ECT 2016
LISBON

14th EUROPEAN CONFERENCE ON THERMOELECTRICS (ECT2016)
Instituto Superior Técnico (IST/C^{2}TN)
Lisbon, Portugal, 20-23 September 2016

BOOK OF ABSTRACTS

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TAP
TAP PORTUGAL
de braços abertos
with arms wide open

Welcome to ECT2016

It is our great pleasure to invite you to participate in the **14th European Conference on Thermoelectrics (ECT2016)**, to be held in Lisbon, PORTUGAL, on September 20-23, 2016.

The European Conferences on Thermoelectrics are high quality scientific forums promoted by the European Thermoelectric Society (ETS) that offer open and informal discussions on Thermoelectrics. The sessions of ECT2016 will cover all aspects on Thermoelectrics, from materials design, synthesis and characterization to application issues, modules and simulations.

Experts, scientists and engineers from Academia and Industry all around Europe and abroad, are invited and expected for attending ECT2016 and discuss the state-of-the-art of the technology, latest advances in material research, device design and market opportunities.

According to the authors preference, papers presented in the Conference may be published in a volume of*Materials Today: Proceedings* or submitted to a regular scientific journal. *The Energy Conversion and Management and Energy* journals have already agreed to receive paper submissions from the conference (please note that a standard peer review process will take place, with no guarantee of acceptance).

We feel confident that you will enjoy ECT2016, which will be also a wonderful opportunity to meet old friends and make new ones, and that the conference will be a memorable event.

On behalf of the Local Organizing Committee

António Pereira Gonçalves
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Contents

Oral Communications

Invited Lectures

I.1

Design of thermoelectrically highly efficient Heusler compounds using phase separations and nano-composites

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Abstract

Half-Heusler compounds are one of the most promising candidates for mid-temperature to high-temperature thermoelectric materials. Currently, they are investigated for automotive and industrial waste heat recovery applications. For both, n- and p-type materials, maximum ZT values of larger than one have been published, and recently first modules have been built.

In this talk, I will give an overview about our recent investigations of phase separations in half Heusler thermoelectrics, focusing on the ternary system TiNiSn-ZrNiSn-HfNiSn. During the last two years, many publications and patents appeared discussing not-single phase samples within the TiNiSn-ZrNiSn-HfNiSn system. I will show how we adapted this knowledge to design a p-type Heusler compound which exhibits a ZT that is increased by 130% compared to the best published bulk p-type Heusler. I will also present how we used the phase separation to design thermoelectric highly efficient nano-composites of different single-phase materials. Since the price for Hafnium was doubled within the last 15 months, our research focused on the design of half-Heusler compounds without Hafnium. I will present a very recent calculation on ZT per € and efficiency per € for various materials followed by our latest very promising results for n-type Heusler compunds without Hafnium.

These results strongly underline the importance of phase separations as a powerful tool for designing highly efficient materials for thermoelectric applications that fulfill the industrial demands for a thermoelectric converter.

I.2

Applications in thermoelectricity

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Abstract

A brief history of Applications in thermoelectricity (TE) is given starting with the first Soviet Union military application; then a review of the 1960's where all ended because the expected breakthrough did not materialize. In the 1970's there was an interest in large cooling systems, but no commercial success. In 1993 after the announcement by Hicks and Dresselhaus that low dimensionality TE materials could produce very high performances; Universities and industry became again interested in TE. The consumer products, and the industrial applications are presented, from applications in cooling and in electricity generation in Space, to the diverse equipment's using thermoelectrics. Today bismuth telluride is still the best for cooling and is expected to remain so. High temperature materials are emerging for electricity generators. The automotive industry, is a key driving factor for electricity generation from exhaust heat. The first industrial cooling large series application was car seat cooling. Laboratory equipment's requiring cooling and heating are less known applications. The overall market size will be estimated.

I.3

Cu-S based synthetic minerals promising as medium-high temperature thermoelectric materials

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Abstract

Copper-sulfur based synthetic minerals have been receiving considerable attention as potential candidates for thermoelectric (TE) materials. They have the advantages of earth abundant, low cost, and less toxic characters of constituent elements. The examples are tetrahedrites $Cu_{12-x}Tr_xSb_4S_{13}$ (Tr = Mn, Fe, Co, Ni, Zn) [1-3] and colusites $Cu_{26}A_2M_6S_{32}$ (A = V, Nb, Ta; M = Ge, Sn) [4, 5], both of which exhibit positive and large thermopower. More importantly, these synthetic minerals—exhibit the lattice thermal conductivity less than 0.5 W/Km, and thereby achieve *ZT* exceeding 0.5 at ~700 K. Our recent studies of the relation between phonon structures and TE properties will be presented.

In search of *n*-type Cu-S based compounds, we have studied $Cu_2TrTi_3S_8$ (Tr = Mn, Fe, Co, Ni) thiospinels. They are derivatives of mineral rhodostannite $Cu_2FeSn_3S_8$. The negative thermopower of –100 μV/K combined with the metallic electrical resistivity and relatively low lattice thermal conductivity of ~1.5 W/Km led to *ZT*~0.2 at 660 K for M = Mn, Co, Ni. The result will be compared with other *n*-type Cu-S and Ti-S based materials.

This work is partly supported by JSPS KAKENHI Grant Number 26820296 and the International Joint Research Program for Innovative Energy Technology funded by METI, Japan.

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[5] Y. Kikuchi *et al*., to be submitted.
[6] K. Hashikuni *et al*., to be submitted.

I.4

The specificities of oxides thermopower investigated in some ruthenates and hollandites

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Abstract

The transport properties of oxides exhibit peculiar characteristics, not easily described by standard Boltzmann equation. In transition metal oxides, the thermopower can be very sensitive to the spin states and oxidation states of the transition metal cations, especially in the case of layered oxides with CdI_2 type layers, which still remain today the best p type oxides. The presence of strong electronic correlations can also be a source for enhanced thermopower.

Following the investigation of these layered oxides, the hollandite family has been considered, due to the presence of edge shared octahedra of the transition metal cation, connected in ribbons forming large tunnels. We will present here the results concerning manganese and vanadium hollandites [1], to show the importance of the spin entropy, the possible doping effect in these structures, and the thermal conductivity of these hollandites.

In a second part, the strong sensitivity of the thermopower to the spin and orbital states of the transition metal cation will be presented in the case of ruthenium oxides. In Sr_2RuO_4, the major role of the spin entropy of Ru^{4+} on the high T Seebeck value has been discussed [2]. Different families of ruthenates (with different ruthenium environment) have been investigated, and the thermopower unexpectedly tends to a similar value at high T, close to 25 – 35μV/K, very close to the one previously measured in $SrRuO_3$ perovskites [3] or in Sr_2RuO_4. The band structure seems thus to play only a minor role at high temperature in these ruthenates.

References:

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I.5

Silicide thermoelectrics: recent progress in research

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Abstract

The silicide family of potential thermoelectrics includes more than 15 compounds, among them at least 2 are semimetals, while the other are semiconductors with band gaps ranging from 0.1 to 2.3 eV. The silicides have obvious attractive features as the materials for thermoelectric energy converters. The most of the constituting elements are abundant, have low price, many of the compounds have good high temperature stability. This is why considerable efforts have been undertaken, especially in the past 10 years, in order to develop efficient silicide-based thermoelectric materials. These efforts have culminated in the creation of Mg_2(Si-Sn) n-type thermoelectric alloys with the proven maximum thermoelectric figure of merit ZT of 1.3. Other silicides were investigated, although to a lesser extend. Currently the most efficient silicide thermoelectrics are based on Mg_2(Si-Sn) alloys (ZT up to 1.3), $MnSi_{1.75}$ (with the highest reported ZT of 1.05) and $ReSi_{1.75}$ (peak ZT about 0.7). For other members of silicide family ZT currently does not exceed 0.25. In this presentation I will review the current status of the research on the silicide-based thermoelectric materials. A particular attention will be paid to the silicide materials, which were not in the research focus; to the recent efforts for enhancement of ZT of $CrSi_2$ and $FeSi_2$; to topologically non-trivial electronic structure of CoSi and $SrSi_2$ and its implications for thermoelectric efficiency.

I.6

Mechanical processing of thermoelectric materials: a solution for material texture inducing

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Abstract

Many conventional thermoelectric materials are anisotropic: the structural complexity, useful to improve the material efficiency, often leads to a strong dependence of the material properties on the different spatial direction considered. This aspect, lately subject of increasing interest, has been often neglected in the study of polycrystalline samples, because of their randomly oriented grain structure. Recently, looking for further improvements in thermoelectric efficiency, techniques for the sintering of polycrystalline samples able to preserve the natural anisotropy of the compounds have been studied and developed. The common target is to produce bulk samples easier to deal with as respect to single crystals, with improved thermal and mechanical properties, preserving the optimal electrical characteristics. In some cases, the latter depending on the crystallographic direction considered.

The present work offers a short review of the results obtained for material texture induction using different techniques, focusing on solutions involving a mechanical processing. Large space is given to the open die pressing sintering technique. The technique results to be effective in material texturing and allows to produce polycrystalline large bulks preserving the anisotropy of electrical properties (α and σ). Both structural analyses and microscopy display strong orientation of the material after sintering. In case of anisotropic materials, thermoelectric analyses performed on processed samples cut in the appropriate direction produced results comparable to the best one reported in literature.

I.7

Thermoelectric applications: from automotive to oil & gas, highlighting design, modeling & testing methodology

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Abstract

This presentation will describe thermoelectric applications such as automotive waste heat recovery as well as the E1TM, an exhaust-gas heat recovery generator, and the Power Generating Combustor (PGC™), which generates electricity from the exhaust heat in enclosed flare stacks, will be introduced and reviewed.

In addition to the applications themselves, this presentation will describe some of the design, modelling, and testing methodology that goes into many of the components that comprise systems in these applications. Many of these applications require targeted modelling to determine the optimal design for the components and system. In the context of application and non-application specific simulation and testing, steady-state and transient/cycling performance, both measured and simulated, will be shown for both PowerCardsTM and PowerModulesTM. Steady-state and transient model validation studies of the PowerCardTM and PowerModuleTM will also be reported.

We will also briefly highlight the four attributes that we believe are required for a thermoelectric material to be successful in waste heat recovery applications. They include 1) an average ZT of at least 0.5 between 100C and 400C, 2) tensile strength of at least 35 MPa with a tight distribution, 3) less than 5% degradation of thermoelectric material with metallization and bond layers when assembled in the package over at least 100 hours and 100 cycles, and 4) existing supply chain must be similar to elements like copper, where global production rate is high and cost is low.

I.8

Chain-forming Zintl phases as promising thermoelectric materials

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Abstract

Significant improvements in thermoelectric efficiency have been achieved in the past decade owing to both innovations in controlling thermal and electronic transport properties and to the discovery of a large number of entirely new thermoelectric materials. Zintl phases represent an important and incredibly diverse new class of thermoelectrics, with promising novel structure types and compounds being reported on a frequent basis. Zintl phases are a subset of intermetallic compounds that are characterized by covalently-bonded anionic "sub-structures", surrounded by highly electropositive cations. They are efficient thermoelectric materials with complex structures and bonding, highly tunable properties, and at times exceptionally low, glass-like lattice thermal conductivity. Several Zintl compounds have been reported with zT values in excess of unity, including $Yb_{14}MnSb_{11}$, YbM_2Sb_2 (M = Zn, Cd), and many others have exciting properties that need only to be optimized. However, the vast majority of Zintl compounds have not been studied beyond the initial crystallographic characterization, suggesting that many potential thermoelectric materials remain "undiscovered". Recognized only in past several years, the chain-forming A_3MPn_3 and $A_5M_2Pn_6$ compounds represent an entirely new class of Zintl thermoelectrics. In these compounds, the cation, A, can be an alkaline earth or divalent rare earth metal (Ca, Sr, Ba Eu, Yb), M is either a triel element (Al, Ga, In) or Sn, and Pn is a pnictogen species (P, As, Sb, Bi). Like $Yb_{14}MnSb_{11}$, they are stable at relatively high temperatures, they exhibit intrinsically low lattice thermal conductivity, and doping can be used to tune their electronic properties. This combination has led to promising zT values in the range of 0.5-1 in initial studies. In this contribution, I will discuss about the crystal structure, tunable electronic transport properties and glass-like lattice thermal conductivity of the chain-forming A_3MPn_3 and $A_5M_2Pn_6$ Zintl compounds.

I.9

Design strategies for thermoelectric half-Heusler compounds

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Large scale utilization of thermoelectric materials is conceivable with the discovery of new efficient materials comprised of Earth abundant and non-toxic constituents. A promising material class in this respect is the half-Heusler compounds (HHCs). They are highly attractive because high conversion efficiencies have been demonstrated in the 500-900 K temperature range as well as the fact that they are generally based on noncritical elements. The chemical complexity of the intermetallic phases both offers a great opportunity for systematically optimizing the thermoelectric performance but also a highly complex and many-dimensional phase space for the optimization.

