute to a concentrated solid solution, the transition to a gapless state, and the semimetal - semiconductor transition, respectively.

The goal of the present work was a detailed study of the heat capacity C - composition dependences of the polycrystalline Bi1-xSbx solid solutions in the range of 0 - 12 at.% Sb. Heat capacity was measured in the temperature range 170-670 K. In the isotherms of C, in the concentration intervals of ~0.5 - 1.0, ~2,5 - 3,0 and 7 - 8 at.% Sb, distinct extrema were observed which indicated qualitative changes occurring in the electron and lattice subsystems of the crystal under changing composition. The presence of the anomalies in the isotherms of C we attributed to the transition from the impurity discontinuum to the impurity continuum and possible self-organization processes accompanying this transition and to the reconstruction of the energy band structure under increasing Sb concentration (transition to a gapless state at certain critical concentrations, inversion of the L bands, semimetal – semiconductor transition, etc.). The obtained data represent additional evidence in favor of our assumptions stated earlier about a significant effect of electronic phase transitions observed in the Bi1-xSbx solid solutions on the concentration dependences of their thermoelectric properties. The obtained results should be taken into account when optimizing thermoelectric properties and developing new materials based on Bi1-xSbx solid solutions.

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The Effect of Equal Channel Angular Pressing on the Thermoelectric Properties of P-Type Bi-Sb-Te

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[1]Korea Institute of Industrial Technology, REPUBLIC OF KOREA; [2]Sejong University, REPUBLIC OF KOREA

In this study, p-type Bi-Sb-Te compounds were prepared by powder metallurgy method. The powders were consolidated by spark plasma sintering method under vacuum. The effect of Equal Channel Angular Pressing (ECAP) on the thermoelectric properties of p-type Bi-Sb-Te was studied. ECAP process was performed at a temperature of 380-500°C, a ram speed of 0.5-2.0mm/s and a pass of 1-4. The thermoelectric properties of the as-sintered and ECAPed compounds were measured at room temperature. Both the as-sintered and ECAPed compounds had the rhombohedral structure. We compared the microstructure, electrical transport, and thermal conductivity of the as-sintered and ECAPed compounds. After the ECAP process, the dynamic recrystallization was accelerated with increasing deformation temperature and lowering ram speed, resulting in a significant decrease in thermal conductivity. The figure of merit of the ECAPed compound was much higher than that of as-sintered compound.

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Macro and Micro Scale Features in the Thermoelectric PbTe (Br, Na) Systems: Micro-FTIR, Micro- Seebeck and SEM/EDX Observations

Stefanaki, E.-C.[1]; Nikolic, P.M.[2]; Papageorgiou, C.[3]; Polymeris, G.S.[1]; Pavlidou, E.[1]; Hatzikraniotis, E.[1]; Kyratsi, T.[3]; Paraskevopoulos, K.M.[1]

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PbTe is a well-known thermoelectric material, since its alloys exhibit properties that are favorable for applications in temperature range between 400 and 800K. In this work, n-type and p-type PbTe doped with Br and Na respectively were thoroughly examined, in the aspect of dopant effect in the microstructure of the samples. Macro and micro homogeneity of the samples were studied by means of micro FTIR, micro Seebeck and SEM-EDX. The experimentally determined U_P parameter, obtained after fitting in micro FTIR data, is used as a probe towards identification of position-sensitive dopant in-homogeneities, due to the dependence of the carrier concentration (N) on the $(U_P)^2$. Furthermore, slight dopant variations are easily detected by changes in Seebeck coefficient and thus micro-Seebeck measurements are ideal for detecting spatial compositional variations that affect the dopant concentration. Finally, SEM-EDX observations can detect the possible different phases that compose the system and map dopant in-homogeneities in micro-scale.

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Influence of Nano-B_4C on Thermoelectric and Mechanical Properties of $Bi_{0.5}Sb_{1.5}Te$ Prepared by Mechanical Alloying and SPS

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Bi_2Te_3-based materials are the most widely used thermoelectric materials for application close to room temperature. Generally, the commercial Bi_2Te_3-based materials are fabricated by zone-melting or vertical Bridgman method, and their ZT value can reach ~1. However, the commercial materials have very poor mechanical properties due to their cleavage fracture problem, and the effect of mechanical properties on TE module performance has often been overlooked. In terms of machining reliability and system integration, the mechanical properties are also essential. Especially for application in space RTGs, where the TE legs need to have higher aspect ratio, and the working environment is very aggressive. Thus, the influence of B_4C nanoparticles on the thermoelectric and mechanical properties of p-type $Bi_{0.5}Sb_{1.5}Te_3$ was investigated.

Highly dense p-type $Bi_{0.5}Sb_{1.5}Te_3$ alloys containing a small amount of B_4C nanoparticles (0, 0.1 0.2 and 0.5 vol%) were prepared by mechanical alloying and spark plasma sintering. The XRD results showed that all the samples were single phase as the small amount of B_4C could not be detected. The SEM micrographs of fracture surfaces revealed that the grain size decreased with increasing B_4C content, which indicated that the nanoparticles suppressed the grain growth of $Bi_{0.5}Sb_{1.5}Te_3$. No apparent preferential orientation was observed, which is consistent with XRD results, so the samples were presumed to be isotropic. With increasing amount of B_4C, the electrical conductivity and Seebeck coefficient changed slightly. The power factor of the sample started to degrade when the amount of B_4C increased to 0.5 vol%. The thermal conductivity was reduced slightly by dispersing B_4C nanoparticles in the $Bi_{0.5}Sb_{1.5}Te_3$ matrix because of increased phonon scattering. The highest ZT value of 1.06 @ 373K was obtained in the $Bi_{0.5}Sb_{1.5}Te_3$+0.1 vol% B_4C material.

The macro-indentation tests were employed to measure the Vickers hardness of all the samples. Different loads (50g, 100g, 200g, 500g and 1000g) were used in the measurements. At each load, the Vickers hardness increased linearly with the increasing amount of B4C. Compared with commercial p-type $Bi_{0.5}Sb_{1.5}Te_3$ materials, the Vickers hardness of $Bi_{0.5}Sb_{1.5}Te_3$ with 0.5 vol% B_4C increased by ~100%, and the machining reliability was significantly improved during cutting and polishing.

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Influence of the Incident Coolant Flow and Thermal Coupling on the Heat Transport of the Cool Side of a Thermoelectric Generator

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A lot of industrial processes consume a huge amount of valuable energy for heating and cooling losing it afterwards to the environment. Looking e.g. at metal forming processes of steel, energy is required to warm up the material to temperatures of 1200 - 1300 °C. Regarding an amount of 3 Mio. tons of steel per year being formed in Germany, this means a huge amount of energy loss connected to about 31,000 jobs within this industry. Thermoelectric generators (TEG) offer in principle the

opportunity to recover this heat energy by transforming it into electrical energy. Main problem is to adopt the thermoelectric generators to the temperatures and process conditions of the industrial processes which are dominated by always changing conditions and temperatures.
To obtain a reasonable amount of electric energy from these processes large areas of heat exchange are required with defined cooling efficiency. To maintain state-of-the-art TEG at their maximum output level, a heat of at least 100 kW/m2 has to be dissipated from the processes. This affords a high efficient heat transport on the cold side of the TEG to keep a sufficient temperature gradient over the device.

Therefore the heat distribution and temperature profiles are simulated in dependence on varying cooling structures and conditions for large area systems. To support the theoretical results the different cooling structures are verified on smaller scale TEG test-systems experimentally. The temperature gradient across the cooling structure and the influence of the incident flow are subject of the experimental and theoretical investigations, depending on the properties of the different cooling structures, the coupling to the TEG, and different cooling media. The results will help to understand the influence of inhomogeneous temperature distributions on the TEG's efficiency and to define an optimum cooling structure.

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Modeling and Design of Tubular Thermoelectric Generator Used for Waste Heat Recovery

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In many energy conversion processes, thermal energy is released to the environment, i.e. it remains unused. With the aid of thermoelectric generators (TEG) a part of this energy can be converted into electrical energy. The efficiency of the process can be increased and the CO2 emissions are therefore reduced. In this contribution, the simulation and the design of a new concept of TEG will be discussed. The TEG is built band-like and is wrapped around an electrically isolated tube, which is heated by waste heat and cooled by water. A numerical model is developed to theoretically study this concept. The goal is to understand the characteristics of the TEG and with it achieve a performance-optimized TEG-design. In order to get the optimal design, parameter-studies were carried out with the numerical model, which should help to determine the performance of the TEG. Geometrical characteristics, thermal resistance and electrical resistance in the components are considered to accurately model the modules. Furthermore the occurring temperatures and heat flows are also studied as small changes of these can often have a direct impact on the system.

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Thermoelectric Power Conditioning with Embedded MPPT Control

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Many thermoelectric generator (TEG) systems have been presented at recent editions of the European and International Conference on Thermoelectrics, as well as in literature. However most of these systems did not include an electronic power conditioning subsystem to maximise the electrical power produced by the TEG, or did not provide sufficient information and experimental results to highlight the importance of such a subsystem within any TEG system.

This work compares the performance of different Maximum Power Point Tracking (MPPT) techniques when tested onto the same DC-DC electronic converter and TEG system. The MPPT algorithms considered are the fractional open-circuit voltage method, the perturb and observe and the extremum seeking control. They are programmed to either a microcontroller or to a Digital Signal Processor in order to obtain an embedded system for stand-alone operation. The power electronic converter used is a 30W-rated synchronous buck-boost that is able to operate in boost, buck or buck-boost mode. The converter interfaces the TEG system to a 12V lead-acid battery load and it starts operating with input voltages as low as 2V. The TEG system comprises of three commercial TEG modules capable of producing output power in excess of 10W each at a temperature difference of 220°C. Extensive experimental results to analyse steady-state and transient performance are presented, as well as a detailed discussion of the benefits and drawbacks of the proposed solutions in terms of performance, cost, sensor requirements and processing power needed. Any of the three solutions proposed ultimately results in a MPPT converter that can potentially be used with any TEG system that can provide the minimum voltage required. If the TEG system can provide more than the converter's rated power or has an open circuit voltage over 55V, multiple converters can be used in a distributed system and connected in parallel to the same battery.

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Thermoelectric Generator for Low Temperature Applications

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Abstract:
The Engineering Center Steyr (ECS) is the commercial vehicle competence center of Magna Powertrain and worldwide well recognized for engineering services and niche production. Thus, several future technologies which will help us to make commercial vehicles more environment-friendly and more efficient are investigated at ECS.

Thermoelectric Generators (TEG) are a mean possibility to reduce CO2-emissions of commercial vehicles and therefore to meet the requirements of future legislation. For example long-haul trucks, which have normally enormous mileages per year, offer interesting application possibilities due to their continuous operation mode. This paper will describe the Thermoelectric Activities at Magna Powertrain and focusses on the conceptual design, mathematical modeling as well as simulation of thermoelectric generators for the exhaust system of diesel-powered commercial vehicles.

Design Studies
Two design studies have been investigated intensively within the last years. The first design study is based on common thermoelectric modules and the second one is characterized by axial cascaded sheets with radial located thermoelectric material (BiTe) and an integrated heat exchanger for hot exhaust gas and cold coolant water. This offers the advantage of a very high degree of integration and a compact design with the possibility to increase the electric power by adding or removing additional sheets.

Simulation models
In an early design phase, the heat exchangers for hot exhaust gas and cold coolant water have been pre-dimensioned by analytic equations in order to get a qualitative and quantitative perspective of main dimensions, weight and power output. With the help of extensive CFD simulations the two design studies have been optimized. The exhaust gas pressure drop is minimized and the exhaust gas flow is as homogenous as possible within the device in order to ensure the best possible efficiency.

Engine test bench
Finally functional prototypes have been realized and verified at an engine test bench. Comprehensive measurements show the challenges of this trendsetting technology and potential for further optimization.

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Design and Simulation of Nanostructure Thermopile Thermal-Based Energy Harvester using ANSYS

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Abstract –This paper presents a thermal energy generator (TEG) designed using ANSYS Multiphysics, a finite element software package which allows coupling of different physical parameters, which will produce heat and electricity. The objectives of this study are to able to simulate the basic operation of a thermoelectric junction using ANSYS Multiphysics, to optimize the dimensions of the thermoelectric junction to maximise voltage output and to design a thermoelectric array which is able to operate according to given device specifications. Based on the required specification, a temperature difference of 100C was chosen as the difference between the hot and cold sides. For a single junction of dimensions 110µm x 30µm x20µm, the Seebeck Voltage generated was 1.02 x10-5V. Thus, for an ideal device to achieve the specifications of 0.5V output a total of 50,000 junctions are required. This corresponds to an ideal total area of 27.5 cm x 6 cm (assuming an array of 2500 x 2000 =50000 junctions). To accommodate for a realistic device, which taken into consideration electrical losses through inter connects, an increase of 50% area is advised as a first approximation. Compatibility of the proposed TEG design with the nanostructure Bi3Te2 processes enables to realize a novel on-chip power supply capable of powering many low-power wireless sensor networks and devices. Index Terms- nanostuctured based TEG, Thermal energy harvesting, Seebeck effect, Thermocouple, Thermoelectric generator..

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Electrical and Configuration Characterization of Thermoelectric Generator Modules

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Abstract - Many electrical appliances and machinery emit wasted heat during their nominal functions. From heavy machinery to even laptops and personal desktop computers emit a significant amount of heat during their operations and even more during processing times. Thermo Electric Generator, TEG function is to convert these waste heats into electricity. In order to be able to harvest the energy efficiently, the need to understand the behavior of current existing thermoelectric modules is essential as an implementation or an application of a TEG in various scenarios. This paper describes the electrical characteristics of a typical TEG module that has

undergone a series of parameter setting using an in-house and cheap solution jig. In specific, the jig evaluation was done to understand the configuration and parameters needed for the TEG module to perform at its best characteristics during applications. To obtain optimum performance from the TEG module, it is important to address several key points and identified the cause that will affect the module performance. Once the characteristic of the TEG module is analyzed and understood, it allows the design of the integration circuit to be more appropriate. Therefore this will allow more sustainable and feasible platform of the Wireless Sensor Network when TEG module is integrated inside the systems. The TEG module that was used in the experiments are from Hi-Z Technology Inc, model HZ-2. Among all of the Hi-Z Technology modules, this model produces the highest possible output with the most minimal ΔT. Index Terms—Energy harvester, Thermal Equilibrium, Thermoelectric Generator Module, Wireless Sensor Networks.

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Optimizing the Heating Equipment of City Gate Station using Thermoelectric Generator

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For longer distance, the natural gas is transferred at high pressure and its pressure reduces in the city gate stations (CGS). In this research, the design and analysis of an electricity generator system for city gate stations using thermoelectric generator, is presented. Through the use of thermoelectric generator Natural Gas Pressure Reduction Stations (GPRS) it is possible to product assured, clean and continual electrical energy. Also To prove the efficient performance of proposed design, measure of generational electricity will be calculate for parameters of Sari natural gas pressure reduction station.

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Thermoelectric Generator Power Converter System Configurations: A Review

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Over the last years, thermoelectric (TE) energy harvesting has been regarded as a promising renewable technology due to the potential of the thermoelectric generator (TEG) to successfully produce electrical energy when exposed to a wide range of temperature difference. In a TEG system, the TE modules can be connected in series, parallel or a combination of both. Independent of the module connection, the power production of the TEG changes with the temperature gradient applied at its input. In consequence, the system requires a power conditioning circuit to deliver a stable and maximized output to the load. The solution is to integrate a DC-DC converter between the TEG and the load. Furthermore, a suitable control strategy is necessary to make the TEG operate at its maximum power point (MPP). Generally, the maximum power point tracking (MPPT) technique is widely used to harvest the maximum powers from the TEGs. The aim of this paper is to create a survey over the existing state-of-the-art TEG system configurations for TE energy harvesting. Depending on the application specifications, a suitable TEG system configuration can be designed with the purpose of improving the power production of the overall system. Section I offers a short introduction on TE existing technologies in terms of modules and applications. In section II, the overall TEG system configurations will be presented step by step. First, the possible connections of the TE modules in a TEG system will be analyzed. Afterwards, the typical converter configurations used in TEG applications will be presented along with their characteristics, followed by a discussion about the role of the MPPT depending on the TE modules connection. Section III discusses and compares the potential of the possible TEG system configurations classified by their TEG connection, with highlight on the main conclusions drawn from this study.

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Finite Element Modeling of a Thermoelectric Generator Based on Novel Phase Separated Chalcogenide Compounds

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Thermoelectric generators fulfill a unique solution of direct and efficient waste-heat recovery systems. Previous modeling of thermoelectric modules has focused mainly on analytical predictions which assume temperature-independent properties, 1-D heat flow and without taking into account the influence of Thomson effect. The current research focuses on a development of a reliable and robust thermoelectric model based on COMSOL Multiphysics 4.2 software, taking into account all of the relevant transport effects, contact resistance and temperature-dependent properties. Validation of the model is done on a mid temperature couple which is consisted of state-of-the-art phase-separated p-type PbTe-GeTe and functionally graded n-type PbTe-PbS

thermoelectric materials electrically connected by copper stripes.

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Transient Thermal Response of Heat Sinks and Its Implication on Power Control Strategies

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Thermoelectric generation has relatively low efficiency and power output, and hence it is necessary to maintain the optimal operating condition for obtaining the maximum power output. In a recent study, it was suggested that a method of optimization that controls the operating voltage to the half of the 'steady-state' open-circuit voltage should be a simple but effective strategy for maintaining the optimal condition. The reason behind this is not that the optimal condition corresponds to the impedance-matching condition, but that typical V-I curves of thermoelectric generators can be approximated by linear relations. The steady-state open-circuit voltage, which is the reference for the optimum voltage is a function of thermal conditions of the system, which may be subject to changes during its operation. In a case where large variation in thermal conditions is expected, it becomes necessary to regularly measure the steady-state open-circuit voltage to estimate the optimum voltage. Since there exists thermal inertia in the system, however, the voltage does not converge to the steady-state open-circuit voltage immediately after the cut-off of the current. The transient response due to the variation of temperature inside the system should be also considered. In order to measure the steady-state open-circuit voltage that is required for the estimation of the optimum voltage, one typically needs to wait for the transient response to decay. Hence, when the convergence towards the steady state is too slow, frequent interruptions of the operation required for the measurement may affect the overall performance of the system. In this study, we investigate the amount of time required for the heat sink to reach the thermal steady state from the instance when the current is cut off. Since a typical heat sink in a thermoelectric system has relatively high thermal resistance, its thermal inertia may become the limiting factor that dominates the transient behavior of the entire system. Both analytic and numerical estimates of the time scale of the transient response are provided, based on which we make some recommendations on power control strategies for thermoelectric generation systems.

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Thermoelectric Coolers with Silver-Sintered Interconnects

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Today, the Bottom-Hole Assembly (BHA) of deep drilling rigs is equipped with various electronic modules for Measurement While Drilling (MWD) and Logging While Drilling (LWD) applications. By MWD the time for well-construction shall be kept as short as possible and drilling costs shall be saved. However, for the deep wells high downhole temperatures of up to 300 °C over long logging periods of 100 - 500 h have to be managed making heavy demands on the electronic components for MWD and LWD. For longer drilling times active heat pumping is necessary, e. g. using thermoelectric (TE) coolers based on the Peltier effect which enables compact on-board cooling in the BHA without moving parts. Unfortunately, TE coolers based on bismuth telluride are limited by the temperature capability of their soldered interconnects. Sn-Sb alloys with a melting temperature of 230°C which have been employed in commercial modules are recommended for operation not above 200°C. In this study, fabrication and test of thermoelectric (TE) Peltier coolers (SPCs) based on bismuth telluride with silver-sintered interconnects for application at temperatures up to 300 °C is described for the first time. Silver sintering enables a die-attach far below its melting temperature of 961 °C offering high bonding strength combined with high thermal and electrical conductivity. SPC modules were assembled using a pick-and-place pressure-assisted silver sintering process at low pressure (5 N/mm^2) and moderate temperature (250 °C) for 2 min. A modified flip-chip bonder combined with screen/stencil printing was used for the pick and place process enabling high positioning accuracy, easy handling of the bismuth telluride pellets, variation of sintering temperature, pressure, and time as well as an immediate process control. The formation of positively locking joints was visually inspected using scanning electron microscopy with cross sections prepared by mechanical and chemical-mechanical polishing. Subsequently, contact resistivity was measured with single pellets yielding $(1.4 \pm 0.1)x10^{-5}$ Ωcm^2 which is below the range of values reported for lead-free or high-lead solder interconnects. The realized SPCs are evaluated at temperatures from RT to 300 °C showing superior cooling performance in comparison with state-of-the-art modules. Even between 250 °C and 300 °C a temperature difference of $\Delta T > 40$ °C between the cold side of the SPC and the ambient was observed. Furthermore, the high-temperature cycling capability of the SPCs was investigated in thermal cycles from 100 °C to 250 °C over more than 200 hours, i.e. 850 cycles. During the cycling tests no degradation of the cooling performance of the SPCs occurred. The fabrication

process of SPCs using pick-and-place pressure-assisted silver sintering will be described in detail.

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Multiscale Modeling of a Thermoelectric Device for the Integration in Wearable Electronics

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The complete understanding of thermoelectric phenomena has concentrated years of intensive work from materials study to device integration in self-powered systems [1] [2]. Thermoelectricity, capitalizing on waste heat recuperation, offers good prospects for the development of autonomous systems in the case of wearable electronics. The most critical obstacle for the technology development is to obtain thermoelectric materials that exhibit high efficiencies under low thermal gradient load, and these target materials should be made of abundant, non-toxic chemical elements in order to replace bismuth telluride and its alloys for applications harnessing body heat harvesting. In this perspective, we choose to study tetrahedrites, a promising p-type thermoelectric material for room temperature applications which transport properties can be significantly improved by chemical doping [3]. Targeting the development of flexible printed thermoelectric devices, as a function of system level efficiency, we propose an innovative approach for device optimization based on the multiscale modeling of a complete thermoelectric system. In this scope, three parallel levels of modeling will be addressed, from nano to macroscale: at the nanoscopic level, quantum density-functional theory is used in conjunction with semi-classical approach using Boltzmann transport theory to calculate electronic properties such as Seebeck coefficient and electrical conductivity and thermal conductivity [4]. The effect of atomic substitutions is more precisely studied and the possibility to find an n-type tetrahedrite based material explored. At the device level, we use material parameters as inputs in order to build a finite-elements virtual prototype of printed thermoelectric device [5], evaluate performance and optimize device architecture. These simulations provide global device parameters used for compact model development. At the system level, we develop a VHDL-AMS compact model to evaluate overall system efficiency as a function of effective electrical operating conditions and establish relevant optimization criteria [6]. The aim of the work is thus to understand each critical aspect of thermoelectric generation and to propose a methodology for evaluating the impact of each level on the global performance of the device when embedded in a complete system. The presented work will then focus on the methodology and models settings.

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Potential Applications of Thermoelectric Generation in the Electric Trains

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In order to increase the energy efficiency of electric trains, various energy harvesting technologies have been researched and deployed in the electric trains. In this study, we introduce potential applications of thermoelectric generation (TEG) in the electric trains and suggest a few conceptual designs for the train's components in which TEGs can be applied.
One of the applications suggested here is the train propulsion system combined with TEG. In general, the conventional train propulsion system consists of inverters, filter reactors, and traction motors, which dissipate about 5 % of total traction energy as heat losses. However, water-cooled designs for the components make it possible not only to improve its capacity but also to harvest a certain amount of electric energy by TEG modules equipped in the heat-exchanger of cooling system.
Other applications are TEG-embedded train braking systems. Most electric trains use regenerative braking system that converts the motor into a braking generator when decelerating the trains. In the ideal operation, up to 70 % of the traction energy can be returned to train power substations, but 20~30 % of the energy is still dissipated as heat at mechanical brakes or over-current resistors in the train control units. Therefore, additional energy harvestings by TEG modules can be expected at the mechanical brakes and the resistors.
The efficiency of TEG modules has been still one of critical issues in deploying them to industrial application. Finally, we suggest the minimum performances of TEG modules to be economically deployed in the electric trains.

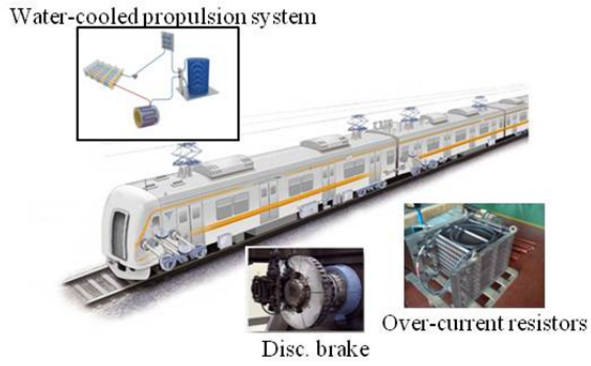

Fig. 1. Components for TEG in the electric trains

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Modelica® Library for Dynamic Simulation of Thermoelectric Generators

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I. Introduction

The contribution presents a new modeling library for dynamic simulation of Thermoelectric Generators (TEG) in 1D spatial resolution. The core of the library is the model of the thermoelectric (TE) material itself, which has already been published by the authors in [1]. In the submitted work, this model was expanded to an overall library for complete TEGs. Due to the concept of the modeling language Modelica, the library can be used by an end-user for direct use as well as by experts, who can do their own extensions.

II. Capabilities of the model library

Modelica is a component-oriented modeling language with an acausal concept. It allows a structure-preserving way of modeling complex physical systems. A further advantage is the reusability of components, supported by graphical model diagrams on distinct hierarchical levels. Fig 1 gives a partial insight into the library. On the left side, the top-level diagram of the TEG is shown; it reflects the concept of the component-oriented modeling. There is the model of the pure TE material in the middle, surrounded by ceramic plates on the left and the right. With the new library, it is possible to adapt the model to one's own TEG type. For instance, there is the choice between different "inner" TE models and different material data, as mentioned in [1]. These models work with the temperature dependencies of material properties, e.g. the Seebeck coefficient and some geometrical parameters, e.g. the thickness of thermoelectric legs. Moreover, there is the option of taking the contact resistances between the legs into account. These options of selection are obviously on the right side of figure 1.

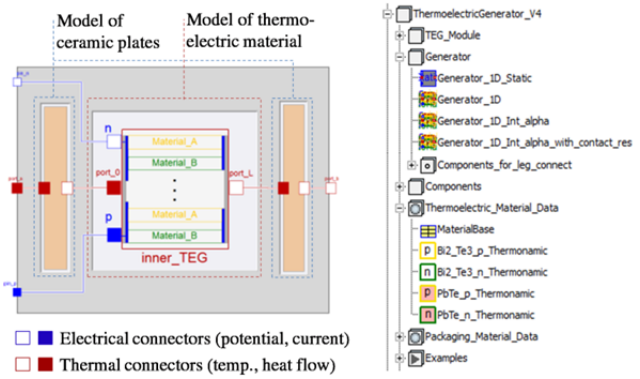

Fig 1: Top-level diagram of TEG model (left) and structure of library (right).