With the advances of computational methodologies, theoretical methods promise to play a important role in exploring and understanding the rules underlying high thermoelectric performance, thereby paving the way for the design new materials. In the present talk, we will present design strategies covering band structure [1,2] and defect engineering[3,4] to optimize the thermoelectric powerfactor, as well as the minimization of lattice thermal conductivity by the combined optimization of alloying and nano-structure.

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I.10

SnTe: an “old” new thermoelectric material

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Abstract

SnTe is a simple cubic binary compound, which has been known for decades to exhibit poor thermoelectric performances due to inherent Sn vacancies that give rise to metallic properties. Yet, this compound came back to the forefront of research in thermoelectricity a couple of years ago leading to high thermoelectric performances with *ZT* values up to 1.35 at 950 K [1-3]. Despite rather high lattice thermal conductivity, these good thermoelectric properties were achieved thanks to its peculiar electronic band structure that can be manipulated through chemical substitutions [4,5]. In this contribution, its main structural, chemical and transport properties will be presented with a particular emphasis on the sensitivity of the vacancy concentration to the synthesis process and the influence of substitutions on the Sn or Te sites on the two-band character of its electronic band structure.

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I.11

Predicting the thermoelectric figure of merit from first principles

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Abstract

First-principles atomistic-scale calculations have been going through a rapid development during the last few years, and the first studies presenting the thermoelectric figure of merit without adjustable parameters are emerging. This now includes computations based on Boltzmann transport theory of both electron and phonon transport. We will in this talk discuss opportunities and limitations within current state-of-the-art electronic structure calculations, with particular emphasis on challenges related to scattering phenomena and possibilities to enhance thermoelectric performance by e.g. energy filtering.[1] Examples are taken from popular materials systems like half-Heusler and Zn-Sb compounds.

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I.12

Thermoelectric interfaces: characterisation and evaluation for manufacturing high-quality thermoelectric modules

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Abstract

Thermoelectric modules are solid-state energy converters that can convert heat into electricity for power generation, or pump heat from one junction to another for refrigeration applications. A key step in the fabrication process of thermoelectric modules is to join an n-type thermoelement with a p-type thermoelement through a metallic contact layer. The existence of various contact layers and their requisite interfaces will inevitably introduce both electrical and thermal contact resistances into a practical thermoelectric device. This will result in the consumption of energy at these interfaces, or a decrease in actual temperature difference across the thermoelement, with a reduction in device performance expected. In order to minimise the performance reduction due to these interfaces, characterisation and evaluation of thermoelectric interfaces plays a crucial role in developing thermoelectric module manufacturing technology. In this talk, we present an overview of an experimental approach for the evaluation of thermoelectric interfaces, which involve preparation of double-interface samples by high temperature soldering or brazing; determination of electrical contact resistivity using scanning voltage probe and thermal contact resistivity using infrared microscopy. In addition, we present a simplified model that facilitates the quantitative analysis of interface's influence on the performances of thermoelectric modules to assist in identifying key factors and challenges that are crucial to obtain satisfactory thermoelectric interfaces for manufacturing high-quality thermoelectric modules.

TransFlexTeg (*TFT*)

TFT.1

AZO thin films deposited by ALD showing state of art thermoelectric properties

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Abstract

The urgent need of non-toxic and abundant thermoelectric materials has become a significant motivation to study the thermoelectric properties of metal oxides in order to overcome barrier towards its widespread use in large scale applications. Thin films enable the use of thermoelectric materials in large areas and on flexible substrates without having prohibiting costs and the need of high ZT values. On the other hand, the great demand for low cost, stable, highly transparent and conductive oxides has contributed to increase the research on the electro-optical properties of zinc oxide and its alloys. In particular, thin films of aluminium doped zinc oxides (AZO) have been one of the most exhaustively studied. However, their thermoelectric properties only recently have started to be more explored with thin films being deposited by rf magnetron sputtering [1], atomic layer deposition –ALD [2] or spray pyrolysis [3] techniques. In this work, AZO thin films have been deposited on different substrates (glass, Kapton CS) by ALD and their properties optimized by varying the deposition temperature (150, 200 and 250ºC).

Thus, we report transparent AZO thin films, with thickness ranging 100nm, showing high Power Factor and ZT values on glass and on Kapton CS (DuPont), at room temperature. Moreover, it is the first time AZO results are shown on flexible/polymeric substrate.

References:

[1] J. Loureiro, *et al.*, Transparent aluminium zinc oxide thin films with enhanced thermoelectric properties. *J. Mater. Chem. A* 2 (2014) 6649-6655.

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TFT.2

Flexible thermoelectric sensor for thermal mapping

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Abstract

Thermocouples are one of the most common ways for measuring temperature. Based on the Seebeck effect, thermocouples create a voltage difference by direct conversion from an applied temperature gradient, thus providing an energy efficient sensor solution.

This work describes our recent progress in designing, prototyping and understanding of a novel flexible thermal touch sensor architechture (Fig. 1). A single conductor line of a traditional thermocouple is replaced by the introduction of a two-dimensional thermoelectric thin film; consequently, the temperature distribution of the thin film may be measured with appropriate contacts. This principle may be liberally applied to a wide range of applications requiring gesture sensing or heat distribution mapping, from industrial scale processes to consumer products and basic research. The proposed device is based on simple and scalable fabrication methods, and it is in principle material independent, durable, and provides passive sensing of its thermal environment.

We illustrate the working principle of the touch panel using atomic layer deposited ZnO thin films as the active material, which combine transparency and flexibility with reasonable electrical properties. The mechanical as well as electrical characteristics of three test devices are presented.

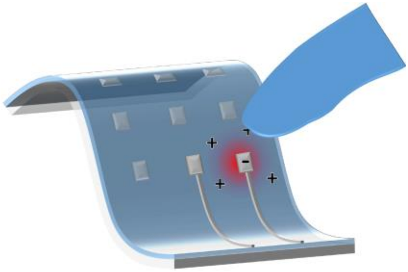

Figure 1: Schematic of the proposed flexible touch sensor.

TFT.3

TransFlexTeg: Large area transparent thin film thermoelectric devices for smart window and flexible applications

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Abstract

The main objective of TransFlexTeg is to develop an innovative large area distributed sensor network integrating transparent thin film thermoelectric devices and sensors for multifunctional smart windows and flexible high impact volume applications. Different breakthrough concepts will be developed:
1) large area high performance transparent thermoelectric thin films deposited on flexible substrates for thermal energy harvesting;
2) low cost high throughput thin film thermal sensors for thermal mapping and gesture sensing;
3) flexible smart windows and walls with energy harvesting, environmental sensing and wireless communication functionalities.

This technology aims to demonstrate the functionalities of a smart window able to measure air quality and environmental parameters such as temperature, sun radiation and humidity. The data is automatically collected and can be utilized for controlling heating, cooling and ventilation systems of indoors. Active radio interface enables long range communication and long term data collection with WiFi or a similar base station. The proposed concept of smart windows replaces several conventional sensors with a distributed sensor network that is integrated invisibly into windows. In addition to the power generated from the thermal energy harvesting, the thermoelectric elements (TE) are also used as temperature sensors that, while being distributed over large area, enable thermal mapping of the area instead of just one or a few values measured from particular points.
This smart window can be produced on glass. The active layer itself can be flexible glass layer or polymer sheet, which will significantly broaden the field of applications and improve business opportunities. Both can be manufactured in batch, or in Roll to Roll Atomic Layer Deposition (R2R ALD) process. High environmental impact is expected with savings of more than 25% of the electrical usage of residential homes and office buildings.

TFT.4

Computational design of thin-film thermoelectric devices for large area applications

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Abstract

Thin-film thermoelectric (TE) devices to be integrated on windows or other suitable surfaces providing thermal gradients for power production are studied by computational methods. Thermodynamic modelling and performance simulations are conducted for a set of selected mechanical designs in order to estimate the available thermal gradients, the performance of the thermoelectric elements and the power available from the TE modules consisting of various geometries, configurations and numbers of the elements. In addition to the electrical properties, an essential part of the model includes the simulations of the heat transfer mechanisms over the TE modules of various geometries. The ultimate goal of the simulations is to find the close to optimal designs for the materials available under the constraints set by the fabrication processes and thermal gradients accessible.

An overview of the main considerations and results will be given for selected geometries. The primary principles and challenges of designing translucent thin-film thermoelectric modules for large area applications are discussed.

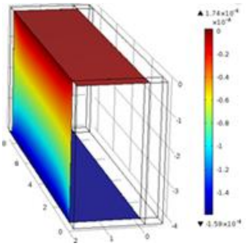

Figure 1: Potential difference generated by a temperature gradient applied over a thin-film thermoelectric device.

TFT.5

Thermoelectric properties of Al-doped ZnO based on ab-initio method and molecular dynamics

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Abstract

ZnO is considered as a promising candidate for thermoelectric applications. The effects of Al-doping on the thermoelectric properties and electronic structures of ZnO have been reported recently [1]. However, enhancement of the thermoelectric properties is not always improving with a higher concentration of doping. Therefore, it is relevant to estimate the figure of merit at different concentrations with Density Functional Theory [2] and Molecular Dynamics simulations [3].

Electronic band structures of Al-doped ZnO were obtained, which have shown band gaps decrease with increasing Al concentrations (Fig. 1a). Seebeck coefficients, electrical conductivities and power factors were calculated by solving Boltzmann Transport Equation [4]. The results (Fig. 1b) confirm that power factor is much improved with 3% and 4% Al doped into ZnO.

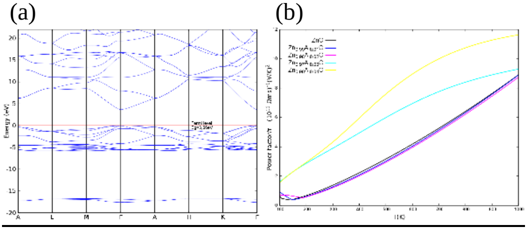

Figure 1:(a) Electronic structure of ZnO (b) Power factor of Al-doped ZnO with concentration of doping from 1% to 4%

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A1. Skutterudites

OA1.1

Skutterudites $Ba_yNi_4(Sb_{1-x}Sn_x)_{12}$; rattling features?

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Abstract

The homogeneity region at 450°C and solidus temperatures have been defined for novel quaternary filled skutterudites $Ba_yNi_4(Sb_{1-x}Sn_x)_{12}$ by means of Electron Probe Microanalysis (EPMA), X-ray Powder Diffraction (XPD) and Differential Thermal Analyses (DTA). For two selected samples, $Ba_{0.73}Ni_4Sb_{8.1}Sn_{3.9}$ and $Ba_{0.95}Ni_4Sb_{6.1}Sn_{5.9}$, temperature dependent single crystal X-ray structure analyses (at 100 K, 200 K, 300 K) revealed the thermal expansion coefficients, Einstein and Debye temperatures and the Debye Waller factors. These Atom Displacement Parameters (ADP's) indicate rather insignificant differences between framework and filler atoms, suggesting a strong coupling of the filler atoms with the framework.

Physical property measurements (i.e. temperature dependent specific heat, electrical resistivity, Seebeck coefficient and thermal conductivity) compare unfilled $Ni_4Sb_{8.2}Sn_{3.8}$ with the Ba-filled samples, $Ba_{0.42}Ni_4Sb_{8.2}Sn_{3.8}$ and $Ba_{0.92}Ni_4Sb_{6.7}Sn_{5.3}$. Small Sommerfeld constants from specific heat data (γ<15 mJ/molK) are consistent for all samples with low carrier concentrations ($n \sim 4 \times 10^{20}/cm^3$) derived from Hall data (n-type from negative Sebeck coefficients). Interestingly Ba-fillers and rising Sn-contents increase the Debye temperatures significantly. Electrical resistivities reveal a crossover from metallic to semiconducting behaviour, which is discussed in terms of a temperature-dependent carrier concentration employing a simple model for a rectangular density of states with the Fermi energy slightly below a narrow gap. In contrast to common features in filled skutterudites, a rising Ba content in $Ba_yNi_4(Sb_{1-x}Sn_x)_{12}$ *enhances* thermal conductivity.

OA1.2

Attempts to further enhance ZT in skutterudites via nano-composites

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Abstract

Skutterudites are known as excellent thermoelectric (TE) materials because they can be produced easily and fast from cheap starting materials, they can be used in a wide temperature range and besides an excellent TE quality they also show stability and a good mechanical performance. The quality of every TE material is represented by the dimensionless figure of merit ZT. Among the filled skutterudites based on CoSb3 high ZTs, (laboratory values: p-type: ZT = 1.3 [1], n-type: ZT = 1.8 [2], values from commercially produced powders by TIAG, Austria: p-type: ZT 1.1 ± 0.1, n-type: ZT = 1.3 ± 0.1) have been gained. Still, there is the urge to further enhance ZT, by simultaneously increase the electrical conductivity and the Seebeck coefficient while maintaining a thermal conductivity as low as possible.

One approach is to form bulk nano-composites where various types of nanoinclusions are dispersed in the CoSb3-based matrix. Provided the phonon mean-free path is reduced by enhanced phonon boundary scattering to a greater degree than any reduction in the mean-free path of charge carriers, the net effect is an improvement in the figure of merit. Moreover, there is also a possibility that the presence of dispersed nanoinclusions will lead to an enhancement in the Seebeck coefficient as a result of energy-dependent scattering of electrons at the interface of nanoinclusions and the matrix.