As the standard interfaces of Modelica (electrical and thermal connectors) were used, it is feasible to integrate the library in other existing Modelica libraries.

III. Example

Fig 2 demonstrates the possibility to combine the TEG library with other Modelica libraries. As an example, an energy harvesting solution for the energy supply of an electronic thermostat on a radiator is chosen. Whereas the heating system is modeled out of components included in the Modelica Standard Library, the presented library is used to model the TEG system. Due to the temperature-dependent internal resistance of the TEG, it is connected to a maximum power point tracker to reach the maximum possible output power. There is no limitation in the simulation time, so short-term and long-term simulations are possible.

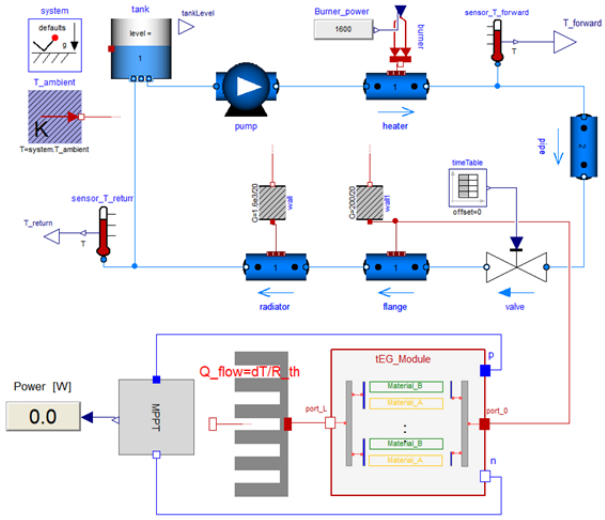

Fig 2 Modelica diagram of a heating unit with integration of a TEG model to simulate energy harvesting for a thermostat.

The results of the simulation will be discussed in the full paper.

IV. References

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Study of Thermally Induced Degradation Effects on Thermoelectric Materials

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Thermoelectric generators (TEG) consist of many thermocouples (pair of n- and p-type materials) which are switched electrically in series and thermally in parallel. During operation the materials are exposed to huge temperature gradients of sometimes several hundred Kelvin per centimetre and an electrical field. These factors can cause thermal degradation (Ludwig-Soret effect) and electromigration. Hitherto, influences on the thermoelectric properties have rarely been investigated, although module properties can significantly deteriorate, especially on a long-term scale. The applicability of new materials under specific thermal and electrical conditions can only be predicted knowing possible degradation effects. Therefore, a better understanding of the occurrent transport processes is essential for ensuring a successful development of future TEGs.

In the ongoing research project we intend to investigate segregation effects in thermoelectric materials caused by temperature gradients. Furthermore, local degradation due to interfacial reactions especially at contact surfaces is studied. For this reason, model systems of lead telluride (PbTe) films on different metal substrates (copper, iron, zinc) are produced and the chemical diffusion at varying temperatures is observed using Time of Flight-Secondary Ion Mass Spectrometry (ToF-SIMS). Sodium cobaltate (Na_xCoO_2) as a good sodium ion conductor is indicating a high tendency to segregation. By applying temperature gradients parallel to the layered structure of the samples, enrichment as well as depletion of sodium ions along the gradient should be observed.

Identifying materials whose thermoelectric properties diminish according to segregation effects as well as materials which show long-term stability against temperature gradients and electric fields is crucial for a purposeful development and improvement of promising systems.

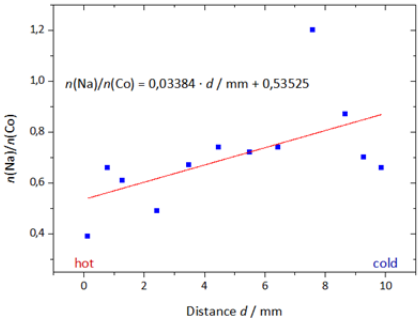

Figure 1: Change of Na_xCoO_2 sample composition after thermal treatment measured by SEM/EDX. Over a distance of 10mm and a period of 16h the hot and cold side temperature was held constant at 600°C and 80°C, respectively. An enrichment of sodium at the cold side could be observed.

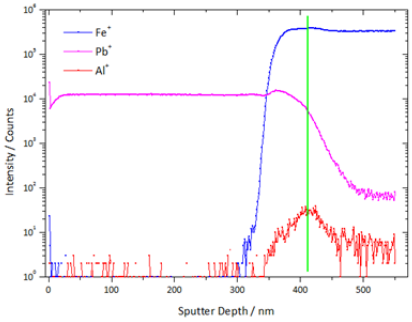

Figure 2: Depth profile of PbTe on an iron substrate using ToF-SIMS analysis. The sample was held constant at 230°C for 8h. The vertical green line marks the initial interface.

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Anodized Aluminum as Effective and Cheap Alternative Substrate for Thermoelectric Generators

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The widely usage of thermoelectric generators (TEG) is still blocked by very high product costs. Almost all nowadays commercially produced TEGs are mounted on ceramics like alumina (Al_2O_3) or aluminum nitride (AlN). On one hand these materials have a very high thermal stability and a rather good thermal conductivity but on the other hand they are also very expensive and their thermal conductivity actually drops with rising temperatures.

Therefore, anodized aluminum could be an effective alternative for this purpose. For good module efficiency the thermal resistance of a TEG substrate must be as low as possible. Aluminum (Al) has a significantly higher thermal conductivity as both named ceramics (see Fig. 1). Secondly, the substrate has to be electrically insulated to separate different thermocouples from each other. So, after anodizing the Al the surface is covered with an about 10 µm thick Al_2O_3 layer which is enough to electrically insulate but does not change the thermal overall resistance of the substrate much (~9 %). And thirdly, the substrate needs to be able to deal with the temperatures used in its application. Since the nowadays most widely used thermoelectric materials are still telluride based the maximum working temperature is located at around 300 °C which is the same or even less than the one of high temperature aluminum alloys. And there are still two more things to be mentioned by comparing anodized Al vs. Al_2O_3 and AlN. Al can be shaped much easier than a ceramic material which could be used for a further reduction of the thermal resistance by more detailed substrate shapes. And the biggest advantage is obviously the price. Anodized Al is around twenty times cheaper than Al_2O_3 and even a thousand times cheaper than AlN (see Table I).

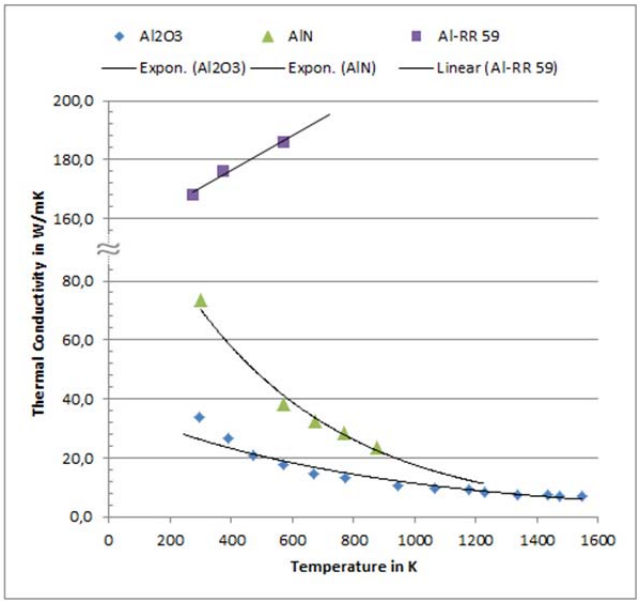

Figure 1: Thermal conductivity of Al_2O_3, AlN and Al vs. temperature [1-3]

Material	Price	Reference
AlN	70 €/cm³	[4]
Al_2O_3	1.3 €/cm³	[5]
Al (elox)	0.06 €/cm³	[6]

Table I: Prices for different materials

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Generalized Heat Equation and the Influence of the Leg Geometry on the Performance of a Thermoelectric Element

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Recently, thermoelectricity as a direct energy conversion technology gained a lot of renewed interest. The physical effects of thermoelectricity as known for long can be applied in solid-state devices, e.g. thermoelectric generators (TEG) which convert heat into electricity or in thermoelectric coolers (TEC) in which an electrical current is used to pump heat against a temperature difference. There are many potential applications of thermoelectric power generation, such as waste heat recovery in energy conversion systems, industrial processes or in automotive applications.

The performance of a thermoelectric (TE) device depends on various factors beyond the material properties which are a focus research target nowadays. Key factors influencing the performance are the working conditions like the junction temperatures and/or heat fluxes at the contacts of the TE material to a metal bridge. In this work we want to focus on the influence of the geometry or the topology of a TE element on the performance of a TE device. The framework of the investigation is delivered by the Onsager-deGroot-Callen theory, a kind of field theory in thermoelectricity which provides a thermal energy balance. A literature review shows that up to now the investigations on TE devices with shaped elements are done mostly in a one-dimensional setup.

Obviously it is clear that for TE elements of non-prismatic, non-cylindrical shape the problem is a priori at least two-dimensional. To investigate the influence of shape the generalized heat balance within the constant properties

material approximation is solved with different techniques and compared to the standard quasi-1D calculation which can be done analytically. Afterwards a truncated cone as a 2D axisymmetric problem is treated and the impact on the performance discussed. Arbitrary shape can be examined numerically by means of the finite element method (FEM). It is used to verify the results from the analytical and approximate solutions.

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Energy Harvesting Wireless Sensor Network

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Energy harvesting is an emerging technology where systems attempt to extract power from the losses or products of other "host" systems. In an industrial environment it can prove hazardous or expensive to have plant monitoring sensors physically connected; one solution is to have such sensors form a wireless network where each "node" generates its own power. This work presents a thermoelectric energy harvester which provides the energy requirements of a wireless sensor which incorporates a data capture and transmission system.

There are many unique challenges to such a system. The Thermoelectric Generator (TEG) must be attached to and clamped firmly between the two parts forming the temperature gradient without introducing a thermal short-circuit between them. The system should be able to operate for extended periods of time from energy previously stored, therefore necessitating exceptionally low operating power. The system should also be uniquely identified physically and on the wireless network and support some form of data security. Lastly, the system should work equally well regardless of the direction of thermal gradient.

The system which will be described analyses the use of a thermoelectric module coupled to a high performance power converter able to provide relatively high voltage and power from a low temperature gradient and with sufficient power production over the target temperature range. An ultra-low power microprocessor design based on the MSP430FR from Texas Instruments is used and careful software programming has enabled an operating current of 270nA at 1MHz clock frequency. The radio system design is based on a 2.4GHz ZigBee transceiver which gives a transmission range of greater than 10 meters. The software stack is adapted from existing wireless sensor network protocols that normally do not take into account the power consumption with the specific aim of reducing power requirements whilst preserving functionality. Data is collected on a central server which has a number of system administration tools and is able to provide system information in real time. An android application is also provided to allow a meaningful way for users to interact with the system via smartphones and tablets.

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Temperature Field Emerging at Unstable Thermal Source and Options to Minimize its Effects on Thermoelectric Generator

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The objective of the presented work is to increase the power of a small thermoelectric generator using the heat of an unstable thermal source combusting wood biomass. It has been found out that due to an uneven spread of heat in a combustion chamber and due to the generator construction significant loss in interconnected thermoelectric modules occurs. This loss increases with a higher temperature difference and the generator power is extensively degraded due to the thermal spread. The influence of the temperature field on the generator power can be partially eliminated using dc/dc converters, their proper ordering and the maximum power point tracking (MPPT) algorithms application. However, their application intensifies the generator complexity and this system might function erroneously more frequently. This is the reason why the potential use of phase-change materials (PCM) is examined. PCM might reduce the temperature fluctuation in a short-term and make the thermal flow more even. A heat exchanger containing PCM material has been designed and constructed and temperatures at the interface of the heat exchanger, i.e. power parameters of a thermoelectric generator, have been measured after its application. The gained results are compared to the original parameters and the effects of PCM on the generator power are analysed.

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Thermoelectric Energy Harvester for Sensor Applications

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With the increasing availability of low-power sensors and the recent advancements in low-power VLSI circuits and ASICs, the use of autonomous systems such as sensor nodes in Wireless Sensor Networks (WSNs) has become very popular. These systems are often connected to an independent power source (solar cells, thermoelectric generators, etc.) and a storage element (battery, super

capacitors, etc.) whose dimensions usually dictates the overall size of the electronic system. For such reasons an important issue to address is the way the maximum power is extracted from the source so that the power budget of the system is met without compromising the size of the system. Thermoelectric generators (TEGs) can be used to power these types of systems from a temperature gradient of a few degrees Celsius. Advantages of using TEGs include that they are physically robust, can be manufactured in very small form factors and weigh a few tens of grams. The thermoelectric energy-harvesting systems presented at recent European and International Conferences on Thermoelectrics did not include a power-conditioning unit to maximize the power produced by the TEG at any temperature difference. In the market there are currently no commercial ready-to-use solutions to interface a thermoelectric energy scavenging system to sensors and low-power processor units. Moreover the available Integrated Circuits (ICs) designed for low-power energy-harvesting systems have some disadvantages: restricted input voltage operation and slow-response or approximate Maximum Power Point Tracking (MPPT) techniques. The main electrical challenge when implementing MPPT with low-power systems is represented by the system standing losses, such as voltage drops across components. Set-point precision is another difficulty when working with small input voltages. This work describes a small-size energy-harvesting circuit that implements MPPT based on the measurement of the open-circuit voltage. The power converter is continuously energized, allowing the system to work with voltages below 80mV after a 330mV cold start-up. Simulation and experimental results confirm the precision and fast-response of the proposed system. This MPPT method is very simple and robust which makes it suitable also for WSNs in the aerospace and automotive industry. The system is versatile and can be used to maximize power production for any low-power system already designed. It is also readily adaptable for use with other types of low power sources such as photovoltaic cells and electromechanical sources.

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Simulation of Power Management Electronics and Energy Storage Unit for MEMS Thermoelectric Generator

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Power management electronics plays a very important role in any energy harvesting system. Harvested electric energy on the output terminals of an energy harvesting module must be tailored for the use with supplied device and the use of an energy storage element is commonly required due to discontinuities in the flow of harvested energy. The power management electronics of energy harvesting systems has to operate around the maximal harvesting point. It is known as the maximum power point tracking (MPPT). This feature is necessary due to the varying conditions in the used energy harvesting system. In the case of thermoelectric generators are the varying conditions represented by the changes in an internal resistance of thermoelectric module.

The main aim of our work is development of the thermoelectric energy harvesting system for critical applications (e.g. aeronautics). This system will be used as a power supply for monitoring and diagnostic wireless sensor units. The further opportunity for using of an autonomous energy source can be observed in a backup source for several applications.

This paper deals with the simulation modelling of the complex energy harvesting unit which is based on MEMS thermoelectric generator. This paper is mainly focused into the first steps in a development process – analysis of demands given on the aircraft-specific thermoelectric harvesting unit, choice of energy storage elements, conceptual architecture of power electronics and simulation of various operating states based on the typical operating envelope. This paper, unlike the commonly used SPICE models, presents a model fully implemented in MATLAB Simulink Simscape. This approach allows using the previously developed Simscape simulation model of TEG without any further improvements.

As the sources of energy are used the commercially achievable thermoelectric modules produced by Micropelt GmbH and Nextreme Thermal Solutions, Inc. The raw power output coming out of each of these modules is in the range of tens of milliwatts. In the developed simulation model are considered several parallel, serial and serial-parallel combinations to obtain the higher levels of harvested power. The special attention is paid to the choice of energy storage unit. Designs using supercapacitors and batteries as the electric energy storage elements are considered and evaluated. Several basic architectures of electronics (boost, buck-boost, SEPIC) are examined through the simulation modelling.

The presented model represents an important step in the process of a mechatronic design of the complex aircraft-specific thermoelectric energy harvesting unit.

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On Permeable Thermoelement Simulation

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The results of the research into prospective applications of permeable thermoelements are presented. Simulation of various permeable structures (planar, channel, porous, segmented and stage) for thermoelements operating in electric energy, thermoelectric heating and cooling modes was performed. Possibilities are described of usage of the combined action of Joule-Thomson and Peltier effects in permeable narrow-channeled thermoelements for gas fluxes cooling. . By way of using Comsol Multiphysics, the applied computer programmes package, a 3D model of a permeable thermopile was created that considers temperature dependences of parameters of the materials used, as well as commutation plates, heat transfer layers and contact resistances presence. The results of studies of a Bi-Te based thermopile are provided. Computation was performed on the impact of coolant flow and electric current density on the temperature and potential distribution and energy characteristics. Optimal values of the said parameters in maximum efficiency and COP modes were defined.

Methods of the mathematical optimal control theory and computer simulation for the solution of multifactor optimization problems in 1D model were described. Computer programmes for estimation of both design and thermal parameters providing maximum values of thermodynamic energy conversion characteristics were developed. Computer aided computations of the optimal parameters for permeable thermoelements fabricated from different materials based on â3-óå, Pb-Te, Si-Ge, Fe-Si, TAGS were performed. The data obtained reveal the possibility of thermoelectric energy conversion improvement by factor of 1.3 to 1.5 as compared to conventional thermoelements.

Samples of permeable thermoelectric piles from the extruded Bi-Te-Se-Sb based materials were developed. The experimental data thus obtained confirm the essentials of the theory which reveals the possibilities of a wider practical application of thermoelectricity.

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Thermoelectric Power Generation Using Waste Heats in Railway Systems

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Due to the increasing demand in energy resources, many efforts in power generation have been given in the field of railway industries, especially, using the waste heats, which are generated during the operation of railway systems. Generally, in railway brake applications, several different types of braking methods are available, such as mechanical braking with disc brake and friction materials, regenerative braking, or eddy current braking. Among the possible braking methods, the mechanical braking is the typical braking type in railway operation. In consideration of mechanical braking, the generation of waste heats is possible during braking with the interaction between brake disc and pad. In this investigation, the thermoelectric power generation using the waste heats in railway systems has been considered. The thermoelectric power generation system was designed using the thermoelectric sensor. Before the actual application on the railway rolling stocks, in this study, the generation system was setup using a full scale dynamometer for railway braking testing at a lab. The thermoelectric sensor was equipped on the back side of pad, and the thermoelectric generator was working at the condition of the temperature change and the generating heat during braking. In this paper, the thermoelectric power generation system using the waste heats from railway braking was introduced, and the efficiency and performance testing results were discussed. Also, the possible suggestions on the actual application on the railway system will be proposed.

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Installation of a Thermal-Buffering Function Using Phase Changing Materials for a Stable Mid-Temperature Thermoelectric Power Generation

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To stabilize the input heat to a thermoelectric generator (TEG) and to protect it from large temperature fluctuations, a thermal buffering device was fabricated and examined in mid-temperature range. To realize a durable thermoelectric power generation system, a heat buffering function in order to avoid TEG breakdown following an unanticipated rise in temperature is needed. The thermal buffering device comprises two adjoining heat storage containers, each containing different alloys, which can be optimized for the temperature range of the TEG. The combination of two alloys in series diminishes

the thermal fluctuations, stabilizing the heat input to the TEG module. This is achieved by having two metallic materials with large enthalpies of fusion that can be placed between the heat source and the TEG. We have developed such a thermal buffering device (TBD) using alloys with eutectic reactions. In a binary alloy system which has a eutectic reaction, it is known the alloy absorbs, when heated, heat equivalent to the enthalpy of fusion in the range from the eutectic temperature to the liquidus temperature. On the other hand, when the liquid of this alloy is cooled down, it releases heat equivalent to the enthalpy of fusion in the range from the liquidus to the eutectic temperature. If we can place alloys with large enthalpies of fusion between the heat source and the TEG, we can expect the alloys to work as heat storage materials. These materials buffer large temperature fluctuations and supply stable heat to the TEG. The combination of the two alloys can be optimized for the temperature ranges of appropriate TEG materials such as Mg2Si or CoSb3. For the Mg2Si TEG, alloys consisting of 20Ni-80Al and 7Si-93Al were used for the heat source side and the TEG side, respectively. In this report, we evaluated a thermal buffering devise by measuring the temperature at the hot side of the module against temperature fluctuations in the heat source. It was also installed to a exhaust duct of a industrial heat treatment furnace with a bellows to absorb thermal expansion of the system, resulting in sufficient durability and stabilized TEG output during long aging test.

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Finite Element Approach for the Evaluation and Optimization of Silicide-Based TEG

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Numerical modeling represents an effective tool for designing and evaluating the performances of thermoelectric power generators (TEG). In particular, the finite element method (FEM) allows to perform multiphysics simulation, that is coupling different physical phenomena, such as heat transfer, thermoelectric effects and Joule heating. In this work, FEM modeling is used to reproduce the results of open circuit voltage and output power measurements on a Mg_2Si based TE-chip under large temperature differences. Furthermore, output power and conversion efficiency of a 16 chips TEG module with different values for the cross sections of the n, p legs have been calculated. In both analyses, thermal and electrical conductivity and Seebeck coefficient are given, as input, as function of temperature. Finite element analysis was carried out in two steps: (i) modeling of single n-type leg, using the measured data of an undoped Mg_2Si chip, in order to evaluate the correspondence of measured results and output values of numerical analysis and (ii) modeling of a 16 legs TEG module to evaluate the dependence of output power and conversion efficiency on the ratio of the cross sections of the p-type (higher manganese silicide, HMS) and the n-type (Bi doped Mg_2Si) legs, and to find the maxima of both functions. The effects of thermal and electrical contact resistances were taken into account, by introducing thin thermally / electrically resistive layers in the numerical model. In the second step, the results of numerical analysis led to an optimal geometrical configuration for the TEG module. Both power density and conversion efficiency were found to increase raising p-type cross section until a maximum value. FEM analysis has been carried out to find these maximum values, useful for further steps in the design of the TEG module. Maximum values of power density and conversion efficiency obtained with FEM modeling have been compared with a different numerical approach, using optimization techniques.

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Silica-Based Materials for Thermoelectric-Legs Embedding

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Sol-gel chemistry was used to synthesize low-density SiO_2 aerogel for matrix embedding of silicide-based (Mg_2Si-and Higher Manganese Silicides, HMS) thermoelectric legs. In TEG modules, the heat conduction in air and the convective and radiative contribution to the heat transfer play an important role on the reduction of the efficiency of the module. Silica aerogel are known for the lowest thermal conductivity of any non-evacuated solid. With this in mind, silica-based aerogel materials were employed to fill the void spaces between the thermoelectric legs of a module. In order to do this, different synthesis procedures were taken into account to produce suitable silica materials. It is important that the silica can be easily cast into place, avoiding mechanical cracks of the matrix. Silica aerogel typically require a supercritical drying step to remove the pore fluid from the SiO_2gel, avoiding the collapse of the pores. This procedure is not practical for TE-legs embedding and it is dangerous, expensive and time-consuming. It is known that replacing the -OH groups with organic hydrophobic substituents in the SiO_2 pores prevents the pore-shrinkage and the sintering of the matrix during solvent evaporation step. This allows to synthesize relatively light materials at low temperature and ambient pressure, with no need of supercritical drying of the gel. The obtained aerogel were characterized by thermogravimetric analysis, differential

scanning calorimetry and FT-IR spectroscopy to determine whether chemical modification occurred and to evaluate the stability of the material with increasing temperature. The thermal expansion of the silica was measured by means of dilatometry. Finally, the thermal diffusivity was measured with the laser flash method to calculate the thermal conductivity of the different specimen. The chemical compatibility between the silica matrix and Mg_2Si and HMS pellet was also investigated.

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Sintered Nano-Ag as Joining Material for Thermoelectric Modules

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We have investigated the use of sintered silver particles as an alternative to other types of brazing materials for the electrical connection between the thermoelectric material and the hot side substrate in thermoelectric generators (TEG). Sintered silver particles have recently gained attention in the field of power electronics due to the high thermal and electrical conductivity of the material. The nanosilver paste used in this work has originally been developed for use as a die attach material, where these properties are important. The sintering process involves a temperature treatment at 320°C under 15 kg mechanical load in a nitrogen atmosphere. Sample TEGs with sintered silver connections are tested mechanically and electrically. Initial results show good performance under 200°C thermal gradient tests. Performance also indicates good contact resistance. Currently, high cost prevents this material from becoming widely used in the thermoelectric field. For low volume, high temperature and high performance applications the use of sintered silver as a brazing material could be an option.

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Thermoelectrics Goes to Both Marine and Automotive Applications–Goals, Agenda and Achievements of the EC PowerDriver Project

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The EC granted PowerDriver project aims to develop thermoelectric generators in the range of 300-600W output electrical power for automotive applications (gasoline engines) by utilizing the waste exhaust heat generated into useful electrical power. The project has also a target of more than 1.5kW for marine (Diesel engines) applications such as leisure boats and several kW for Large Diesel/Gas engines. Although several automotive companies like General Motors and BMW had recently demonstrated the high potential of thermoelectric converters to utilize the large extent (>60%) of the waste exhaust heat generated in automotive applications into electricity, the PowerDriver project applies for the first time to marine applications, showing several clear advantages. Since maximizing the thermoelectric efficiency (in order to be closer to the theoretical Carnot efficiency) requires maximizing the hot side temperature and minimizing the cold side temperature, it is clear that marine applications are capable of much more effectively cooling the cold side using the large reservoir of cold sea water, compared to automotive applications which are limited by the coolant flow rate through the cars radiator. There are difference in operation between automotive applications and marine application on the hot side as well. Automotive applications will tend to show variable temperature through a driving cycle; Marine engines are typically run at 75 - 80% of rated power for extended periods allowing for consistent power generation. Furthermore, the thermoelectric semiconducting materials are usually mechanically weak and prone to mechanical failure due to thermal cycling. In a normal driving profile of cars, on average, the engine is turned on and off several times a day. In the large boat application, the engine is turned on only once per cruise. Therefore it is clear that the marine thermoelectric applications are also very interesting. Since both the automotive and the marine applications seem very promising, both of the approaches are investigated in the PowerDriver project. For the automotive application, we consider a gasoline engine, generating a maximal temperature of ~650^{o}C (in NEDC condition operations), while for the marine application, we consider a diesel engine, generating a maximal temperature of 450^{o}C. Therefore, silicide and telluride based thermoelectric materials are considered for those applications, respectively. So far very promising thermoelectric properties were obtained for the various developed thermoelectric materials. The goals, agenda and preliminary achievements will be reviewed in the current presentation.

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Viper Automotive Thermo-Electric Generator Mechanical Design Development

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This paper describes the design and development process that was used to create a thermo-electric generator for application in the automotive sector. The process started with basic analysis of an initial simple concept from which temperature gradients along the surface of the heat exchanger were calculated and predicted using numerical methods. The results obtained were analysed and compared to well established, classical solutions that are typical of what one would expect to see. From this exercise confidence was gained of the methods and models applied.

With the methodology established, the next step was to optimise the pellet length and cross sectional area to achieve maximum power output with high efficiency. The geometric optimisation exercises as well as mechanical strength and robustness of the design analysis were carried out using three dimensional (3D) Computational Fluid Dynamics (CFD), Finite Element Analysis (FEA) and 1D analysis. This was followed by the determination of the minimum surface area required to achieve a total thermo-electric generator (TEG) power output of 300W. Brainstorm sessions were used to generate many ideas from which TEG design concepts were created. The concepts were then assessed and selection made based on the following driving parameters: minimum surface area, valve types, and the use of bypasses to ensure it would fit within the specified space volume. Back pressure and flow uniformity analysis were carried out and several iterations were executed to create optimised flow characteristics.