It was demonstrated by the authors [3] that a homogeneous nanoscale distribution of Yb_2O_3 in n-type $Sr_{0.09}Ba_{0.11}Yb_{0.05}Co_4Sb_{12}$ improved the TE performance, resulting in an enhancement of ZT from 1.4 to 1.6. Based on such inspiring results, further similar experiments were carried out. In this paper not only the influence of addition of oxide nanoparticles (Al_2O_3, Cu_2O and $La_{1.85}Sr_{0.15}CuO_4$) in various wt. % but also of borides in various wt. % ($Fe_{2.25}Co_{0.75}B$ and $Ta_{0.8}Zr_{0.2}B$) to p- and n-type skutterudites (commercially produced) under various preparation methods will be discussed. In some cases the thermoelectric properties led to a higher ZT, but even if this was not the case, the investigated mechanical properties changed to the better.

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OA1.3

Thermoelectric properties of skutterudite materials made from lower purity elements

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Abstract

Skutterudite materials have been the subject of renewed interest in the 1990's and have since been intensively investigated as thermoelectric power generation materials. There are a number of binary, ternary, and filled skutterudite materials with diverse transport properties, making this class of materials attractive for thermoelectric applications. Today, they are one of the leading classes of materials considered for several power generation applications including automotive and space. The cost of the thermoelectric materials may be one of the important factors that may limit the commercial viability of some of these applications. Most of skutterudite materials R&D is performed using high purity starting elements which tend to be expensive. This paper reports on the initial assessment of using lower purity elements to synthesize n- and p-type selected skutterudite materials and provides an initial sensitivity comparison of the thermoelectric properties for materials made from high- and low-purity elements. A brief cost analysis is also presented.

OA1.4

Effect of framework substitution on the thermal conductivity of skutterudites

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Abstract

Compounds with the skutterudite structure have been studied extensively since they were reported as potential thermoelectric materials at elevated temperatures [1]. Typically, the thermal conductivity (κ) of skutterudites is reduced by the introduction of filler species into the cavities within the structure. In this work we propose a new approach to reduce the thermal conductivity via isoelectronic framework substitution. Materials of the form $Co_{1-2x}Fe_xNi_xSb_3$ ($0 \leq x \leq 0.5$), isoelectronic with the archetypal $CoSb_3$, have been synthesized by conventional solid-state methods. All phases are cubic and crystallise in the $Im\bar{3}$ space group. Surprisingly, even in the absence of a filler species, κ is reduced substantially ($\kappa_L \approx 3.7 – 4.7$ W m^{-1} K^{-1} at 300 K) from that of $CoSb_3$ ($\kappa_L \approx 8.5$ W m^{-1}K^{-1} at 300 K) (Fig. 1a). Given the very similar atomic masses of Co, Fe and Ni, mass fluctuation scattering of phonons in the mixed-metal frameworks is unlikely to play a major part in lowering κ.

A pair distribution analysis (PDF) by neutron diffraction suggests changes in local structure (Fig 1b) which may be related to the reduction in thermal conductivity through a perturbation of the phonon propagation. Furthermore, inelastic neutron scattering measurements reveal differences in the vibrational spectrum associated with the transition-metal based modes (Fig 1c). Rietveld refinement using neutron diffraction data, SEM coupled with XEDS, XANES spectroscopy, Seebeck coefficient and electrical conductivity measurements have also been performed for $Co_{1-2x}Fe_xNi_xSb_3$ and will be presented and discussed.

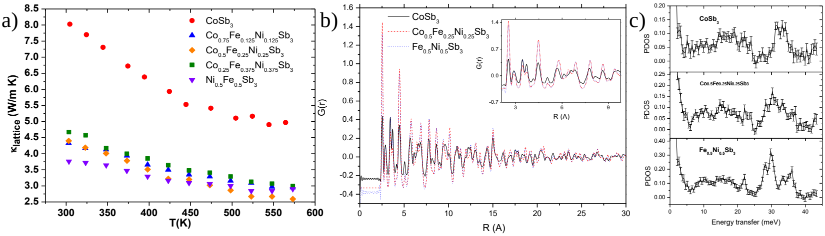

Figure 1: $Co_{1-2x}Fe_xNi_xSb_3$ ($0 \leq x \leq 0.5$) a) Temperature dependence of the lattice thermal conductivity, b) PDF data at RT, c) Neutron Phonon Density Of States (PDOS) data at 5 K.

References:

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OA1.5

$In_{0.25}Co_4Sb_{12}$ nanocomposites with improved ZT

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Abstract

$In_{0.25}Co_4Sb_{12}$ is a n-type thermoelectric skutterudites which displays a moderately large figure of merit ZT = 1 at 550 K[1]. $In_{0.25}Co_4Sb_{12}$ shows a large power factor (~ 3.4 mW. $m^{-1}K^{-2}$ at 300K) but its lattice thermal conductivity which amounts to λ_L = 3.8 $W.m^{-1}.K^{-1}$ could nonetheless be reduced. Several studies have shown that the reduction of the grain size to a mesoscopic scale (~ 200 nm) or the addition of nanoparticles (~ 20 nm) lead to a reduction of the lattice thermal conductivity and to an increase of ZT. The phonons are indeed scattered by the numerous grain boundaries or by the nanoparticles.

$In_{0.25}Co_4Sb_{12}$ is synthesized by melting and annealing the elements. Grain size reduction is obtained by ball milling in a planetary mill. To inhibit the grain size growth which occurs during densification by Spark Plasma Sintering, CeO_2 nanoparticles (~ 20 nm) are added. This leads to $In_{0.25}Co_4Sb_{12}$ compacts with small grain sizes in the 200 – 400 nm range. The lattice thermal conductivity is strongly reduced (λ_L = 2.2 W m^{-1} K^{-1} at 300K) (Fig. 1) and the figure oh merit is strongly enhanced to ZT = 1.4 at 750 K.

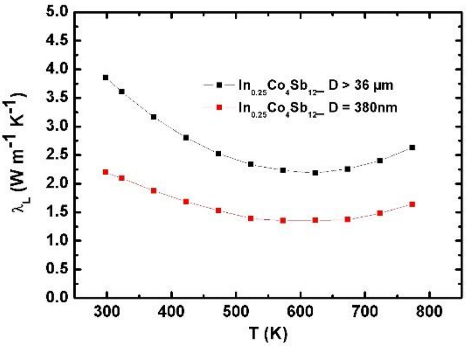

Figure 1: Lattice thermal conductivity in $In_{0.25}Co_4Sb_{12}$ nanocomposites.

References:

[1] He, T., *et al.*, Thermoelectric properties of indium filled skutterudites. *Chemistry of Materials* 18 (2006) 759.

OA1.6

Long term stability tests on commercially produced skutterudites

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Abstract

Long-term (8880 hours) thermal stability tests (TST) were performed at a temperature of 600°C for p- and n-type skutterudites (p-$(RE)_yFe_3CoSb_{12}$, $(RE)_yCo_4Sb_{12}$, RE is rare earth) produced from industrial powders supplied by Treibacher Industrie AG (production Nov. 2012). The TE properties and thermal stability for specimens hot pressed under industrial and reference laboratory conditions were compared. The partial oxidation of the p-type material during hot pressing results in a significant degradation of the TE performance: the figure of merit at 800K is reduced to 0.9 in comparison to the reference sample (ZT_{800K} = 1.1). The better oxidation resistance of n-type material results in almost identical ZT_{800K}=1.3±0.1 for samples hot-pressed in both conditions.

The experimental set-up for TST was designed in a way that allows (i) gas transport between n- and p-type legs located at 600°C (hot side) and (ii) sublimation of antimony from this couple at the cold side (at 80°C) of the silica tubes. The results obtained show an enhanced stability of n-type against thermal decomposition. P-type materials show stronger Sb-evaporation resulting in weight losses of ~0.0001 wt %/h (or 0.001 mg/cm^2), however, the decomposition occurs only in the surface zone of the specimens with a thickness of 25-50 μm and this insulating layer does not affect the thermoelectric performance of the legs. Unusual weight exchange between p- and n-legs, observed for the specimens hot-pressed in an industrial equipment is attributed to partial oxidation of p-type materials, however, this effect is absent for the samples compacted under reference laboratory conditions.

The figure of merit during the entire TST period remains in the range of 0.9±0.1 for p-type but it slightly decreases from 1.3±0.1 to 1.1±0.1 for the n-type material. The decrease of the TE performance for n-type materials is explained with a gradual decrease of the filling level from y=0.17 (start of the TST) to y=0.11 (after 8880 h of TST). Considering that in TE modules only a small part of the legs will be subjected to high temperatures (600°C), the observed decrease of ZT for the n-type materials will have only a very small effect on the overall TE performance of the TE modules built on the base of these materials.

OA1.7

Thermoelectric properties of melt-spun and crystalline $Co_4Sb_{11.6}Te_{0.4}$ ribbons

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Abstract

Melt-spinning nowadays is widely used as a method of non-equilibrium synthesis of thermoelectric materials [1]. It has several very important advantages in comparison with conventional procedures. Due to very high cooling rate it allows to quench high-temperature phases and avoid long-time annealing procedures. The resulting materials have amorphous or quasi-amorphous structure, which helps to reduce lattice thermal conductivity. Usually, the melt-spinnig is only the first step in sample preparation procedure. To prepare bulk samples for measurements of thermoelectric properties, the ribbons, produced by melt-spinning, are crushed to powder, which compacted by hot pressing (HP) or spark plasma sintering (SPS). The material undergoes at least partial crystallization during the sintering process. Thermoelectric properties of the initial, as prepared ribbons and, consequently, the effect of the re-crystallization remains largely unknown. In this work we study thermopower and electrical resistivity of as prepared ribbons of $Co_4Sb_{11.6}Te_{0.4}$ scutterudite. The ribbons were produced by melt-spinning. Skutterudite samples had width about 0.25 mm, length 30 mm and thickness about 0.01 mm. The properties were measured during in-situ annealing of the ribbon samples, using home made equipment [2]. We found that initial state of the ribbons is stable up to about 620 K. At this temperature sharp changes of both, the thermopower and the resistivity were observed, see Fig.1. These changes indicate onset of crystallization.

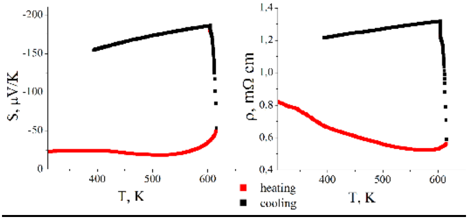

Figure 1: Temperature dependences of thermopower (S) and resistivity (ρ) of amorphous ribbon $Co_4Sb_{11.6}Te_{0.4}$.

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OA1.8

Thermoelectric properties and stability of filled skutterudite materials under large temperature gradient and thermal cycling

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Abstract

Filled Skutterudite materials are among the most promising high performance (zT) candidates for building up thermoelectric (TE) modules [1]. Besides the high zT values, the stability of the materials under dynamic conditions is equally important, and it plays a crucial role in the performance of TE module. In this work, the TE properties and stability of filled skutterudites are investigated under a large temperature difference of 397 K (T_{hot} = 773 K; T_{cold} = 376 K) and thermal cycling from RT up to 773 K. The results showed that after 20th thermal cycles zT values of 1.3 for p-type and 1.6 for n-type at 773 K materials are maintained. However, under operating conditions of ΔT = 397 K for 600 hours, the maximum output power was degraded resulting from the increase in the total electrical resistances. The effect is very substantial with the p-type, while the change in the resistance of n-type is less than 7% after 300 h. Microstructures at the interfaces as well as of the materials were carried out and correlated with the observed TE performance.

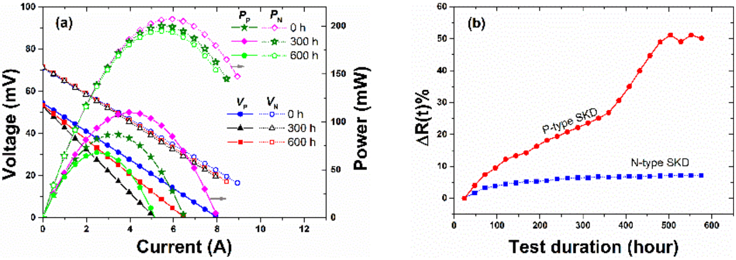

Figure 1: (a) Power generation characteristics, and (b) the change in total electrical resistances of single p-type and n-type legs under temperature gradient of 397 K for 600 hours.

References:

[1] G. Rogl, A. Grytsiv, P. Rogl, E. Bauer, M. Hochenhofer, R. Anbalagan, *et al.* Nanostructuring of p- and n-type skutterudites reaching figures of merit of approximately 1.3 and 1.6, respectively, *Acta Mater* 76 (2014) 434–48, doi:10.1016/j.actamat.2014.05.051.

A2. Heusler-based phases

OA2.1

Theoretical and experimental investigation of the electronic structure and thermoelectric properties of Fe_2VAl

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Abstract

In today’s world, the energy demand has been increased enormously driven by population growth and increase in living standards. There is an urgent requirement of efficient and eco-friendly thermoelectric devices to recover energy losses. Heusler-type Fe_2VAl compounds attained a great attention due to their semiconducting nature over a wide temperature range up to 1200 K. First principles calculations are performed to study the electronic structure of the full Heusler compound Fe_2VAl and the formation energy of the intrinsic point defects such as vacancies, antisites and interstitials is analyzed as well. The *ab initio* calculations show that Fe_2VAl is a non-magnetic semimetal. The density of states reveals a sharp pseudogap at the Fermi level, which is a beneficial aspect for thermoelectricity. The electronic transport properties of Fe_2VAl and the most favorable defects are analyzed based on the Boltzmann transport theory within the constant relaxation time approach. The lattice thermal conductivity is also being analyzed by using the sets of second- and third-order interatomic force constants which can be calculated from *ab intio* methods. Pure Fe_2VAl compounds in parallel have been synthesized by the combination of mechanical alloying and spark plasma sintering. The transport properties obtained from the experiments are compared with the calculated values.

OA2.2

Large Seebeck coefficient in a novel thermoelectric V doped Fe_2TiSi Full Heusler alloy

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Abstract

Full Heusler alloys such as Fe_2VAl are one of the potential candidates for practical use because they are typically composed of the earth-abundant elements [1]. Recently, by first principle calculations, we discovered a novel composition: Fe_2TiSi with possible high Seebeck cofficient [2]. So far, there has been no experimental evidence for their thermoelectric properties. In this study, we investigated the effect of V doping on thermoeletcic properties in Fe_2TiSi films and found the high Seebeck coefficient of -159 μV/K by controlling the valence electron concentration (VEC).

200 nm-thick $Fe_2(TiV)Si$ films were deposited on MgO(001) single crystal substrates by magnetron sputtering and then annealed at 800°C in order to crystallize the as-sputtered films from amorphous state. The VEC was changed by using V-doped Fe_2TiSi targets and resultantly the V doping concentration was varied from 0 to 10 at%. The crystal structures of the films were analyzed by X-ray diffraction and cross-sectional TEM images. The Seebeck coefficients and the resistivity were measured by dc four-probe method at 50 °C.

The annealed $Fe_2(TiV)Si$ films are found to have highly Fm3m symmetry. The non - doped Fe_2TiSi film, in which the differential VEC (ΔVEC) is 0.00, shows the S of -13.2 μV/K. When the V substitution increases, the $|S|$ takes a maximum value of -80.4 μV/K at ΔVEC of 0.05. This behavior can be caused by the carrier concentraiton modulation through the ΔVEC change. Finally, by optimizing the E_F level, the Al-doped $Fe_2(TiV)Si$ alloy shows the S as large as -158.9μV/K. The obtained large S could originate from a narrow energy gap near Fermi level (E_F) and flat-bands are located in the bottom of conduction band.

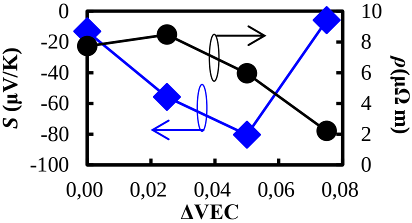

Figure 1: Thermoelectric properties of $Fe_2(TiV)Si$.

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OA.2.3

$Fe_2TiSn_{1-x}Si_x$ Heusler alloys: influence of sintering conditions on crystal structure and thermoelectric properties

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Abstract

Among a variety of thermoelectric materials, half Heusler NiMSn (M = Ti, Zr, Hf) and full Heusler Fe_2VAl semiconducting alloys have been attracted considerable attention over last years. Other representatives of the semiconducting Heusler alloys, Fe_2TiSi and Fe_2TiSn, have enjoyed recently growing interest. Results of first principles calculations [1] have indicated that a large Seebeck coefficient, up to – 300 μV/K, can be expected in $Fe_2TiSn_{1-x}Si_x$ alloys. On the other hand, experimental investigations [2] have shown that physical properties of Fe_2TiSn significantly depend on both atomic disorder and stoichiometry. Although a secondary phase is presented in bulk samples of Fe_2TiSi, the single Heusler phase can be stabilized in thin films of Fe_2TiSi [3]. The mentioned above facts imply that precipitations of the secondary phase in Fe_2TiSi and the physical properties of Fe_2TiSn can be controlled by preparation method and/or thermal treatment. In order to check this we have studied $Fe_2TiSn_{1-x}Si_x$ alloys prepared by induction melting and mechanical alloying.

Results of this study revealed that a secondary phase appears in both induction melted and ball milled samples with $x > 0$. Consolidation of the ball-milled powder by Spark Plasma Sintering (SPS) brings about even more complex phase coexistence. Comparison of electrical resistivity ρ, Seebeck coefficient S and thermal conductivity κ measured in induction melted and SPS sintered samples of the same composition indicates that thermoelectric properties of $Fe_2TiSn_{1-x}Si_x$ depend on the preparation method. Details of these measurements shall be given in the presentation.

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OA2.4

Role of point defects for thermoelectric properties of ZrNiSn and ZrCoBi

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Abstract

Density functional theory calculations using both the PBE and the HSE06 functional are employed to investigate the role of intrinsic point defects for the thermoelectric properties of the semiconducting half-Heusler alloys ZrNiSn and ZrCoBi. In ZrNiSn, the interstitial Ni atom (Ni_i) as well as the $V_{Ni}Ni_i$ complex introduce defect states in the band gap, whereas just a minor reduction of the band gap is associated with the Ni vacancy (V_{Ni}). While Ni_i is electrically active and may act as a donor, the other two types of defects may compensate extrinsic doping. In ZrCoBi, defect formation energies are found to be higher than in ZrNiSn, and only the $V_{Co}Co_i$ complex introduces a defect state in the band gap. Motivated by the reported use of ZrNiSn for thermoelectric applications, the Seebeck coefficient of both materials, both in the p-type and the n-type regime, is calculated. We find ZrCoBi to display a large thermopower of up to 500 µV/K when p-doped, whereas the maximum thermopower of ZrNiSn is in the n-type regime. The reported difficulties in achieving p-type doping in ZrNiSn could be rationalised by the unintended formation of Ni_i^{2+} in conjunction with extrinsic acceptors, resulting in their compensation. Moreover, our calculations show that all types of defects considered, when present in concentrations as large as 3%, tend to reduce the thermopower compared to ideal bulk crystals at T=600K. For ZrNiSn, the calculated thermodynamic data suggest that excess Ni could be removed by annealing, leading to precipitation of a metallic Ni_2ZrSn phase.

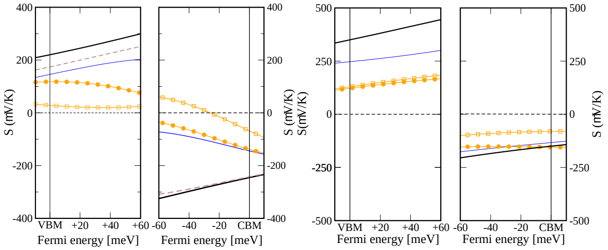

Figure: Seebeck coefficient for ZrNiSn (left) and ZrCoBi (right) for Fermi levels close to the band edges, for pure materials (thick line), interstitial Ni or Co (thin blue line), Ni vacancies (dashed) and $V_{Co}Co_i$ or $V_{Ni}Ni_i$ complexes (orange lines with symbols).

References:

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A3. Clathrates
&
A6. Zintl Phases

OA3-6.1

Thermoelectric properties of a sodium indium tin compound

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Abstract

A ternary Zintl phase, $NaInSn_2$, reported by Blase *et al*. [1] has a crystal structure similar to that of $Na_{1+x}Ga_{1+x}Sn_{2-x}$ showing relatively high ZT values of 0.12–0.98 at 295 K [2]. In the structure of $NaInSn_2$, Na atoms are located in helical tunnels of In-Sn framework as shown in Fig. 1(a). The objective of the present study was to prepare $NaInSn_2$ polycrystalline samples by sintering and to clarify the thermoelectric properties. The Seebeck coefficient (S) of a sintered sample of $NaInSn_2$, having a relative density of ca.100%, was -130 μV K^{-1} at 295 K and the absolute S value showed a maximum of $|-151|$ μV K^{-1} at 358 K (Fig. 1(b)). The electrical conductivity (σ) of the sample was increased from 0.89×10^5 to 1.37×10^5 Sm^{-1} with increasing temperature. The thermal conductivity (κ) measurement was carried out by the hot-disk method for two samples prepared at the same condition. The κ was increased from 1.49 to 2.17 $Wm^{-1}K^{-1}$ at 295–380 K. ZT values calculated from these data were 0.30–0.48. Low-temperature X-ray diffraction of a single crystal revealed a large dynamical positional disorder of Na atoms in the structure of $NaInSn_2$, which is probably responsible for the low thermal conductivity.

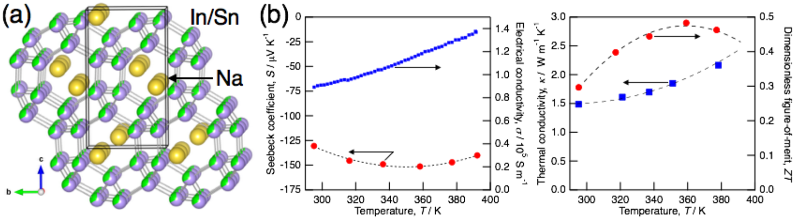

Figure 1: Crystal structure of $NaInSn_2$ (a) and thermoelectric properties of a polycrystalline sintered sample of $NaInSn_2$ (b).

References:

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OA3-6.2

Type II Sn clathrates – unexpected outcomes from cage disorder and gas encapsulation

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Abstract

Clathrate systems are cage-like formations which can host different guest atoms and molecules. The relationship between the particular structure and its transport properties is of fundamental importance for their basic understanding and technological importance. The relatively high electron mobility and low thermal conductivity are particularly attractive features of these systems for potential applications in thermoelectricity. The focus of our investigation are type II Sn clathrates, which have been explored to a lesser extent as compared to Si or Ge materials. We present results for calculated lattice structure, electronic structure and phonon dynamics properties based on first principles calculations. Comparison with available experimental data is also performed. Our comprehensive investigation shows that the type of guest atoms and cage substitution via Ga atoms strongly affect the energy band structure coupled with anharmonicity effects originating from the guest atoms. Unusual effects arising from weak van der Waals interactions and negative Gruneisen parameters have also been identified. Our study expands and improves the fundamental understanding of clathrate materials in general and it gives new perspectives for experimental applications.

OA3-6.3

Thermoelectric properties of the ternary phosphide $Ag_6Ge_{10}P_{12}$

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Abstract

The ternary phosphide $Ag_6Ge_{10}P_{12}$ [1], exhibiting a complex crystal structure, is build up by octahedral Ag_6-clusters embedded in a three-dimensional phosphorous-germanium anionic-covalent-framework (Fig. 1). The material contains sub-valent silver (Ag_6^{4+}), mixed-valent germanium (Ge^{2+}/Ge^{4+}), it is stable in air, and its structure is closely related to the tetrahedrite, $Cu_{12}Sb_4S_{13}$: $Ag_6\square Ge_4Ge_6P_{12} \equiv Cu_6SSb_4Cu_6S_{12}$. As later one is attributed to have prominent thermoelectric properties it seemed to be worthwhile to investigate $Ag_6Ge_{10}P_{12}$ in more detail.

The semiconducting character of this material is reflected in band structure calculations, which reveal an indirect band gap of about 0.46 eV. Measurements of the thermal diffusivity exhibit a very small thermal conductivity ($\kappa \sim 1$ W/m·K) across the temperature range of 300-700 K. This directly reflects the strong lattice anharmonicity of the material. Combining this with an adequate electrical conductivity (σ) and a high Seebeck coefficient (S) results in a remarkable high figure of merit ($ZT = (S^2 \cdot \sigma \cdot T)/\kappa$) of about 0.5 at 700 K (Fig. 2). The coexistence of these properties suggests that $Ag_6Ge_{10}P_{12}$ is one of the first phosphides having potential as a thermoelectric material.

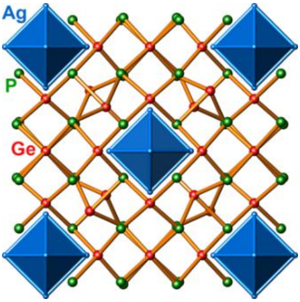

Figure 1: Representation of the crystal structure of $Ag_6Ge_{10}P_{12}$.

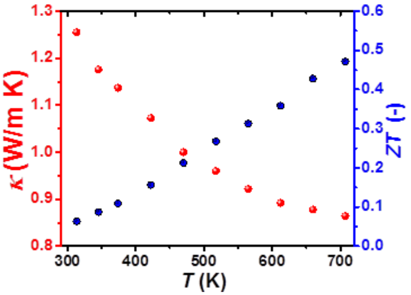

Figure 2: Thermal conductivity κ and figure of merit ZT of $Ag_6Ge_{10}P_{12}$.