Upon achieving an optimum size design that fitted well within the specified enveloped, the fin selection process was started. This included analysis of various types of fins that were to be selected based on the performance characteristics of their pressure drop versus thermal conductivity. When all elements of the TEG design were selected, a final structural FEA analysis exercise was carried out including buckling. The purpose of this exercise was to ensure the robustness and structural integrity of the finalised design.

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Assessment of Thermoelectric Power Generation for Hybrid Electric Vehicles Based on Tracked Data

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Many factors, like shortage of oil or environmental pollution, lead to the need for a new and highly efficient engine generation in passenger vehicles. Plug-in hybrid electric vehicles (PHEV) are a promising approach. The combination of an electric motor and a combustion engine enables the range of modern vehicles and the enhanced efficiency of electric power trains at the same time. This reduces the exhaust emissions and the fuel consumption to a minimum. Most car manufactures therefore offer at least one hybrid vehicle. Even in these highly efficient vehicles, there is still an amount of waste-heat of the combustion engine, which is not used. To further increase the overall efficiency of the car this heat is to be used.

The idea is to integrate a TEG into the exhaust gas system of a PHEV. This is already done/ tested with internal combustion engine vehicles (ICEVs). In comparison to the ICEVs, the combustion temperature throughout a typical drive of a PHEV shows a distinct different characteristic (temperature gradient) and therefore other materials can be used. High temperature materials are not sufficiently investigated, whereas with low and middle temperature materials already promising results were achieved. Hence fully developed materials can be applied in PHEV. Due to the fact that the combustion engine is only used temporarily, the electric yield might be lower. On the other hand, the load is more constant and uniform, which affects the thermomechanical stress positively. Lower stress inside the module leads to a higher durability and lower deformation guaranties a good thermal contact to both, the heat source and the heat sink. The generated electrical energy furthermore can be easily stored and extends the range of the PHEV. Since the voltage used in PHEV power-trains differs from the usually used 14V in vehicles, this high voltage storage could also be used for the TEG, which potentially enables more efficient ways of interconnection. All in all PHEV appear to be one promising field of application for TEG. [YANG] and [KIM] already investigated the potential of the combination of HEVs and TEGs.

In the present study tracked drive data of a PHEV is used to evaluate the capability of a TEG integrated in the exhaust gas system of a hybrid electric vehicle. Additionally, a FEM-simulation of the stress under realistic load is carried out. The stress as well as the overall energy output of the TEG is then compared to its potential using a conventional vehicle.

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Simulation of Design and Operating Modes of Thermoelectric Generators for Vehicles

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The project of development of thermoelectric generators utilizing the combustion engines waste heat is still topical. But, as previous experience has shown, one can surely face multiple obstacles caused by both dynamic modes of engine operation and interaction between the generator and various systems in the vehicle. Although permanent endeavors aimed at the development of a vehicular thermoelectric generator have been taken, no industrial sample of the said generator still exists at present. It is absolutely clear that an effective sample of the generator in question can be developed by way of optimal constructions simulation considering the specific features of its operation only. We have developed a theory of thermoelectric generators for automobile waste heat utilization that considers the specific features of the automobile engine operation. Basic correlations for estimation of electric power and efficiency of vehicular thermoelectric generators in different model approximations are provided. Essential mechanisms of operation of the generator were defined on the basis of a prime model, such as optimal thermal conditions, correlation between heat fluxes at both input and output of the generator and demands to thermoelectric materials used. Application of more complex 3D models with distributed parameters allowed studying the generator under dynamic operating modes where real temperature dependences of the parameters of thermoelectric materials and the generator constructional elements are considered. The results are given of the sectional design of the generator that provides its maximum efficiency. Computation of the generator efficiency was performed considering its interaction with the vehicle, namely, heat supply and rejection waste and additional weight effect. A measuring test bench for collection of the information on the vehicle during movement and for testing of the generator mounted on it was developed. The information thus collected on temperature and exhaust gas thermal power enables the thermoelectric generator optimal designing for the certain class of a vehicle and its preferable operating mode.

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Research on Design Method for Degree of Hybridization of HEV Integrated with TEG

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The vehicle waste heat recovery based on thermoelectric technology has traded a new way to automotive energy saving and emission reduction. The muti-energy system integrated with thermoelectric generator iTEG jin hybrid vehicle will be the trend of the future. The current researches have primarily focused on the construction of TEG system which only aims at the energy harvesting in order to solve the problem of maximizing TEG's power-output . However, more efforts should be made on how to integrate TEG system on the hybrid vehicle so as to improve the power utilization of the muti-energy system. Aiming at a HEV with TEG , a design method of degree of hybridization iDOH j, mainly about the constraint, boundary conditions condition and calculator method on DOH was introduced. At last, a case study of hybrid SUV is provided by employing this method mentioned above and is proved to be rationally and effectively.

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Design and Evaluation on the Device Integrated by the Thermoelectric Generation and the Automotive Muffler

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Abstract: The thermoelectric generator (TEG) is one of the most effective technologies of the vehicle energy saving. In order to improve the compatibility between the TEG and the exhaust system, the design of the combination by TEG and the automotive muffler is imperative. Based on the performance requirement of the on-board automotive muffler and the TEG, the two kinds of projects have been proposed. The simulation analysis was used for evaluated the Thermal field performance and the sound field performance of the two kinds of project to find the advantage and disadvantage of both of them and come up with the better one. This work has provided the basis for the further research of the combination by TEG and the automotive muffler. Keywords: The thermoelectric generator, the automotive muffler, the design of the integrated device,simulation analysis

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Thermoelectric Inventions and European Patents

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The European Patent Office (EPO), the patent granting authority for Europe, grants patent rights in its 38 member states. By a single, centralised application process, an inventor can obtain Europe-wide patent rights.

The number of patent applications received in the field of thermoelectrics will be presented and analysed according to their technical content and geographical origin of the applicants.

A brief overview of recently patented thermoelectric inventions will also be presented.

In addition, it is pointed out that patent publications are freely accessible online and provide an invaluable, classified source of information for researchers in this technical field.

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Novel Process for Metal Silicide Nanostructures Regarding Cheap and Large Scale Material Synthesis

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Thermoelectric power generation presents a most promising and attractive way to utilize waste heat and to generate electricity in remote situations. Thanks to continuing technology development an outlook of converting a significant amount of waste energy comes within reach. The class of silicide materials is considered to be a sustainable and cost effective candidate for an application of thermo electrics. One approach to improve effectiveness of these materials is by nanostructuring. Nanostructured metal silicide can be obtained by using a rapid solidification technology (RGS, ribbon growth on substrate). This technology allows for low-cost and high throughput synthesis of silicide material. The possibility of this technology to control the microstructure offers the opportunity of optimizing the thermoelectric properties of the silicide. This paper describes the current status of development and validation process, as well as future perspectives for TE applications.

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Thermoelectric Properties of Mg_2Si-Mg_2Sn Solid Solution When Substituting the Magnesium

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In this work the effects of addition Zn, Cd and Ca instead of Mg atom on thermoelectric properties are investigated. Samples of $Mg_{2-x}A_xSi_ySn_{1-y}$ solid solution (A=Zn, Cd, Ca; x up to 4%, y=0 and 0.3) were prepared. Seebeck and Hall coefficients, electrical end thermal conductivity were measured from room temperature up to 700 K. Some parameters of band structure were calculated. It was shown that addition of isovalent atoms increase energy gap in Mg_2Sn compound, whereas there is no such effect in solid solution. 1% Cd, Zn and Cd addition leads to slight decrease of thermal conductivity. However, thermal conductivity increases with increasing the impurity atoms, and it becomes higher than that for the pure solid solution $Mg_2Si_ySn_{1-y}$ when Zn and Cd atoms exceed 2%.

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Structural Characterization and Thermoelectric Properties of Hot-Pressed CoSi Nanocomposite Materials

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Silicides have found widespread acceptance in semiconductor technology. They were suggested as potential thermoelectric materials by E.N. Nikitin with emphasis on MnSi, MnSi2, CrSi2, and CoSi. These compounds are mechanically and chemically strong and often can be used in hostile environments without any protection. The figure-of-merit of selected members was found to be high. In this work, CoSi is studied where nano-metal-oxides were incorporated aiming to fabricate nanocomposites. CoSi was prepared through solid state reaction, ground with the nano-metal-oxides and finally was sintered using hot press for the formation of the nanocomposites. The structural and morphological modifications were studied with Powder X-ray diffraction, Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy. The thermoelectric properties of CoSi nanocomposites were studied in terms of Seebeck coefficient, electrical and thermal conductivity at high temperature range (300-1000 K).

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The Effect of Ge on $Mg_2Si_{0.6-x}Sn_{0.4}Ge_x$ Materials

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Mg2Si-based alloys have attracted much attention as they are composed of cheap, abundant, and friendly (non toxic) raw materials, have a high figure of merit and the lowest density amongst all efficient thermoelectrics. Mg2Si1-xSnx has been found to be the most favorable in terms of thermoelectric energy conversion, while Bi-doped materials such as Mg2Si0.4Sn0.6 and Mg2Si0.55Sn0.4Ge0.05 exhibited ZT of 1.4. In this work, we investigate the influence of the introduction of Ge on the thermoelectric properties of the Bi- and Sb- doped quaternary Mg2Si0.6-xSn0.4Gex series with 0¡Ü x¡Ü0.4 were fabricated by a combination of ball milling and solid-state reaction method, followed by hot pressing. Structure and phase composition were studied by X-ray diffraction (XRD) and analyzed by applying Reitveld refinement. Morphology and chemical composition were monitored by Scanning Electron Microscopy equipped with Energy Dispersive X-ray Spectroscopy for elemental mapping. The thermoelectric properties are studied in terms of Hall Effect, Seebeck coefficient and electrical and thermal conductivity measurements. The Bi- and Sb-doped materials exhibit high ZT reaching, 1.4 and 1.3, respectively.

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Structural Properties of Ag/Mg_2Si Composites

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Magnesium silicide (Mg_2Si) and its solid solutions stand among the most prospective candidate materials suitable for thermoelectric energy conversion, due to a number of favorable properties such as high thermoelectric figure of merit (ZT), low density, high melting point, mechanical stability as well as its low-cost and environmentally friendly fabrication. Pure (Mg_2Si) is an indirect-bandgap semiconductor with less interesting thermoelectric properties. Therefore, a plethora of dopants has been proposed in order to improve its thermoelectric properties. Among these dopants, the most commonly applied are Sb and Bi for n-type materials. Recently, silver (Ag) has been suggested as convenient dopant for p-type materials [1]. So far, the literature lacks of detailed morphological/structural characterization of Ag-doped materials; this is attempted in the present study for the case of hot pressed pellets fabricated by self-propagating high-temperature synthesis (SHS) under argon. Dopant was introduced in two ways: (a) by mixing Ag_2CO_4 with Mg and Si elemental powders (in situ doping); (b) by mixing Ag_2CO_4 with the synthesized Mg_2Si powder before sintering (ex situ doping). Structural characterization was monitored by using Transmission Electron Microscopy of moderate and high resolution (TEM & HRTEM), Scanning Electron Microscopy (SEM) equipped with EDS analyzer, as well as conventional Fourier transform infrared spectroscopy (FTIR) in the reflectivity mode. For both doping processes, in SEM micrographs the presence of bright silver-rich spots in the matrix of hot pressed Mg_2Si is indicative. Spot EDS analysis on bright positions reveal the presence of both Ag and Mg suggesting the possible formation of AgMg intermetallic precipitates instead of elemental Ag. This result is also heavily supported by the fitted FTIR spectra adopting the concept of effective, or macroscopic dielectric constant $å_{eff}$ and the approximation of Landau-Lifshitz-Looyenga [2 and references therein]. The presence of stoichiometric magnesium silicide [3], magnesium oxide and intermetallic Ag/Mg compound was identified while each volume fraction was calculated. The TEM diffraction patterns also support the aforementioned result. Finally, doping in-homogeneities were monitored by applying a micro Seebeck hot probe scanning procedure resulting in detection of spatial compositional variations that affect the dopant concentration.

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Formation of Thermoelectric Candidate Chromium Silicide by Pack Cementation Process

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Transition-metal (TM) silicides are reported as good candidates for thermoelectric applications due to their thermal and structural stability, high electrical conductivity and thermoelectric power at elevated temperature. Moreover, in most cases their constituent elements are abundant which decrease the cost of fabrication. Chromium disilicide (CrSi2) is a narrow-gap semiconductor with band gap of 0.30 eV and is referred as a potential p-type thermoelectric (TE) material because it exhibits high-temperature. The most frequently used techniques for the formation of thermoelectric silicides, are magnetron spattering, RF-plasma and ball milling in

inert atmosphere. Most of these techniques are highly sophisticated or the equipment apparatus has increased cost. Chemical vapor deposition by pack cementation process is a simple and costless technique, for the formation of aluminium, chromium, silicon and zinc coatings. The process was recently applied for the synthesis of thermoelectric compounds, such as Mg2Si. The aim of this work is to form transition chromium silicides and for this reason Si wafer pieces were placed in sealed porcelain crucibles filled with a powder mixture of the donor material and the halide activator and heated to 1000oC in Ar atmosphere. Results showed that at first step Cr3Si phase was formed and on a second step Cr3Si samples were siliconized with the same technique at 1050oC for 2h. The final product was pure CrSi2 phase. SEM/EDS, XRD and IR studies were performed for the phase identification while the thermal stability was evaluated by TG measurements.