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OA3-6.4

Physical properties of the new rare earth clathrates $Ba_{8-x}Eu_xAu_ySi_{46-y}$

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Abstract

Intermetallic clathrates have potential as thermoelectric materials for waste-heat recovery application, in particular if based on a silicon framework [1]. Substitutions with transition metal atoms add flexibility in tuning the charge carrier concentration. $Ba_8Au_ySi_{46-y}$, for instance, shows a metal-insulator transition as function of y [2,3]. The incorporation of some rare-earth elements into the clathrate cages leads to an enhancement of the Seebeck coefficient via electronic correlation effects [4,5]. Here, we report a study of the low-temperature transport and magnetic properties of single-crystalline $Ba_{8-x}Eu_xAu_ySi_{46-y}$ (x = 1.0, 1.7 and y = 4.8, 5.3) type-I clathrates. Our investigations show that a transition from *n*- to *p*-type conduction takes place with increasing the Au content. The *n*-type sample presents a large maximum in the phonon thermal conductivity κ_{ph} due to the freezing of three phonon Umklapp scattering processes at low temperatures. The maximum of κ_{ph} in the *p*-type sample is strongly reduced, which we attribute to an enhanced phonon-electron coupling and to a larger Eu content. The Seebeck coefficient is well described by a diffusion term, evaluated in the free-electron approximation. Both samples are metallic and ferromagnetic, with Curie temperatures T_C of 3.1 K and 10 K for x = 1.0 and 1.7, respectively, and effective magnetic moments of ~ 7.2 μ_B, confirming the Eu^{2+} state.

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

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A4. Tellurides

OA4.1

Electronic structure and thermoelectric properties of As_2Te_3 studied from first principles

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Abstract

As_2Te_3 belongs to the tetradymite family of materials. Unlike Bi_2Te_3, it may be synthesized in two polymorphic phases, rhombohedral (β) and monoclinic (α). Interesting thermoelectric properties of both phases of As_2Te_3 have been recently reported [1, 2]. In this work, electronic structure and transport properties of n- and p-type, alpha and beta phases of As_2Te_3 are studied using first principles calculations methods, in order to understand and optimize the thermoelectric performance of this material. For the pure compounds of both rhombohedral and monoclinic As_2Te_3, band structures and Fermi surfaces (Fig. 1) are computed, and the transport properties are studied using the Boltzmann approach. Electronic structures of the realistic cases of materials containing defects, vacancies and various dopants, are studied basing on the KKR-CPA method [3]. Theoretical results are compared to the experimental findings and help to design the efficient doping strategy, which involves classical and resonant impurities.

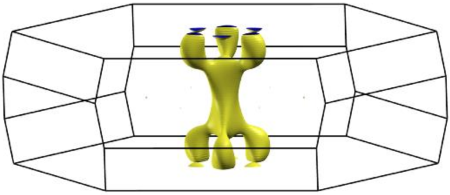

Figure 1: Fermi surface of n-type β-As_2Te_3

References:

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OA4.2

Synthesis of $AgSbTe_2$-based thermoelectric compounds by rapid solidification and hot pressing

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Abstract

$AgSbTe_2$-based compounds attract interest both from the experimental and computational points of view [1] owing to their good thermoelectric (TE) properties in the medium temperature range [2], and since they are constituents in high performance *LAST* alloys [3]. The δ-phase of the Ag-Sb-Te system, which is a Sb-rich off-stoichiometric $AgSbTe_2$ compound, decomposes below 633 K into Ag_2Te and Sb_2Te_3. Upon cooling, a microstructure of interconnected Sb_2Te_3/δ-$AgSbTe_2$ phases typically forms due to fast heterogeneous nucleation of Sb_2Te_3 on planar defects and grain boundaries [4], with consequent deterioration of TE properties.

The aim of this work is the stabilization of a homogeneous δ-$AgSbTe_2$ single phase by rapid solidification techniques (planar-flow casting and melt-spinning), avoiding the formation of primary Sb_2Te_3 lamellae upon quenching.

Rapidly solidified samples are in form of flakes with different thickness (60-400 µm). The cross section of the flakes shows a columnar microstructure with grains that are getting smaller with decreasing flake thickness. Thick flakes (thickness above 100 µm) exhibit isolated Sb_2Te_3 precipitates dispersed in the δ-$AgSbTe_2$ matrix, with no apparent continuous interconnected Widmanstätten microstructure. Conversely, thin flakes (thickness below 100 µm) consist of a homogeneous δ-$AgSbTe_2$ single phase with no residues of the Sb_2Te_3-phase. The lattice parameter of the δ-$AgSbTe_2$ phase progressively increases with the cooling rate, indicating progressive supersaturation of the matrix for high degree of super-cooling.

Bulk samples were obtained by hot pressing of the as-milled rapidly solidified flakes. Sintered samples show lower thermal conductivity (κ), higher Seebeck coefficient (S) and lower electrical conductivity (σ) values with respect to as-cast samples. On the one hand, the decrease of κ and the increase of S can be related to the stabilization of the δ-$AgSbTe_2$ single phase. On the other hand, the decrease of σ can be likely explained by the lattice distortion of supersaturated δ-$AgSbTe_2$ single phase and the presence of a high density of defects, due to the rapid solidification process. Further heat treatments under controlled conditions are expected to further homogenize the microstructure, providing enhanced TE performance.

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OA4.3

Materials for high temperature thermoelectric power generation (>1100 K)

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[2]*California State Polytechnic University, Pomona, California, USA*
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Abstract

In addition to the well-established need for highly reliable space power systems, there is renewed interest in developing practical new materials capable of efficient thermal-to-electric conversion by coupling to high grade heat sources (1100 K up to 2000 K), such as generated through fossil fuel combustion or produced from a high temperature waste exhaust stream. Segmented and cascaded modular device architectures that combine multiple materials, each operating at high efficiency, provide unique flexibility when designing for maximum thermoelectric converter performance and robustness.

Proven state-of–practice $Si_{0.8}Ge_{0.2}$ alloys are unpractical, due to the cost of Ge but more importantly because of their low thermoelectric and mechanical compatibility with the most mature lower temperature materials, such as skutterudites, that are available today.

Refractory n-type rare-earth based selenides and sulphides, as well as p-type boride compounds have been explored in the 1980's for use in devices up to 1800 K. For applications below 1300 K, complex p-type 14-1-11 Zintl antimonides have been more recently identified as practical high performance thermoelectric materials and they, just like their n-type rare earth tellurides counterpart, typically share similar favorable characteristics for their use at high temperatures. In addition to good mechanical compatibility with each other and with skutterudites, they exhibit semi-metallic behavior, with low to very low lattice thermal conductivity values and reasonably large thermopower values near their peak operating temperatures. Approaches for tuning the properties of these rare earth compounds have focused on suitable chemical substitutions and inert particles compositing coupled with guidance from first principle electronic structure simulations. We present an overview of recent collaborative research efforts aimed at optimizing the performance of these materials and facilitating their integration into thermally and mechanically stable high efficiency (≥15%) segmented devices.

OA4.4

Influence of powder size on thermoelectric properties of p-type 25%Bi_2Te_3-75%Sb_2Te_3 alloys fabricated using gas-atomization and spark-plasma sintering processes

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Abstract

Developing high efficient thermoelectric materials is one of the essential aspects for energy conversion applications[1]. In order to investigate the effect of grain size on thermoelectric performance, different size range of powder particles of 25%Bi_2Te_3-75%Sb_2Te_3 thermoelectric alloys were successfully fabricated by Gas-atomization and spark plasma sintering (SPS) processes[2,3]. The crystal structures of as-atomized powders and SPSed bulk samples were analyzed by X-ray diffraction (XRD) and their cross-sectional microstructures were observed by the scanning electron microscopy (SEM). The micro hardness values were increased with decreasing grain size and obtained maximum 80 Hv for <30μm SPSed samples. The Seebeck coefficient values were greatly enhanced by 52% for <30μm powder SPSed sample compared to GA sample through potential barrier scattering mechanism. The electrical conductivity and thermal conductivity values were decreased with decreasing the grain size. The thermal conductivity of <30μm powder SPSed sample is around 0.85 $Wm^{-1}K^{-1}$ which is decreased by 36% of its GA powder sample thermal conductivity, due to the fine microstructure which enables scattering of carriers at grain boundaries. The ZT value for <30μm and 32~75μm bulk samples exhibits a ZT of 1.1 at 300 K and 1.23 at 350 K respectively.

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OA4.5

Thermoelectric properties of PbTe films and PbTe-based superlattices

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Abstract

Thermoelectric properties of PbTe films and PbTe-based superlattices are discussed. Bi doped PbTe, EuTe/PbTe, and PbTe/PbSnTe superlattices were prepared by hot wall epitaxy, and temperature dependence of electrical conductivity and Seebeck coefficient were measured. In the n-type films and superlattices, main scattering mechanisms are nonpolar phonon scatterings, and temperature dependence of conductivity and Seebeck coefficient are well explained by the theoretical calculation. Electrical conductivity and Seebeck coefficient of p-type PbTe are well explained by considering indirect Σ valleys with heavy effective masses. GeS/PbTe amorphous / epitaxial superlattices useful to decrease the thermal conductivity are presented also.

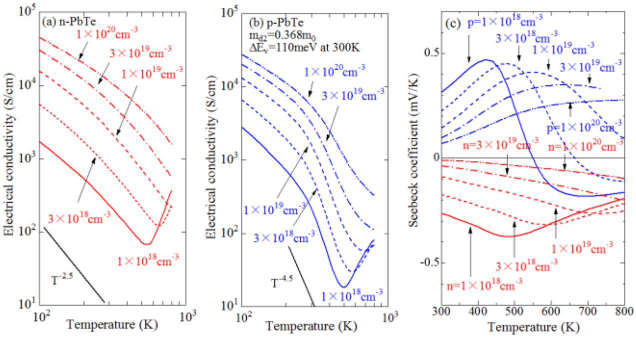

Figure 1: Theoretical temperature dependence of conductivity for (a) n-type PbTe, (b) p-type PbTe, and (c) temperature dependence of Seebeck coefficient for n- and p-type PbTe.

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A5. Bismuth and related materials
&
A8. Silicides

OA5-8.1

Increasing the figure of merit of Bi2TexSe3-x alloy for thermoelectric power generation applications by optimization of the preparation process

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Abstract

In an attempt to find new alternative energy resources new technological developments must be made to bring society one step closer to a cleaner environment. The rising awareness of the global warming effect as well as the steady decline in the quantity of current resources and subsequently the climb in their price drive the search for improving current energy usage and finding new energy resources. Thermoelectric devices take thermal heat, either directly from solar energy or as a byproduct of fuel burn, and transform it to electricity.

The efficiency of thermoelectric devices can be gauged by the dimensionless figure of merit ZT of the material, defined as $ZT = \alpha^2\sigma T/k$, where α, σ, k and T are the Seebeck coefficient, the electrical conductivity, the thermal conductivity and the temperature in Kelvin, respectively. The inter-correlated σ, α and k make it difficult to improve the thermoelectric performance in a satisfactory way just by electronic doping approaches.

Bismuth–telluride-based alloys are of great importance not only as the best thermoelectric materials with the maximum ZT values close to unity near room temperature, but also due to the potential for further performance improvement.

Since these alloys are highly anisotropic, there is a direct relation between the orientation and the thermoelectric properties of the ingots. Hence, higher ZT values can be achieved by improving the orientation anisotropy of the ingots. In this study the Bi2TexSex composition was optimized by various CHI3 doping, preferred alignment of the crystallographic orientation, and lattice thermal conductivity minimization. The synthesis route included rocking furnace melting, energetic ball milling or by mortar and pestle and hot pressing with optimal parameters for enhancement of the thermoelectric figure of merit, ZT, at temperatures higher than 200oC, commonly applied in low temperature power generation applications. The transport properties in the directions perpendicular to the pressing direction were examined was achieved.

OA5-8.2

Thermoelectric properties of isotropic $Bi_xSb_{2-x}Te_3$ by mechanical alloying and followed by hot pressing

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Abstract

Bi_2Te_3–Sb_2Te_3 solid solution has a rhombohedral crystal structure with the *R3m* space group, and anisotropic physical and thermoelectric properties [1]. The anisotropies of the electrical and phonon thermal conductivities of Bi_2Te_3 are respectively estimated to be $\sigma_{/\!/}/\sigma_{\perp} \approx 3$ and $\kappa_{/\!/}/\kappa_{\perp} \approx 0.47$, for the values parallel and perpendicular to the *c*-basal plane, but the Seebeck coefficient is isotropic in case of melt growth [1]. Fine-grained and isotropic materials are prepared by mechanical alloying (MA). Inside of sintered compacts MA powders by hot pressing (HP) have random crystal orientations and refined structures, which decrease the thermal conductivity [2]. However the preferred orientation affects the electrical and thermal conductivities on the surface of the Bi_2Te_3-related materials sintered compacts as a result of thermal stress of heterojunction between the HP mold and sintered compacts arising from hot deformation process [3].

In present study, the isotropic $Bi_xSb_{2-x}Te_3$ were prepared by MA and followed by HP. Only millimeter-scale grains of the bismuth (5N), antimony (5N), and tellurium (6N) were used, to suppress contamination by a surface oxide layer. The raw materials were placed in a stainless-steel vessel with a milling ball made of a silicon nitride ceramic in a glove box filled with argon. MA was performed in a Fritch P-5 planetary ball mill at a maximum speed of 180 rpm for 30 h. The MAed powder was sintered by HP at 623 K under a uniaxial pressure of 147 MPa in an argon atmosphere. All sintered compacts were eliminated approximately 1 mm of the sintered compact surface. The Seebeck coefficient, electrical and thermal conductivities at room temperature were measured by constructed thermal contact, four point probe, and static comparison methods, respectively. The accuracies of these instruments were less than ±1%. The temperature dependence of Seebeck coefficient and electrical conductivity were measured by ZEM-3 from 300 K to 573 K (Advance-Rico). The accuracy of ZEM-3 was around ±7%.

As results, an isotropic $Bi_{0.3}Sb_{1.7}Te_3$ with a maximum dimensionless figure of merit $ZT = 1.16$ at 367 K was obtained by MA–HP.

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OA5-8.3

Fabrication of large scale Bi-Te based materials using gas atomization and spark plasma sintering process

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Abstract

Thermoelectric materials (TE) are playing a vital role in limiting greenhouse gas emissions, through their unique application in renewable energy technologies, which includes automobiles, power generators, refrigerators, gas sensors, aerospace and defense applications. In particular, Bi_2Te_3 based materials exhibits high thermoelectric performance at room temperature. However, these materials have poor mechanical properties and low productivity, which limits their broader applications. To resolve this problem, the powder metallurgy processes are beneficial for producing an efficient thermoelectric performance with high mechanical properties.

The purpose of this study is fabrication of large scale p-type Bi-Te based powder using gas atomization and subsequently consolidated to large diameter pellets around 25mm with 16-17mm thickness by spark plasma sintering techniques. The sintered bulk samples thermoelectric properties were analyzed at different positions pellets.

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OA5-8.4

Recycling Si kerf from Photovoltaics to Thermoelectrics.

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Abstract

The Mg_2Si compound is a very good candidate for thermoelectrics since it combines high ZT and environmentally friendly features. ZT up to 1.0 has been reported for the binary Mg_2Si system and reached 1.4 for the multinary $Mg_2(Si,Sn,Ge)$ materials. On the other hand, its availability in nature as well as its non-toxicity are significant advantages.

Although Si is a widely available material, recycling process is always a priority, when possible, in technology. Several processes have been developed to recover Si from the slurry waste produced during wire saw cutting of Si photovoltaic cells. In this work, high-density liquid and gravitational settling technique were used to separate Si and SiC powders after removal of organic medium and metallic impurities. The recovered powder was used as starting material and only Si source for Mg_2Si synthesis in order to evaluate its feasibility as well as to study its effect on the thermoelectric performance. The formation of Mg_2Si compound via solid state reaction was successful with the products containing also silicon carbide. Moreover, Bi was used as dopant and the thermoelectric properties of the doped Mg_2Si are also discussed.

OA5-8.5

First-principles study on thermal conductivity, Seebeck coefficient and electrical conductivity of Ca_3Si_4

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Abstract

Silicide semiconductors have attracted much attention for in-vehicle applications of thermoelectric materials Among a variety of silicides, Ca_3Si_4 has been predicted as a semiconducting material with 42 atoms in unit cell[1]. The complex hexagonal crystal structure could realize a low lattice thermal conductivity. We have previously reported the Seebeck coefficients and the phonon properties of Ca_3Si_4[2]. However, the thermal conductivity and the figure of merit (ZT) have not been clarified both experimentally and theoretically. In this study, we evaluated ZT value by calculating the lattice thermal conductivity and Seebeck coefficients using first-principles calculations. Figure 1(a) shows the cumulative lattice thermal conductivities of Ca_3Si_4 as a function of mean free path of the phonons. The main contribution of lattice thermal conductivity comes from phonons with the mean free path of over 10 nm. Figure 1(b) shows the carrier concentration dependence of ZT value of Ca_3Si_4 at 800K. The maximum ZT value of bulk Ca_3Si_4 reaches 0.8 while the ZT value exceeds 1.5 in the case of the grain size of around 10 nm. In the conference, we will report the thermoelectric properties of Ca_3Si_4 in detail. This work is based on results obtained from the Future Pioneering Program “Research and Development of Thermal Management and Technology” commissioned by the New Energy and Industrial Technology Development Organization (NEDO). This work is also supported by TherMAT.

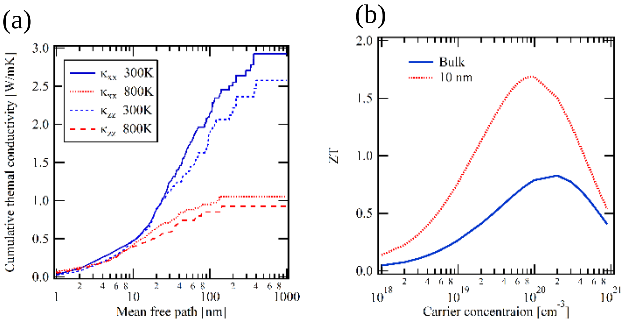

Figure 1: (a) Cumulative thermal conductivity of Ca_3Si_4, (b) Carrier concentration dependence of ZT (P-type) at 800 K.

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A7. Oxides

OA7.1

Effect of sintering aids and annealing time on the thermoelectric properties of $Sr_{0.61}Ba_{0.39}Nb_2O_{6-\delta}$

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Abstract

Morphology, crystal structure and thermoelectric behaviour of $Sr_{0.61}Ba_{0.39}Nb_2O_6$ (SBN61) were investigated as a function of sintering aid (0.5wt% MnO or B_2O_3) and annealing time in Ar/H_2 5% reducing atmosphere. Density measurements showed that SBN61 prepared with MnO or B_2O_3 sintered for 4h at 1598 K and at 1573 K respectively and annealed for 12h at 1623 K were at least 98% dense. SEM analysis showed that the grain sizes of sample with MnO and B_2O_3 annealed for 12h are 15.6 µm and 7.3µm respectively, but only MnO doped samples are completely crack free. XRD spectra indicated that all annealed SBN61 samples are predominantly single phase (tetragonal crystal structure) at room temperature; it was identified the presence of very small amounts of $MnNb_2O_6$ with NbO_2 and just NbO_2 secondary phases in samples prepared with MnO and B_2O_3 respectively. SEM and XRD analysis suggests tendency for Mn to react with Nb and tendency of B to cause sample micro and macro cracking in any Ar/H_2 5% reduction conditions. Measurement of thermoelectric properties revealed that samples annealed for 12h and prepared with MnO exhibited significantly higher Power factor (PF) values $\approx$ 490 µW/mK^2 and Figure of merit (zT) values $\approx$ 0.176 at 870 K, whilst sample's with B_2O_3 PF $\approx$ 375 µW/mK^2 and zT $\approx$ 0.157 at 870 K. The significant enhancement in PF and zT in samples prepared with MnO is attributed to the very high density, absence of micro-cracks and higher average grain size.

OA7.2

Promising thermoelectric properties of oxygen deficient (K,Na)NbO_3 ceramics

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Abstract

$(K_{0.5}Na_{0.5})NbO_3$ is a white compound that presents a perovskite structure [1]. Since Saito et al. [2] have reported a large d_{33} value in 2004, $(K_{0.5}Na_{0.5})NbO_3$ is largely studied as a lead free piezoelectric material to substitute to lead–zirconate–titanates. In a recent paper, Bah et al. [3] have shown that spark plasma sintering (SPS) allow synthesizing dense $(K_{0.5}Na_{0.5})NbO_3$ ceramics. However, these authors have shown that such sintering route leads to the formation of dark pellets that require air annealing to restore the white colour and present the piezoelectric properties. Indeed, without such an air annealing the dark $(K_{0.5}Na_{0.5})NbO_3$ samples breaks at low voltage during poling and present high electrical losses. They have attributed such a behaviour to an oxygen deficiency that leads to increase the electrical conductivity of such perovskites. Many oxides with a high electrical conductivity are studied for thermoelectric applications since the discovery of a large thermopower in the metallic oxide Na_xCoO_2. Among them, perovskites present some of the best n-type properties: recently, doped-$SrTiO_3$ ceramics have exhibited ZT values close to 0.4 at 1000 K [4]. Oxygen deficient $(K_{0.5}Na_{0.5})NbO_3$ present promising n-type thermoelectric properties. The electrical conductivity is still limited (circa 10^2 S/m) but the Seebeck coefficient is high (-(600-700) µV/K). The most remarkable feature compared to doped-$SrTiO_3$ is that thermal conductivity is low and stable over the 325-1000 K temperature range between 3.5 to 4 $Wm^{-1}K^{-1}$. These promising results will now have to be improved by controlled annealing, through cations substitutions on both alkaline or niobium sites or nanostructuration. The thermoelectric properties of $KNbO_3$ and $NaNbO_3$ will also be presented.

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OA7.3

Metal oxides thin films for transparent thermoelectric applications

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Abstract

The continuous search for environmentally friendly and abundant materials for efficient thermoelectric (TE) devices has lead to growing interest in the research of metal oxides, mainly transition metal oxides.

While bulk TE materials are foremost applied in high power and high temperature regimes, TE thin films (TE-TF) have their main field of application in low temperature and low power consumption electronic devices. Along with a reduction in material usage, TE-TF materials have also other advantages when compared to the bulk: higher degrees of freedom with in-plane geometry being adapted to the application requirements; possibility to be deposited on flexible substrates; and high transmittance in the visible range.

In this work, we present an overview of the TE optimization of eco-friendly metal oxides thin films, deposited either by rf magnetron sputtering or thermal evaporation, having transmittances up to 80% in the visible range: AZO [1], Cr/V_2O_5[2], graphite/V_2O_5[3], SnO_2[4] and Cu_2O. These films can be used in different type of applications from energy harvesting in large areas (as they have room temperature ZT up to 0.2) to transparent electronic devices, like temperature sensors or touch triggers (as they have Seebeck coefficients up to 1mV/K).

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OA7.4

Thermoelectric properties of amorphous InGaZnO thin film

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Abstract

Amorphous InGaZnO (*a*-InGaZnO) is n-type semiconductor material and has enormous potential such as transparency, a low temperature fabrication process. Thus, the application of *a*-InGaZnO to flexible electronics (thin film transistor) has been studied. Low thermal conductivity and a low temperature process are merit for a transparent and a flexible thermoelectric (TE) module application. Oxide TE materials can be also used for high temperature applications. Our group researched the dependence of carrier density in the *a*-InGaZnO thermoelectric properties [1,2]. Additionally, a transparent TE device was demonstrated using *a*-InGaZnO and ITO electrode. In this study, we evaluated a thermoelectric properties at high temperature range. Effects of a film thickness and a surface roughness were also measured. *ZT* value was 0.02 ~ 0.03 at 300 K and 0.14 ~ 0.2 at ~800 K (k = 1.0~1.4 W/mK ref [3,4]). Even amorphous material, the *ZT* value of *a*-InGaZnO was almost comparable with InGeO and AlZnO bulk materials (Fig.1). *PF* was decreased when the film thickness becomes thinner than 100 nm. This result was caused by a surface and an interface effect. By increasing surface roughness of substrate, defects were formed at the *a*-InGaZnO /sub interface. As a results, the electrical conductivity increased and the thickness effect was recovered.

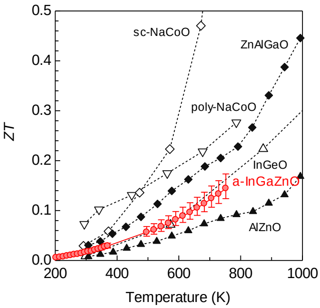

Figure 1: *ZT* values of various oxide materials [5-7] and *a*-InGaZnO film.

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OA7.5

Dependence of thermoelectric properties of CaO(CaMnO$_3$)$_m$ (m=1,2,3,∞) based oxides on lattice periodicity

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Abstract

Calcium-manganate based thermoelectric (TE) oxides of the CaO(CaMnO$_3$)$_m$ (m=1,2,3,∞)-form are good candidates for high-temperature power generation, and their TE performance strongly depends on their composition, as reflected by the m-value [1]. We study electronic and vibrational transport properties of these compounds applying the density functional theory (DFT) to elucidate their electrical and thermal transport behavior. The electronic properties of these compounds are analyzed in terms of band structure at the vicinity of the Fermi level (E_F). It is shown that the total density of states (DOS) values at E_F increase with increasing the m-value, which implies on increase of the electrical conductivity, σ, with increasing m-values, in full accordance with experimental results. Additionally, the calculated values of the relative slopes of the DOSs at E_F correlate with the experimentally-measured Seebeck coefficients [1].

The electrical conductivity was calculated in the framework of the constant relaxation time approximation. It is shown that the σ behavior is dominated by electron scattering on the boundaries between perovskite (CaMnO$_3$) and Ca oxide (CaO) layers inside the crystal lattice.