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A Study on Magnesium Oxide Uptake in Mg_2Si-Based Materials

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The magnesium silicides (Mg2Si) based alloys are promising candidates for thermoelectric (TE) energy conversion in the middle-high temperature range. These materials are a candidate to replace lead-based TE materials thanks to the abundance of their constituent elements in the earth's crust, their nontoxicity and their low density.
One of the main hindrances to Mg2Si use is its tendency to oxidation. It is well known that careful procedures have to be employed in order to produce MgO free pellets. Furthermore both doping elements and pellets density play an important role to prevent a dramatic degradation of these materials at high temperature. In this work the influence of the synthesis procedures and conditions on the MgO amount and its effect on the thermoelectrical properties are discussed. Structural and morphologic characterizations, obtained by X-Ray diffraction analyses and scanning electron microscope, are reported, together with Seebeck coefficient analyses and electrical and thermal conductivity measurements. Furthermore, a study on the stability of magnesium silicide based materials has been performed by thermogravimetric analyses of doped Mg2Si powders and pellets with different densities and under different atmospheres. Some ageing tests at intermediate temperature are also reported.

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Synthesis and Thermoelectric Characterization of Type-I $Ba_8Ga_{16}Ge_{30}$ and Type-VIII $Ba_8Ga_{16-x}Cu_xSn_{30}$ Clathrates Thin Film

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Intermetallic clathrate compounds have become recent object of study as thermoelectric materials, important because of the environmental preservation and energy conservation issues. The purpose of this work is to grow p-type and n-type single crystals of type I Ba8Ga16Ge30 by a self-flux method using excess Ga and single crystals of type-VIII clathrate Ba8Ga16-xCuxSn30 (x=0,03; 0,06 e 0,15) with p- and n-type carriers grown from Ga flux and Sn flux, respectively. The single crystals Ba8Ga16Ge30 and Ba8Ga16-xCuxSn30 were used as targets for deposition of thin films. Clathrates thin films have been prepared on silicon (1 0 0) substrates by physical vapour deposition (PVD) techniques. The layer structure in the as-deposited films was confirmed by X-ray diffraction (XRD) and the microstructures analyzed by scanning electron microscopy (SEM). In addition, the surface morphology and the roughness of the deposited clathrates thin films were characterized by atomic force microscopy (AFM). Efficient thermoelectric materials must have low electrical resistivity, low thermal conductivity and a large Seebeck coefficient. The thin films were thermoelectrically characterized with electrical resistivity and thermopower measurements as functions of temperature, which showed strong microstructure-dependent behaviors. The relationship between morphologies and transport properties of the thin films was explored. We analyze the combined results of Seebeck coefficients, electrical resistivities and Hall effects for the deposited clathrate thin films in comparison with the single crystals.

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Study of Host-atoms Substitution Effects for Electronic Structure and Thermoelectric Properties on Sn-based Clathrates

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Tin based semiconducting clathrates Ba-Ga-Sn are caged materials with the type-8 structure, and those materials have good thermoelectric properties due to low thermal lattice conductivities like glasses. [1] In addition, by guest atoms substitution for Ba-Ga-Sn clathrates it has been reported that carrier mobility of electrons and thermometric figure of merit ZT was enhanced. [2] On the other hand, for p-type cases the mobility is low and it is an issue to be increase of ZT. Recently, the ZT enhancement in p-type polycrystalline and single

crystalline samples was reported by Ge substitution, respectively. [3,4] In the present study we study the substitution effects for electronic structures and thermoelectric properties based on the calculated band structure.

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Thermoelectric Properties of Hot-Pressed $K_2Bi_{8-x}Sb_xSe_{13}$ Materials

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Alkali bismuth chalcogenides are promising for thermoelectric applications as suggested by previous works. The K2Bi8Se13 compounds were grown from melt as polycrystalline ingots or from Bridgman technique as highly-oriented polycrystalline ingots. However, even if high ZT is achieved, the mechanical properties of such ingots can be major problem on the thermoelectric devices assembly. Powder techniques have been recently applied on K2Bi8Se13-xSx series in order to fabricate, for the first time, hot pressed pellets. The pellets had high density and performed ZT of about 0.5 at 800K. In this work, we apply powder techniques on the Sb-series, where hot-pressed pellets of K2Bi8-xSbxSe13 are fabricated. The hot pressing conditions were selected based on the previously applied statistical Design of Experiments optimization approach. The effect of the sintering process and the Sb concentration on the thermoelectric properties of the series is discussed.

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Hybrid Si/AlO_x Thin Films of the Electron Crystal-Phonon Glass Type as a Thermoelectric Material

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Thermoelectric materials require for high ZT values a low thermal conductivity, as indicated in phonon glasses. On the other hand, a high electrical conductivity is required. A thermoelectric material is effective, if it is of the electron crystal-phonon glass type. Hybrid materials enable the research on nontoxic, cheap and common materials with a good thermoelectric performance. We studied the structural and thermoelectric properties of silicon particles formed in an aluminum oxide matrix. The samples were synthesized by means of a physicochemical process. A thin film of aluminum has been deposited on different glass substrates followed by a thermal annealing step in argon atmosphere. Silicon oxide reduces during the heat treatment to silicon, whereas the aluminum is oxidized. For annealing temperatures between 540°C and 600°C, the size, shape and distribution of the silicon particles was found to be interesting for thermoelectric applications. We present the structural chararacterization of hybrid Si/AlO_x films along with measurements of the electrical and thermal conductivity.

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Thermoelectric Properties of $Cu_2HgSnSe_4$-$Cu_2HgSnTe_4$ Solid Solutions

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Copper-based semiconductors of the family Cu2-II-IV-VI4 have attracted recently a great deal of attention because of their promising thermoelectric properties. Polycrystalline samples of Cu2HgSnSe(x)Te(4-x) (x=0,0.8,2,3.2,4) solid solutions were prepared. The phase purity of the prepared samples was checked by means of powder x-ray diffractiction. Transport, thermoelectric and thermal properties of hot-pressed samples were characterized.

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Anisotropic Thermopower of the Kondo Insulator $CeRu_4Sn_6$

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Kondo insulators are materials in which an energy gap in the electronic density of states (DOS) opens at the Fermi level as a consequence of strong electronic correlations. The gap arises from a half-filled conduction band hybridized with the almost localized f-levels (c-f hybridization). The gap width of Kondo insulators is typically of the order of 1 to 10 meV [1].

A particularly interesting situation arises when the c-f hybridization is strongly anisotropic or develops nodes along certain directions in k space [2, 3]. The tetragonal compound $CeRu_4Sn_6$ shows pronounced anisotropy between the crystallographic c axis and the directions within the tetragonal plane (a and c' directions) [4,5]: characteristics of a Kondo insulator are seen within the tetragonal plane but heavy fermion behaviour dominates along the c axis [5].

Thermopower and Nernst effect are extremely sensitive to details in the electronic DOS close to the Fermi level. Thus, measurements on single crystals along different crystallographic axes may shed light on the underlying electronic correlation phenomena. Here we present our investigations of the thermoelectric properties of single crystalline $CeRu_4Sn_6$ at low temperatures and under magnetic fields. Our aim is to reveal the topology of the Fermi surface and its relation to the anisotropy of the energy gap.

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Metallurgical and Thermoelectric Properties in $Co_{1-x}Pd_xSb_3$ and $Co_{1-x}NixSb_3$ Revisited

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Because of their simplicity, the $Co_{1-x}M_xSb_3$ (M = Ni, Pd) skutterudites have often been considered as candidates for nanostructuring with the objective of reducing their lattice thermal conductivity. It is important to know in detail these systems to choose the composition corresponding to the largest power factor, prior to any nanostructuring operation. We thus re-examined their metallurgy and electronic transport properties. Pollycristalline samples have been synthesized by melting, annealing, and spark plasma sintering. The solubility limit of Pd and Ni are determined to be respectively $x_{max} = 0.03$ and $x_{max} = 0.09$. The density of states effective masses range between 2.0 m_0 and 4 m_0 in both systems. These values are consistent with the effective band mass ($0.3m_0$) and the degeneracy number $N_v = 36$ derived from band structure calculations. Power factor measurements and calculations in $Co_{1-x}Pd_xSb_3$ show that at 300K, the optimum electron concentration would be $[n]_{opt} = 1.4 \times 10^{20}$ cm^{-3}, slightly beyond the electron concentration (1.1×10^{20} cm^{-3}) of the solubility limit composition $Co_{0.97}Pd_{0.03}Sb_3$. The maximum power factor is effectively obtained for the composition $Co_{0.97}Pd_{0.03}Sb_3$ and reaches 4.3 mW m^{-1} K^{-2} at 700 K. An activation energy, which can correspond to the intrinsic gap $\varepsilon_G = 0.13$ eV, is determined in $Co_{0.98}Ni_{0.02}Sb_3$. $Co_{1-x}Ni_xSb_3$ displays smaller electronic mobilities than $Co_{1-x}Pd_xSb_3$ leading to smaller power factors. Best properties (3.4 mW m^{-1} K^{-2}) are observed at 700K in $Co_{0.95}Ni_{0.05}Sb_3$ - $Co_{0.94}Ni_{0.06}Sb_3$.

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Effect of Te Substitution on the Thermoelectric Properties of $Ag_{3.8}Mo_9Se_{11-y}Te_y$ Compounds

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Currently, there is a resurgence of interest in thermoelectric materials with enhanced efficiency. Among investigated classes of bulk thermoelectrics such as partially filled-skutterudites, Zn4Sb3-based materials or clathrates, novel polycrystalline Mo9 cluster-based chalcogenides were reported recently. Among those, AgxMo9Se11 (with $3.4 \leq x \leq 3.9$) compounds have shown interesting thermoelectric properties compared to Chevrel phases based on Mo6Se8. AgxMo9Se11 materials possess a complex crystallographic structure, built up by stacking Mo9Se11 units, leaving Chevrel-phase like channels accommodating Ag atoms. In this paper, we describe the synthesis route we used to prepare quaternary Ag-Mo-Se-Te compositions and involving a combination of powder metallurgy and spark plasma sintering techniques. Physical and chemical characterizations were performed by means of X-ray diffraction, scanning electron microscopy analysis,

electrical and thermal measurements. The results obtained with compounds Ag3.8Mo9Se11-yTey (with 0 ≤ y ≤ 0.75) are discussed and compared to the parent ternary compound Ag3.8Mo9Se11 in the temperature range 300 - 800 K.

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Commercial, High Through-put Skutterudites of High ZT and TE Efficiency

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During the development of highly efficient p- and n-type skutterudites under laboratory conditions, high ZT values (ZT=1.2 for didymium filled Fe/Co substituted skutterudites and ZT=1.4 for multi-filled Sb-based n-type skutterudites) were obtained. These ZT values were further increased to 1.4 and 1.9, respectively, by nano-structuring via high-energy ball milling and/or severe plastic deformation introduced by high-pressure torsion (HPT).
Commercial production of skutterudite materials with high ZTs and high thermal-electric conversion efficiencies for applications requests fast and reproducible methods. Such materials are already available on the market from Treibacher Industrie AG and they exhibit ZT=1.0±0.1 and ZT=1.2±0.1 for p- and n-type, respectively, which we will show in this presentation.

Furthermore we will demonstrate how the figure of merit of these commercial materials can be further improved (up to 30%) by nano-structuring and/or HPT.

Research from the Austrian Christian Doppler Laboratory (CDL) for Thermoelectric Research.

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Effect of Structure and Microstructure on the Thermoelectric Properties of $Yb_{0.19}Co_4Sb_{12}$ Alloy

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In this work, we report results about the synthesis and characterization of the n-type Yb0.19Co4Sb12 thermoelectric (TE) alloy that is among the most promising materials for automotive applications with a value of ZT ranging around 1 at 600 K [1]. Samples were prepared in a BN coated quartz crucible with a sequence of three steps: 1) a solid/liquid reaction between the pure elements at 780°C in a resistance furnace; 2) complete melting in an induction furnace; 3) annealing at 850°C in a resistance furnace for 0.75h, 1.5h, 3h and 6h. A small excess of Sb (about 3%) was added in order to compensate the loss of this element due to evaporation during the thermal treatments. Microstructure and phase composition were investigated by scanning electron microscopy (SEM) equipped with an energy dispersion spectroscopy (EDS) microprobe. Structural analysis was performed by powder X-ray diffraction (XRD). Electrical conductivity (σ) was measured with the four-probe method. The Seebeck coefficient (α) was obtained from the relationship $\alpha = \alpha_{wires} - (\Delta V/\Delta T)$, where α_{wires} represents Seebeck coefficient of the thermocouple wires, ΔV is the measured potential difference and ΔT is the applied temperature difference. Thermal conductivity (k) was determined using the Fourier's law, $Q = (\Delta T \cdot k \cdot S)/l$, where Q is the heat flow, S and l are the section area and the length of the sample, respectively. AISI 304 steel, thermally connected in series with respect to the sample, was used as a reference standard.
The non-annealed samples consist of a mixture of Sb, YbSb2, CoSb, CoSb2 and CoSb3. Only a fraction (about 50%) of the thermodynamically stable Yb0.19Co4Sb12 phase could be obtained by free cooling of the melt. This is due to the complex solidification path, involving two peritectic and one eutectic transformations, that does not allow the system to reach the equilibrium. Annealing at 850°C promotes the formation of the desired CoSb3-type phase up to fractions between 95% and 98%, as a consequence of the faster diffusion. Concerning TE properties, annealing brought, as expected, to a decrease of α and k because of the higher fraction of the Yb0.19Co4Sb12 phase. Unexpectedly, also σ decreases after annealing, likely because of the formation of pores as a consequence of Sb evaporation.
The combination of TE parameters results in an increases of ZT with increasing annealing time. The values of ZT, obtained at room temperature for the samples containing 95-98% CoSb3, range between 0.14 and 0.18.

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Phase Selection and Microstructure Refinement of Melt-Spun Zn_4Sb_3-type Compound

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Zintl phases show thermoelectric (TE) properties close to the skutterudites ones: the mechanism involved in their efficiency is related to efficient carriers doping and disordered structures [1]. The Zn4Sb3 phase is considered one of the most interesting compounds for TE application inside the Zintl phases family due to its very low thermal conductivity [2]. Despite of the mechanical brittleness, Zn4Sb3 has attracted much attention for its TE application in the intermediate temperature range (400-600 K). Typical processing routes of this material for technological applications require several steps, in order to obtain an homogeneous single phase with fine microstructure [3]. In fact, it is well known that phonon contribution to thermal conductivity can be significantly depressed increasing the grain boundaries density, leading to a higher figure of merit ZT.

Among the preparation techniques used for improving structural homogenization and microstructure refinement, rapid solidification has the advantage of being fast and reducing contamination from the working atmosphere.
In this study, the effect of rapid solidification on the phase stability and microstructure of pure and Al- and Ag- doped Zn4Sb3 was investigated.

Zn4Sb3, Zn3.96Al0.04Sb3 and Zn3.96Ag0.04Sb3 bulk compounds were obtained by a solid state synthesis using a muffle furnace. Subsequently, rapidly solidified samples in form of small flakes were obtained by melt spinning. All the sample were studied in terms of crystal structure by X-ray diffraction (XRD), morphology and phase composition by scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS), respectively, and thermal stability by differential scanning calorimetry (DSC).
All the bulk samples are characterized by the Zn4Sb3-type single phase.

Melt spun flakes show, on the one hand, other crystalline phases in addition to the expected Zn4Sb3-type phase, probably because the high cooling rate did not allow the system to reach the thermodynamic equilibrium. On the other hand, rapid solidification induced a remarkable decrease of crystallites size down to the limit of the nanoscale, as estimated by the peak broadening in the XRD patterns. Additionally, the presence of an irreversible exothermic peak in the DSC trace can be likely related to the crystallization of a small amount of amorphous phase, formed because of the high cooling rate, that could not be detected by XRD.

The results suggest that melt spun flakes can be used as a starting material in the subsequent compaction steps [5].

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Electrical Characterization of Ni(Ge-Sn-Si) Nanowires for Thermoelectric Application

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In this study, the electrical properties of Ni(Ge-Sn-Si) nanowires for thermoelectric application have been investigated. The purpose of preparing such materials was mainly to reduce the contact resistance of the wires, where the electrical and thermal conductance was tailored by the size of wires, their composition and formed Ni phases. More attention was paid to relate these properties to ZT, which is the figure-of-merit for thermoelectric materials.

Strained or relaxed Ge1-x-ySnxSiy ($0.01 \le x \le 0.10$ and $0 \le y \le 0.30$) epi-layers were grown at low temperatures on SOI substrates by RPCVD technique. The strain in these layers was controlled by material composition and/or a buffer layer on the Si substrates.
The nanowires were fabricated through a CMOS compatible process comprising I-line lithography and dry-etching. Ni was deposited either on the whole nanowires or only the contact areas. The wires went through rapid thermal annealing at 400 to 600 °C for 30s in N2 ambient. The phase formation of Ni(GeSnSi) layers was examined by x-ray diffraction (XRD) and the residual strain (both parallel and perpendicular to the growth direction) also measured by high-resolution reciprocal lattice mapping

(HRRLM). The surface morphology and the layer thickness were revealed by scanning electron microscopy (SEM). The transmission electron microscopy (TEM) was used to observe the defects in the formed layers. The formation and thermal stability of Ni(GeSnSi) was strongly dependent on the Sn content in GeSnSi alloys. The thermal stability is discussed in terms of strain and layer quality. When the Sn content is high (above ~6%) the epi-layers suffer from Sn segregation. The Sn-rich surface impedes remarkably the Ni diffusion. In the last step, thin Pt/Ti electrodes were fabricated and electrical conductivity was measured. The results of this work provide an understanding of how Ni interacts with GeSnSi materials and how GeSnSi nanowires can be designed to increase ZT for thermoelectric devices in future.

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Nanovoid Formation and Dynamics in He^+-Implanted Nanocrystalline Silicon

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Helium implantation in single crystal silicon is known to lead, after a proper thermal treatment, to the formation of mesovoids with diameters ranging between 10 and 30 nm [1−3]. Formation of mesovoids is governed by the coalescence of vacancies created by implantation, initially trapping helium atoms. At high temperatures (≥700 °C) helium leaves the nanobubbles and outdiffuses, while the now empty voids grow up in size and eventually change their shape to form tetrakaidecahedra (Wulff construction).

In this communication we report how He^+ implantation in heavily boron or phosphorus doped nanocrystalline silicon shows a completely different dynamics. Annealing to 500 °C leads to the formation of large voids, located around gran boundaries, along with a large number of nanocavities with an average diameter of 2 nm and an estimated density of $2x10^{19}$ void/cm^3 distributed throughout the grains. Further annealing (up to 1000 °C) induces a decrease of the nanovoid size (but no observable changes in their uniform distribution) due to evaporation up to a depth of 80−100 nm from the outer surface; and to the migration of vacancies toward the larger voids located at grain boundaries. The possibility of obtaining a stable, uniform distribution of nanometer-sized voids is of major relevance as a novel tool for phonon and electron engineering in thermoelectric materials. Expected effects on the power factor and on the thermal conductivity will be discussed.

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Bismuth Nanotubes Included in $Bi_{1-x}Sb_x$ Alloys and their Thermoelectric Characterization

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The aim of this work is the synthesis of bismuth nanotubes (BiNT´s) and the inclusion of these in Bi1 xSbx – nanoalloys, as well as the thermoelectric characterization of the alloy-nanotube composites. The nano sized tubular bismuth structures were synthetized through a transformation of a β – BiI precursor with a n – BuLi solution. The corresponding nanoalloys, acting as a matrix material, were produced by ball milling. In those alloys different quantities of nanotubes were included, resulting in three series: an alloy series without inclusions and two series with BiNT´s contents of 3 and 5 percent. The bulk powder was milled under argon atmosphere for 20 hours at 450 rpm and with a ball-to-powder ratio of 7.5:1. After the synthesis the thermoelectric and structural properties were characterized, revealing a decrease in thermal conductivity in alloys including BiNT´s up to 40 % in comparison to inclusion - free alloys due to the enhanced phonon scattering. The Seebeck-effect efficiency became optimized simultaneously.

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CMOS Compatible Planar Thermoelectric Microgenerator Based on Thin Si Membranes

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Nanostructured semiconductors offer a promising route towards the fabrication of miniature chip-based TE devices. In particular, Si has emerged as a potential TE candidate since the discovery that small diameter NWs conduct heat like a disordered solid, maintaining reasonable values for both electrical conductivity and

Seebeck coefficient. In this context, the fabrication of miniature chips formed by Si NWs arrays may yield efficient conversion devices. While bottom-up strategies for the synthesis of NWs allow the realization of highly-dense large-area arrays of NWs, they often lack enough reproducibility. Here, we present a planar TE microgenerator based on an ultrathin Si membrane with a high-density of n, p regions that can work up to T ~ 400°C. To obtain the appropriate doping level we carried out detailed TRIM simulations and multiple implantation and annealing experiments. Doping levels in the range of 1-5x1019 at/cm3 both in n and p-type regions are obtained and epitaxial re-crystallization of the 100 nm thick Si layer is reached during post-implantation thermal treatments. Suitable electrical contact resistances, i.e. 1.7x10-6 Ωcm2, were achieved by using 50-100 nm Ni thin layers and post-deposition annealing. Several devices with ultrathin membranes and microribbons (2µm width and 100 µm long) have been tested. Power efficiencies of 5 µW/cm2 under temperature differences of 5 K are currently achieved in non-optimized devices.

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Data Analysis for Seebeck Coefficient Measurements

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The Seebeck coefficient is one of the key characteristics of a thermoelectric material and is routinely measured in several laboratories. There are, however, several ways to extract the Seebeck coefficient from the raw measurement data. We will present details about the data analysis of Seebeck measurements as well as consistency checks and tools to check and increase the trustworthiness of the obtained results. Using a custom-build system as exemplary setup we have performed a thorough analysis of the data obtained from quasi-stationary measurements. Comparing different, physically equivalent, equations to calculate the Seebeck coefficient from measured voltages and temperatures one easily finds that equations based on a single reading of voltages/temperatures can lead to erroneous results as they are affected by spurious voltages inherent to all measurement systems. If repeated measurements are obtained in a variable temperature gradient we can experimentally show excellent agreement between three redundant approaches to evaluate the Seebeck coefficient in one and the same setup. This, however, holds only true if the analysis is not based on the internal voltage to temperature conversion of the employed digital multimeter. Another point that is important for precise non-stationary Seebeck measurements is the simultaneous acquisition of the measured temperatures and voltages. If an exactly equitemporal reading is not feasible we show that data interpolation over time is reliable to obtain correct results by avoiding uncertainties in the lower percentage range. Finally we discuss several indicators that can be used to evaluate the trustworthiness of the data or indicate experimental deficiencies. These are the linear correlation coefficient of the linear fits used to calculate the Seebeck coefficient, the offset of these fits, the agreement between different redundant equations to calculate the Seebeck coefficient and the two-point resistances of the different measurement loops.

In recent years there have been considerable efforts to increase the quality of thermo-electric measurements in general and in the Seebeck coefficient measurements in particular. Many problems are hardware-related and are addressed in other publications. However, several problems can also be identified and monitored by a thorough data analysis which increases the accuracy and the trustworthiness of the obtained measurement results. This in turn is indispensable for efficient optimization of thermoelectric materials and their application.

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Simultaneous Measurements of Seebeck Coefficient and Electrical Conductivity up to 860 K

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The European metrology organization (EURAMET) opened a call in 2009 to advance measurement science and technology in the field of Energy [1] by providing funding for Joint Research Projects. The project "Metrology for Energy Harvesting" started in September 2010 and had a scheduled end in 2013. In the frame of this project, Physikalisch-Technische Bundesanstalt, PTB, was assigned to provide reference materials for Seebeck coefficients of thermoelectric bulk materials in the temperature range from 300 K to 860 K.

The performance of a thermoelectric material scales with the thermoelectric figure of merit (ZT) of the active material, which is defined as $ZT = S2\delta T/_{k}$, with S, δ, $_{k}$ and T are the Seebeck coefficient, the electrical conductivity, the thermal conductivity, and the absolute temperature, respectively. The simultaneous measurement of the Seebeck coefficient and the electrical conductivity enables to calculate the so called power factor (PF = S2δ) in one step. Therefore this results in lower uncertainties of PF other than if S and δ are measured separately.

The paper describes the measuring system which is used to calculate PF on basis of the simultaneously measured

quantities S and δ [2-4], and the four probe method to determine the electrical conductivity δ in particular. The power factors are given for the both reference materials for Seebeck coefficients, ISOTAN® and bismuth-doped lead telluride (PbTe) (Fig. 1), which were certified by PTB in the frame of this project.

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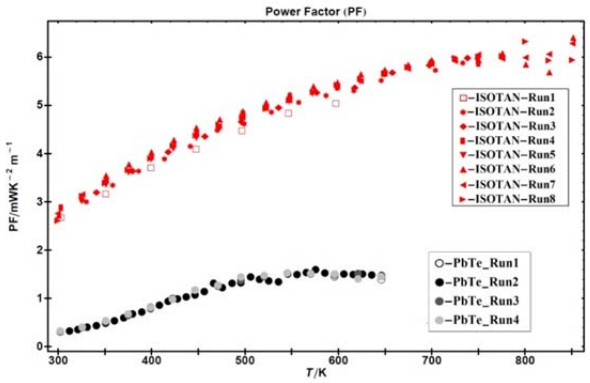

Fig. 1: Power factor (PF) of the reference materials for Seebeck coefficients ISOTAN® and bismuth-doped lead telluride.

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Methodology and Implementation of Electrical Contact Resistance Measurement

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In recent years, a lot of progress was made in terms of improving the performance of thermoelectric materials. However, in order to be able to convert heat into electrical power it is essential to have a contacting technology which guarantees minimum ohmic contact resistances at the interface between the thermoelectric material and the electrodes. Furthermore the electrical contacts have to be long term stable under the influence of large temperature variations. For the support of the development of thermoelectric module contacting technologies, Fraunhofer IPM has developed an automated contact measurement setup which is capable of performing a two-dimensional mapping of the electrical resistances of a sample. The performance of this measurement setup is demonstrated for different thermoelectric samples like thin composite thermoelectric wafers and sintered contacts.

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Investigations on Novel Thermoelectric Materials Using a High Temperature Hall-Measurement-Setup

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Novel thermoelectric materials especially for medium and high temperature application are in the focus for waste heat recovering systems not only in automotive applications. Beside the accurate determination of all thermoelectric properties and thereby the ZT-value, a detailed understanding of the processes inside the materials is needed. Hall-measurements are the well-known tool to investigate carrier concentration and mobility within metals, semiconductors and of course thermoelectric materials. Up to now, most commercial setups are only suitable for temperatures up to 400°C. The full characterization of high temperature materials like Oxides or Silicides require measurement temperatures of 600°C and above. Therefore Fraunhofer IPM developed a high temperature Hall-measurement-setup which allows measurements in this range. We will present first high temperature measurements on different materials and sample geometries performed with our new IPM-HT-Hall setup.