To elucidate the thermal conductivity behavior, the various contributions to the phonon relaxation time (τ) were calculated and analyzed applying well-established approaches [2]. We found that the thermal conductivity of CaO(CaMnO$_3$)$_m$ is governed by contributions from phonon scattering on CaO/CaMnO$_3$ layer boundaries (for m=1, 2, and 3) and Umklapp processes having characteristic relaxation times which are inversely proportional to the square Grüneisen parameter, γ [2]. Our calculated γ–values are close to 3 on average, a value which exceeds the typical value of γ~2. Our computational approach enables illuminating the TE behavior of these compounds.

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OA7.6

Design of structural defects in $SrTiO_3$-based materials for enhanced thermoelectric performance

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Abstract

Very recent works have highlighted good prospects for boosting thermoelectric performance in $SrTiO_3$ –based materials by introducing A-site deficiency [1,2]. This work focuses on detailed analysis of the changes in performance promoted by altering the defect chemistry. To compare the impacts from defect structure on thermoelectric properties, Ta- and Nb-substituted strontium titanates were selected as model systems. The prevailing defect types were controlled by introducing nominal A-site deficiency, from Ruddlesden-Popper-type (RP) and other oxygen-rich defects, confirmed by TEM (Fig. 1), to oxygen nonstoichiometry, estimated by TG. Combined electrical conductivity/TG/XPS studies suggest that presence of cation- and oxygen vacancies is favourable for high mobility of the charge carriers (Fig. 1). Noticeable deviations from stoichiometric oxygen content were found to decrease the lattice thermal conductivity (Fig. 1), suggesting good phonon scattering ability for oxygen vacancies, vacant A-sites and oxygen-excessive defects.

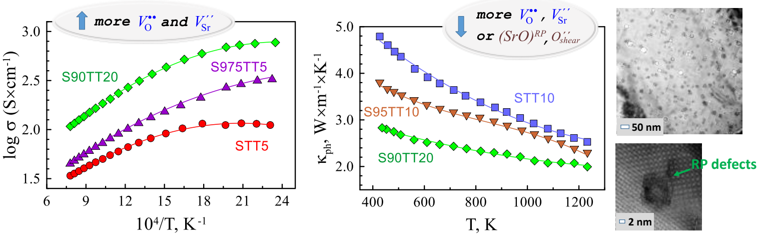

Figure 1: Temperature dependencies of the electrical conductivity (left), lattice thermal conductivity (centre) and high-resolutions TEM images (right) of $Sr_{1.05}Ti_{0.9}Nb_{0.1}O_{3\pm\delta}$ sample. The sample denominations correspond to $SrTi_{0.95}Ta_{0.05}O_{3\pm\delta}$ (STT5), $Sr_{0.975}Ti_{0.95}Ta_{0.05}O_{3\pm\delta}$ (S975TT5), $SrTi_{0.90}Ta_{0.10}O_{3\pm\delta}$ (STT10), $Sr_{0.95}Ti_{0.90}Ta_{0.10}O_{3\pm\delta}$ (S95TT10) and $Sr_{0.90}Ti_{0.80}Ta_{0.20}O_{3\pm\delta}$ (S90TT20).

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OA7.7

Materials for high temperature thermoelectric converters

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Abstract

Nanostructured chalcogenides (600 K < T < 700 K), half-Heusler compounds (700 K < T < 1000 K), and perovskite-type oxides (T > 1000 K), have been developed and tested for a large range of high operating temperature. The relation between sample preparation methods, microstructure, and transport properties are investigated to obtain high efficiency thermoelectric materials and devices. Perovskite-type ceramics as well as their nanocomposites are prospective candidates for the high temperature side of thermoelectric energy conversion processes [1-3] in exhaust gas catalysts, solar furnaces and solid oxide fuel cells. Here they are combining their catalytic activity with the thermoelectric function. Their good performance can be explained based on e.g. their suitable band structures, adjusted charge carrier density, effective mass and - mobility, hindered phonon transport, electron filtering potentials, and strongly correlated electronic systems. These properties are tuneable by changing the composition, structure, crystallites size, interfaces and materials combinations with tailor-made scalable synthesis procedures. The resulting improved thermoelectric generators are characterised and tested in diverse high temperature applications to improve the efficiency and energy density of the thermoelectric conversion process. The goal is to finally utilize the investigated materials to convert large temperature gradients from concentrated solar systems and other forms of wasted heat into electricity.how to prepare your camera-ready to A5 format (14.8 × 21 cm or 5.8 × 8 inches); with the margins: bottom 1.5 cm (0.59 in) and top 2 cm (0.79 in), right/left margins must be 2 cm (0.79 in).

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OA7.8

Improved thermoelectric properties of $Sr_{0.9}Nd_{0.1}TiO_3$ co-doped with boron and zirconium

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Abstract

Donor-doped $SrTiO_3$ ceramics show promising features for thermoelectric applications [1]. In this study, high density $Sr_{0.9}Nd_{0.1}TiO_3$ ceramics with 0.5 wt% B_2O_3 and varying ZrO_2 content (x=0, 0.2, 0.3, 0,4 and 0.8 wt%) were prepared by the mixed oxide route. B_2O_3 addition allowed densification of the samples at low temperature of 1673 K in a single step sintering process under reducing atmosphere. Additionally, the effect of different sintering times (4 to 24 hours) on microstructural development and thermoelectric properties was investigated.

Structural characterisation of the samples was carried out by both Synchrotron X-ray diffraction and electron diffraction techniques. Study revealed that the samples had tetragonal symmetry (S.G. I4/mcm). Microstructural analysis by HRTEM and aberration corrected STEM-HAADF showed a high density of dislocations and phase-transformation induced sub-grain boundaries acting as source of phonon scattering, promoting a low thermal conductivity of ~3.3 W/Km at 1000 K. XPS results revealed that there was a slight increase in [Ti^{3+}] with ZrO_2 content up to 0.3 wt.%. Furthermore, additions of ZrO_2, up to 0.3 wt%, significantly improved electrical conductivity, resulting from enhanced carrier mobility. This was supported by transport property measurements showing an increase in power factor mainly resulting from enhanced electrical conductivity while the Seebeck coefficient was in the same range for all the samples. In the optimised samples a power factor of 2.0 x 10^{-3} W/mK^2 was obtained at 500 K. This is a ~ 30% improvement with regards the highest values reported value for un-doped $Sr_{0.9}Nd_{0.1}TiO_3$ [2]. The highest ZT value was 0.33 at 1000 K for $Sr_{0.9}Nd_{0.1}TiO_3$ with 0.5 wt% B_2O_3 and 0.3 wt% ZrO_2 additions prepared by sintering at 1673 K for 12 hours under reducing atmosphere.

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OA7.9

The effect of stoichiometry on the crystal structure and thermoelectric properties of $Bi_{2+x}Sr_2Co_2O_y$

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Abstract

(Bi – Sr – Co – O) based compounds are among the candidate materials for high temperature applications as *p* – type thermoelectrics [1]. High quality $Bi_{2+x}Sr_2Co_2O_y$ (X= 0.0, 0.1, 0.2) ceramics were prepared by the mixed-oxide and Spark Plasma Sintering (SPS) method. Structural characterisation of the samples was carried out by both Synchrotron X-ray diffraction and electron diffraction techniques. The results revealed that the samples had misfit type structure with a doubled c-axis. Structural observations along [100], [010] and [110] directions using aberration corrected STEM-HAADF showed three distinct arrangements between Cobalt oxide layers CdI_2 type hexagonal structure layers and $Bi_2Sr_2O_4$ Rock Salt layers. The secondary phase $Bi_{0.75}Sr_{0.25}O_{1.375}$ was observed in the microstructure, increasing with the amount of bismuth doping. HRTEM study showed an ordered Aurivillius type structure for this phase. The effect of these phases on thermoelectric properties was evaluated. Samples of $Bi_{2.2}Sr_2Co_2O_y$ showed lowest electrical resistivity leading to ZT of 0.10 at 900K. $Bi_{2.2}Sr_2Co_2O_y$ exhibited the following thermoelectric properties: Electrical resistivity, ρ=18-21 mΩ.cm, Seebeck coefficient, S = 110-155 μV/K, thermal conductivity, κ = 0.6-0.8 W/m.K, and ZT = 0.04 - 0.1 over 300-900K temperature range.

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OA7.10

An innovative n-type thermoelectric oxide: the adaptive structure of the tetragonal tungsten bronzes $Nb_{8-x}W_{9+x}O_{47}$

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Abstract

Materials for thermoelectric applications are required to possess a low thermal conductivity combined with good electrical properties to fulfil the concept of "phonon-glass electron-crystal". In this scenario, materials with an engineered nanostructure can offer an important contribution. Within the structural family of the tetragonal tungsten bronzes (TTB), the tungsten niobium oxides $(Nb,W)_{17}O_{47}$ [1] seem to be promising n-type oxides for thermoelectric applications. The general stoichiometry of these compounds is $Nb_{8-x}W_{9+x}O_{47}$, with $x = 4$ representing the upper limit of the series. Upon substitution of Nb^{5+} by W^{6+}, the overall charge carrier concentration can be manipulated to reduce the electrical resistivity down to values proper of a doped semiconductor material. At the same time thanks to a layered nanostructure and to the presence of intrinsic crystallographic shear planes, the thermal conductivity is expected to be maintained constantly low over the whole substitution range.

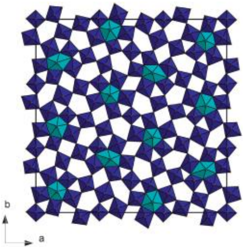

Figure 1: Crystal structure of the TTB $Nb_{8-x}W_{9+x}O_{47}$ viewed along the c axis. The dark blue and turquoise polyhedra represent distorted mixed metal-centered octahedra and pentagonal bipyramids, respectively, with oxygen atoms situated on the corners and a mixed Nb/W occupancy of the central cation. [2]

Starting from this idea, we synthesized the whole series $Nb_{8-x}W_{9+x}O_{47}$ $(0 \leq x \leq 4)$ and we carried out a complete high temperature (above 1100 K) thermoelectric characterization of the phase pure compounds.

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OA7.11

Crystal and electronic structure of thermoelectric $[Bi_{0.87}SrO_2]_2[CoO_2]_{1.82}$

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Abstract

$[Bi_{0.87}SrO_2]_2[CoO_2]_{1.82}$ (BSCO) is one of the best *p*-type thermoelectric oxide materials but its structural and electronic properties are little understood. Here we investigate the crystallographic and electronic structure as well as thermoelectric transport properties using density functional theory and Boltzmann transport calculations. BSCO is a misfit-layered compound composed of two incommensurate subsystems – crystalline hexagonal CoO_2 layers and double rocksalt-type $BiSrO_2$ layers and we identify the most stable structures by considering different structural approximations between these subsystems. We present a structural model for BSCO that agrees well with the X-ray data and high-angle annular dark-field imaging and provide data on its electronic, magnetic and transport properties. We show that Bi-deficiency leads to a band-gap opening and increases p-type electronic conductivity of the material due to formation of Co^{4+} species that serve as itinerant holes within the predominantly Co^{3+} framework of CoO_2 layer. The relationship between the hole-doping mechanism and the Bi defect, through the changes of the local structure is evaluated. The reliability of the simulations is supported by the calculated temperature dependence of the Seebeck coefficient for the Bi-deficient BSCO, which is in good agreement with the measurements further stressing the importance of the Bi deficiency for this material. Moreover, we shed light on the apparent stacking disorder of the $BiSrO_2$ layers that can take different arrangements between CoO_2 layers. We find that such a disorder arises from the minor energetic difference between different relative arrangements of CoO_2 and BiSrO layers in consecutive layers of BSCO and can be related to the low thermal conductivity of the material. Our study shows that the first principle calculations can provide detailed understanding of the properties of this complex material, which make them a valuable tool for developing and testing new oxide thermoelectric materials.

A9. Selenides and Sulfides

OA9.1

Thermoelectric properties of nanostructured SnSe derivatives prepared by arc-melting technique

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Abstract

Unprecedented thermoelectric properties have been recently reported in p-type single crystal SnSe with extraordinarily high, positive, Seebeck coefficient and an extremely low thermal conductivity. These excellent features are described in the threshold temperature of a structural phase transition from the low temperature *Pnma* structure to the high temperature *Cmcm* structure.

In order to enhance thermoelectric efficiency through proper tuning of this material we report on the structural characterization and assessment of the thermoelectric properties of doped tin selenide compounds prepared by a straightforward arc-melting method, which yields nanostructured polycrystalline materials.

SnSe pellets prepared by arc-melting present a nearly perfect stoichiometric structure, higher Seebeck coefficients and even slightly lower thermal conductivity than single crystals.[1]

Electron donor effect by Sb doping produces a change in the type of primary charge carriers, which turnouts into large, negative Seebeck coefficients. Moreover, the increased amount of Sn defects and the mentioned layered nanostructure, accounts for a reduction of the thermal conductivity, which is highly desirable for thermoelectric materials.

Lattice point defects in Ge-doped SnSe have been found to produce a notable effect in the thermoelectric properties, yet the electrical properties show a semiconductor behavior with resistivity values higher than that of the parent compound, whereas the Seebeck coefficient is higher and thermal conductivity lower, favorable to a better ZT figure of merit.