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A Platform for the Characterization of Thermoelectric Properties of Nanowires

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For determining all three thermoelectric quantities, the Seebeck coefficient S, the electrical conductivity σ, and the thermal conductivity κ, of a single nanowire, a measurement platform has been developed that combines the advantages of the two setups in [1] and [2]. On the one hand, a single nanowire is truly suspended between two 180 nm thin silicon nitride membrane islands that themselves are suspended by 200 µm long beams; on the other hand, thermometers are directly attached to the nanowire, serving as voltage probes of its four-probe resistance measurement at the same time.

The fabrication process involves dry etching and anisotropic KOH wet etching on the back side of the substrate. Contact pads are defined by photolithography, and leads, heaters, and electrodes are defined by electron beam lithography, as is the final etch mask that defines the islands and their supporting beams.

A nanowire is then positioned onto our platform with a micromanipulator inside a dual focussed ion beam/scanning electron microscopy instrument. An additional advantage of our setup is the possibility to investigate by transmission electron microscopy the very same nanowire that is measured.

We acknowledge financial support from the Austrian Science Fund (FWF project I623-N16).

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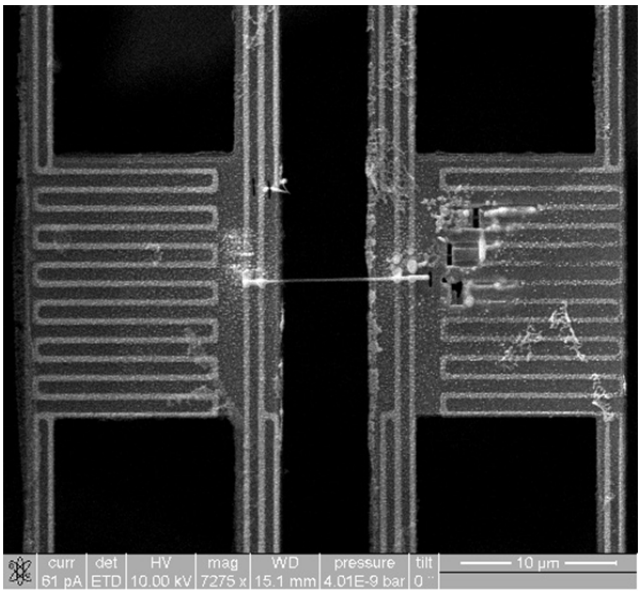

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Characterisation of Thermoelectric Generators: Impact Factors on the Accuracy of the Reference Principle for Heat Flow Determination and Current State of the International Round Robin Campaign

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Thermoelectric materials convert thermal energy directly into electrical energy, without the loop of performing mechanical work in between and with high durability. Hence, thermoelectric energy conversion becomes continuously more import for energy recuperation applications, especially within the temperature range between 300 K to 1000 K. Due to different continuing difficulties measurement errors distinctly higher than 15 % can be observed repeatedly during characterisation of thermoelectric generators (TEG), which is still too high for an industrial benchmark and deficient for many scientific investigations and technological developments. We describe main methodical and practical influences on the accuracy of the favoured TEG efficiency determination employing a reference principle. Collateral experiments, performed by use of thermal reference materials, and results from comprehensive finite element modelling (FEM) shall provide an indication of typical error levels during determination of incident heat flow, effective temperature differences and heat flow density at a TEG for varying measurement conditions. As described earlier [1], the TESt-project addresses the development of an absolute heat flow measurement in order to achieve a traceable metrology for TEG, by employing a guarded hot plate method (GHP) as an alternative to the conventional reference principle. Results obtained from finite element modelling assisted parametric studies on a design concept of a GHP-apparatus shall demonstrate the enhanced accuracy and give proof of the effectiveness of active thermal guarding for TEG characterisation. Furthermore an international Round Robin (RR) campaign for TEG metrology was started within the framework of the TESt-project. A set of two samples will be send to 18 laboratories in order to investigate the applicability for the use as standard reference samples and for the reflection of current measurement uncertainties during TEG characterisation. In this context we will present measurement data of the ongoing RR test, which was obtained so far.

Acknowledgments: The authors thank the German Federal Ministry of Education and Research for funding the TESt-project at the Institute of Materials Research of the German Aerospace Center (Grant: 03X3550B).

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High Resolution Neutron Spectroscopy and Ab Initio Powder Averaged Lattice Dynamics Calculations: Complementary Tools for the Study of Complex Functional Materials

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Advanced functionalized materials become progressively vital to our everyday life and indispensable to industrial engineering, energy supply and sustainability, healthcare, environment as well as life sciences. The development of novel materials with tailored macroscopic properties and optimized performance calls for a comprehensive understanding of chemical and physical principles underlying the material properties which can be only accomplished at the microscopic level through careful experimental, simulation, and theoretical studies. Neutron scattering experiments - probing the structure and dynamics on a nanometer and Tera-Hertz scales - and ab initio calculations - sampling microscopic characteristics by approximating the electronic structure - are the tools of choice to tackle this challenge.

The fundamental obstacle for a comprehensive study of advanced functionalized materials is their easy formation in polycrystalline form. Consequently, any deeper understanding of the complex physics requires dedicated computation of powder averaged spectra and thence powder averaged lattice dynamics (PALD) calculations. We discuss some examples of functionalized materials and the experimental and computational approaches we apply and combine to study polycrystalline matter. We focus on materials supposed to be suitable for energy conversion for thermoelectric applications. The combination of ab initio PALD calculations with high quality inelastic neutron scattering results from polycrystalline matter is however a generic approach becoming progressively attractive with increasing computation power and improved performance of neutron spectrometers.

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Characterisation of a Thermoelectric Heat Pump

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Various applications of thermoelectric devices as heat pumps have been shown in the literature, however these have primarily focused on their maximum cooling ability. The efficiency of the thermoelectric device has only recently become the focus of work in the field. In this paper a method of measuring the performance of the thermoelectric device in heat pumping mode is presented, the device's underlying physics is explained briefly and a test system is described.

Thermoelectric heat pumps operate by driving a current through the n-type and p-type semiconductor materials of the device and exploiting the Peltier effect. The amount of thermal energy transported across the device is proportional to the current flowing and the polarity of the temperature difference determines the direction in which heat is pumped.

This paper presents an innovative measurement system that evaluates the performance and characteristics of a heat pump. Traditional heat pumps are tested in a similar fashion to refrigerators where the chamber temperature is of paramount importance, this system implements a controllable heat source isolated from the environment and allows the amount of thermal energy emitted to be measured.

The system comprises a labyrinth heat exchanger to remove thermal energy and an electrical heater to provide the input thermal energy. Temperature is measured on both faces of the TE module as well as in the entry and exit of the labyrinth heat exchanger. Full control of all system parameters, including the clamping force, is under computer control with a specially written programme that automates the measurement.

The test system presented aims to characterise a thermoelectric heat pump at various temperature differentials and input powers. The coefficient of performance is calculated and shows the device's efficiency at transporting thermal power. The aim is to produce a set of curves that describe the device coefficient of performance in heat pumping mode over a range of operating conditions.

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Energy Harvesting for Low Power Demands on Space Systems: Thermoelectric Generators Under Extreme Environments

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To provide some efforts in closing the gap between recent improvements in material science of thermoelectrics and the integration into potential applications, TU Dresden investigates the application of commercial miniaturized

TEGs for the use in space with out radioistopic decay as heat source (no RTGs) - within the scope of a project funded by the German Space Agency DLR, support code 50RM1114. On the ICT conference 2013 in Kobe, Japan, the working group presented already a detailed system study for the use of TEGs on communication satellites to generate power for the communication between a failed satellite and a service orbiter (von Lucowicz, Schmiel, Rosenfeld, Tajmar). As the next important step straight forward, this paper and its presentation as foreseen for the ECT conference at ESA ESTEC combine both, the investigation (analysis and test) of miniaturized thermoelectric generators (TEGs) for space application concerning operational, mechanical, thermal and environmental aspects, and the development steps necessary for a space proved TEG system on board of future satellites. TEGs without RTGs are supposed to be attractive concerning moderate temperature levels and gradients. External and internal thermal heat loads, especially electronic devices, induce high heat flows within the spacecraft. This thermal energy is emitted to space unused via radiators so far. Using this available waste heat is promising for autonomous supply of low-power-loads, although the efficiency of TEGs is expected to be low. Radiation and vacuum conditions as well as thermal cycling and extreme vibrations during launch make high demands on thermoelectric devices, integration and power management. Furthermore, the system design has to ensure high reliability over the entire duration of operation. In order to evaluate the potential of space applications extensive analysis and tests regarding TEG-characteristics are essential. Since the datasheets of commercial TEGs are terrestrial oriented, they are insufficient and inconsistent for space applications. Especially thermal and electrical characteristics have to be identified for various thermoelectric devices in detail. Hence, the working group developed a test bed in order to prepare the design of a technology demonstrator, applied e.g. on pico- or nano-satellites. The first space demonstrator will be launched on the SOMP2 satellite.

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New Technologies of Modules for Space Applications

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The paper presents the results of creation of new technologies for space-purpose thermoelectric devices: film radiation detectors, film solar generators, cooling modules. Detectors based on high-performance films prepared by ion-plasma sputtering of thermoelectric materials of optimized composition have been developed for orientation systems of low-altitude satellites by the horizon line. To form the legs layout, lift-off photolithography method with selective etching of thermoelectric materials has been elaborated. The detectors possess volt-watt sensitivity 150 V/W and detectability 8o10^{8} cm·Hz$^{1/2}$· W^{-1}.

The same technologies were employed when creating film batteries for space solar generators. Two-year testing of prototype under open space conditions has shown its resistance to space radiation exposure. Such batteries are of interest for future developments of high-power solar electric stations, sources of energy for ion-plasma engines of solar sail spacecrafts.

Technology of producing thermoelectric materials for space-purpose cooling modules assuring increased shock resistance of stage modules has been developed. New technologies of creating particularly reliable contacts of thermoelectric material to connecting plates have been elaborated. To increase the reliability of modules, the method for redundancy with passive elements built into ceramic thermal spreaders has been developed. The method for redundancy with thin-film metal spirals deposited on the surface of legs has been created as well. Developed with employment of new technologies, stage modules with shock resistance 2000g and over assure temperature reduction of large-size CCD arrays (16o30 and 20o20 mm) by 70 °ñ from + 65 °ñ with power requirement about 4 W. The modules have found wide application in space products. At the present time they have been installed on more than 200 space objects.

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Thermoelectric Heat Pump As a Better Solution For Energy Saving In Water Purification Systems On The Manned Spaceships

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A new generation of apparatus for provision of the astronauts with water during long-term space flights is described in this report.

The apparatus have two basic components, namely a centrifugal vacuum distiller (CVD) and a thermoelectric heat pump (THP). Critical parameters of the complex are as follows: efficiency up to 5 l per hour, specific energy consumption less than 100 W per hour/l, degree of the initial water concentration from 92 to 95 %, capacity less than 0.1 m^3 and weight 30 kg.

The apparatus improved characteristics were primarily obtained due to the use of the quality thermoelectric pump. Computer simulation methods utilizing the optimal control theory were used for its design as well as optimal thermoelectric materials and operation modes, all those making the heating coefficient indications twice as good. The distillation system combining CVD and THP was designed and developed on the base of scientific achievements of the National Technical University of Ukraine "Kyiv Polytechnic Institute", the Institute of Thermoelectricity of the National Academy of Sciences and the Ministry of Education and Science of Ukraine and the company "Thermodistillation RV" Ltd.

The testing results of the complex CD and THP on the test bench "Thermodistillation RV" Ltd., Honeywell International, Inc. and NASA are given. The use of the THP system for energy regeneration allows reducing energy consumption by 1.6 times as compared to a vapor compression distiller (VCD). In that case a CD and THP system is running stable at the concentration up to 95^{o} C.

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Notes: .....

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	Monday 18 November	
time start	"Newton" room	"Einstein" room
09:00		
09:20		
09:40		
10:00	*Registration*	
10:20		
10:40		
11:00	**Opening Ceremony**	
11:20	**Invited Speaker: Jeffrey Snyder**	**Thin Films**
11:40		
12:00	**Oxides**	
12:20		
12:40		
13:00	*Lunch Break*	
13:20		
13:40		
14:00	**Oxides**	**Invited Speaker: Xanthippi Zianni**
14:20		
14:40		**Theory**
15:00		
15:20		
15:40	**Poster Session 1 & Coffee Break**	
16:00		
16:20		
16:40	**Invited Speaker: Sylvie Hebert**	**Theory**
17:00		
17:20	**Oxides**	
17:40		
18:00		
18:20	*Welcome drinks*	
18:40		
19:00		
19:20		
19:40		
20:00		

	Tuesday 19 November	
	"Newton" room	"Einstein" room
	Invited Speaker: Tsutomu Iida	**Nano-structures**
	Silicides, Stannides and Germanides	
	Coffee break	
	Silicides, Stannides and Germanides	**Nano-structures**
	Lunch Break	
	Chalcogenides	**TE Modules and Generators**
	Poster Session 2 & Coffee Break	
	Invited Speaker: Qiang Li	**TE Modules and Generators**
	New Materials	
	Conference Dinner	

	Wednesday 20 November	
	"Newton" room	"Einstein" room
	Invited Speaker: Jan König	**Skutterudites, Half-Heusler and Zintls**
	Measurements	
	Coffee break	
	Measurements	**Sulfides and Clathrates**
	Lunch Break	
	Invited Speaker: Mauro Brignone	**Organic Materials and Ionic Liquids**
	Automotive Applications	
	Poster Session 3 & Coffee Break	
	Space Applications	
	Closing Remarks and Goodbye Drinks	