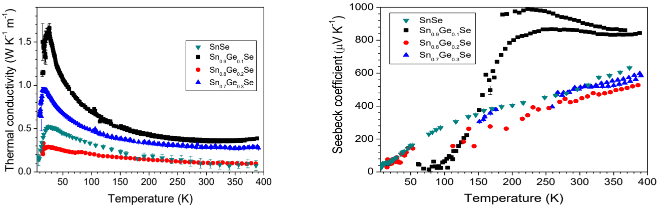

Figure 1: a) thermal conductivity and b) Seebeck coefficient vs temperature for $Sn_{1-x}Ge_xSe$ (x= 0.1, 0.2, 0.3) compounds.

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A9.2

Non-stoichiometry in TiS_2-based thermoelectrics induced by pulsed-electric-current sintering

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Abstract

Thermoelectric materials based on non-toxic and abundant titanium disulphide have been recognised as a possible alternative for the telluride-based alloys utilized at near-room and mid-temperatures [1]. Several studies have demonstrated a promising potential of TiS_2 below 670K, with PF over 1.7 mW/mK at room temperature, and ZT up to 0.5 at 700 K [1-3]. However, at temperatures above 770K, which are necessary for the solid-state synthesis of TiS_2, self-intercalation of Ti atoms into van der Waals gap occurs due to deviation from stoichiometry caused by sulphur volatilisation. Such structural changes affect the charge-carrier concentration and consequently significantly impact the thermoelectric properties of TiS_2 [2]. Moreover, sulphur losses during the solid-state synthesis and consolidation have been found to deteriorate thermoelectric properties in several TiS_2-based materials [2-4]. Determination of sulphur losses during processing is thus necessary for optimization of thermoelectric performance of TiS_2-based materials. By performing an accurate analysis of stoichiometry using XRD, TGA and ICP-AES, we determined that substantial off-stoichiometry can occur during consolidation of TiS_2, and that self-intercalation of Ti-atoms is progressively induced with higher sintering temperatures, which significantly affects the ZT of the material. We identified pulsed-electric-current sintering conditions (temperature and pressure) at which bulk TiS_2 can be prepared highly stoichiometric with high bulk density. Furthermore, we found that it is possible to diminish the sulphur volatilization and suppress the sulphur deficiency even at high sintering temperatures by using a gas-tight sintering mould. The ability to consolidate TiS_2-based materials without sulphur deficiency is of crucial importance for the future engineering of optimal transport properties for achieving high ZT values.

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OA9.3

The effect of electron and hole doping on the thermoelectric properties of the shandite $Co_3Sn_2S_2$

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The scarcity and cost of tellurium coupled with the limited thermal stability of Bi_2Te_3 have motivated the search for new Te-free materials for energy recovery, particularly at temperatures appropriate to low to medium-grade waste heat. Metal sulphides are attractive candidate thermoelectric (TE) materials, owing to the low cost and ready availability of sulphur. Here we describe the impact of chemical substitution on the TE properties of the metal-rich sulphide, shandite, $Co_3Sn_2S_2$.

The shandite structure consists of two-dimensional kagome-like Co_3Sn layers capped by sulphur and linked through trigonal antiprismatically coordinated Sn atoms (Fig. 1). Following our recent demonstration that substitution at the tin site markedly improves the TE figure-of-merit [1], we will describe here the effect of substitution at the transition-metal site.

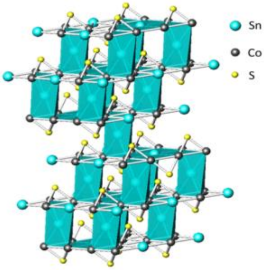

Figure 1: Shandite Structure.

Preparation of series $Co_{3-x}M_xSn_2S_2$ has enabled the impact on TE properties of both electron (M = Ni) and hole (M = Fe) doping to be explored. Nickel substitution increases the metallic character of the materials, leading to increased electrical and thermal conductivities. Conversely, iron substitution leads to a transition from metallic to n-type semiconducting behaviour and improves the TE properties. Furthermore, we have combined iron substitution with substitution at the tin site to optimise the TE properties through synthesis of materials $Co_{2.667}Fe_{0.333}Sn_{2-y}In_yS_2$ ($0 \leq y \leq 0.7$). Physical property measurements reveal a large increase in the Seebeck coefficient, which in combination with the reduction of thermal conductivity, contributes to a further rise of the figure-of-merit, ZT = 0.28 at 473 K.

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OA9.4

Scalable fast route for Ni and Zn doped tetrahedrite thermoelectric material production

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Abstract

Tetrahedrite mineral family, one of the most widespread sulfosalts on Earth's crust, seems to meet the right features for an attractive sustainable p-Type Pb-free thermoelectric material, showing relatively high conversion efficiency, achieving a figure of merit value of almost 1 at 450°C [1,2].

In this work, Ni-Zn co-doped tetrahedrite samples were prepared by Open Die Pressing one step reactive consolidation method [3], employing previously ball milled sulphide powder precursors, in order to identify a simple cheap scalable fast production route for thermoelectric pellets.

The influence of dopant presence and reactive consolidation process parameters on the tetrahedrite phase content, stoichiometry and density of the samples were investigated by X-ray diffraction, scanning electron microscope (equipped with energy dispersive X-ray spectroscopy), and thermogravimetric analysis. Laser Flash Analysis, electrical conductivity, and Seebeck coefficient measurements were carried out for obtaining a complete thermoelectric characterization.

Acknowledgments

The authors are grateful to Stefano Boldrini (CNR-ICMATE) for the valuable discussion about the results, to Enrico Bassani (CNR-ICMATE) for his essential technical supports, and Raul Carampin (CNR-IGG) for the inestimable help, advices and data discussion about the quantitative EDS analyses.

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OA9.5

Investigation of some new sulfides based thermoelectric materials

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Abstract

Over the last decade, thermoelectric (TE) materials have considerably drawn global interest in research and development due to the need to find a sustainable future source of energy. Indeed, numerous sectors could take advantage of the thermoelectric materials capacity to directly convert the waste-heat into electrical energy and then contribute to close energy crisis and global climate change. For low and medium temperature range applications (*i.e.* below 700 K) best performances are currently obtained by $AgPb_mSbTe_{2+m}$ and Zn_4Sb_3 compounds which exhibit ZT values higher than 1.70 and 1.35 at 700 K respectively [1]. Nevertheless, the generally complex and costly synthesis processes, together with the scarce and toxic compounds used, prevent the use of these complex thermoelectric materials for large scale applications. Many efforts were therefore been made in order to find new environmentally-friendly TE compounds which not only exhibits high performance, but also possess the potential to be produced on large scale. Based on this trend, the high TE performance together with the potential for economical, large scale production makes sulfide based TE materials very promising candidates for the construction of competitive TE generators [2]. In that respect, the high Power Factor (PF) value reported for copper based ternary sulfides, together with the cheap, non-toxic and abundant precursors used for synthesizing them, prompted us to further investigations regarding this system.

Thus, through this presentation, we will describe and discuss the TE properties of some promising new sulphide compounds.

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OA9.6

Thin films of Cu_2Se with high thermoelectric efficiency grown by pulse controlled reactive sputtering

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Current interest in thermoelectric materials (TE) focuses on their ability to transform a temperature difference in a voltage difference (Seebeck effect). Similarly, the obtention of a temperature difference due to an applied electric voltage (Peltier effect), allows to use them as heat sources and sinks in industrial applications as an alternative cooling devices. Recently crystalline p-type Cu_2Se bulk material has been synthesized with excellent thermoelectric properties [2]. In this work we report a novel approach on the growth of highly efficient thermoelectric materials via pulse controlled reactive magnetron sputtering. This technique allows for a fine control of the stoichiometry of the films, of their texture or crystallographic orientation and of their thermoelectric properties and it is shown to be fully reproducible and scalable to the industry. Moreover, the whole process takes place at low room temperature without further post-selenization or post-annealing treatments, which allows the production of excellent polycrystalline selenide films even on polymer or flexible substrates. Figure 1 shows experimental results on the promising thermoelectric properties of thin films of p-type $Cu_{2+x}Se$, deposited by our particular reactive sputtering method both at 200ºC and at room substrate temperature. The extremely wide range of Cu to Se ratio in the grown films with nearly constant Seebeck and electrical conductivity values is due to the segregation of excess Cu atoms in the matrix to Cu nano-clusters at grain boundaries as observed on TEM images. These results, along with fact that this material is a high temperature stable super ionic conductor, makes it especially encouraging for a wide range of applications, reaching a thermoelectric figure of merit of 1.5 at 1000 K [2].

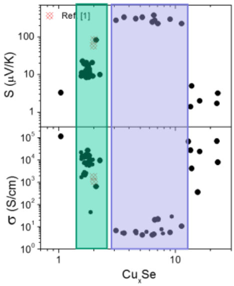

Figure 1: Seebeck and electrical conductivity at room temperature as a function of the compositional ratio Cu/Se @ RT. The values marked with a red cross are taken from [2].

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OA9.7

Microstructure and thermoelectric properties of mixtures of natural and synthetic tetrahedrite

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Abstract

Recently, naturally occurring sulfosalt minerals from the tetrahedrite-tennantite series $(Cu,Ag)_{10}(Fe,Zn,Cu,\dots)_2(Sb,As)_4S_{13}$ have been proposed for direct use in manufacturing moderate temperature thermoelectric devices [1,2]. The high thermoelectric potential of these abundant sulfosalt minerals lies within their extremely low lattice thermal conductivity and high Seebeck coefficient, giving rise to *ZT* values close to unity.

It has been shown that mechanical alloying can be used for their rapid synthesis, either making use of natural minerals as a starting material [2,3] or even directly from stoichiometric mixtures of elements [4]. In this contribution, we report on the microstructure and thermoelectric properties of mixtures of natural and synthetic tetrahedrite prepared via two different routes: simple mixing and grinding in an agate mortar and high energetic ball milling.

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OA9.8

Influence of selenium for sulfur substitution on high temperature thermoelectric properties of Bornite

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Abstract

Sulfosalt minerals such as tetrahedrite and bornite [1,2,3,4] exhibit promising thermoelectric properties thanks to their intrinsic low thermal conductivity and tunable electronic transport properties. In the present work, we have investigated the thermoelectric transport properties of solid solution of bornite $Cu_5FeS_{4-x}Se_x$ ($0 \leq x \leq 0.6$) compositions in the temperature range of 300-620 K. Selenium for sulfur substitution results in a significant reduction in electrical resistivity over the pristine Cu_5FeS_4, which leads to an improvement in the power-factor. The electrical resistivity has been reduced effectively by nearly an order of magnitude compared to the pristine bornite with selenium substitution. The electrical resistivity reduces from ~ 22 mΩ cm for the pristine Cu_5FeS_4 to ~ 3.95 mΩ cm for $Cu_5FeS_{3.4}Se_{0.6}$ at room temperature as shown in Figure 1. A maximum power factor of 5.2×10^{-4} W/mK^2 is attained at 615 K for x = 0.3 composition. Thermal transport measurements indicate a reduction in lattice thermal conductivity by introduction of selenium at the sulfur site. Surprisingly, the Hall effect measurements indicate that the carrier concentration decreases with the increase of selenium concentration. Single parabolic band approximation calculations indicate that the reduction in electrical resistivity with selenium substitution is mainly attributed to the reduction of carriers effective mass and increase in mobility which is originating from the broadening of the valence band. A maximum ZT of 0.57 is attained at 620K for $Cu_5FeS_{3.8}Se_{0.2}$ composition.

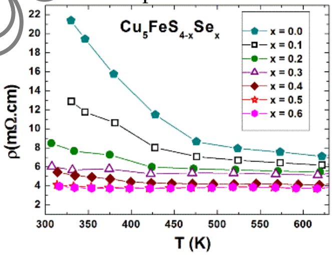

Figure 1. Temperature dependence of the electrical resistivity in the series $Cu_5FeS_{4-x}Se_x$ ($0 \leq x \leq 0.6$).

References:

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A10. Organics

OA10.1

Flexible thermoelectric generators using organic materials by printing process

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Abstract

Thermoelectric energy conversion is an attractive and environmentally friendly way to recover energy from industrial waste heat or natural heat because of its potential for improving the energy efficiency. As thermoelectric materials, organic materials have unique advantages, such as cost effectiveness, low intrinsic thermal conductivity, high flexibility, and amenability to large area applications. Therefore, organic conducting polymers, which possess good electrical conductivity, have been actively researched. Herein, we present a convenient method for enhancing the thermoelectric properties of inorganic-based nanostructures coated with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (PEDOT:PSS hybrid) by simple chemical treatment. Significant enhancement of the electrical conductivity of PEDOT:PSS hybrids was achieved by simple chemical treatment with H_2SO_4. The power factor of the developed materials could be effectively tuned over a very wide range depending on the concentration of the H_2SO_4 solution used in the chemical treatment. The power factors of the developed thermoelectric materials were optimized to 284 μW $m^{-1}K^{-2}$. Using the BiTe-PEDOT:PSS hybrids, a flexible thermoelectric generator that could be embedded in textiles was fabricated by a printing process. This thermoelectric array generates a thermoelectric voltage of 2 mV using human body heat [1,2].

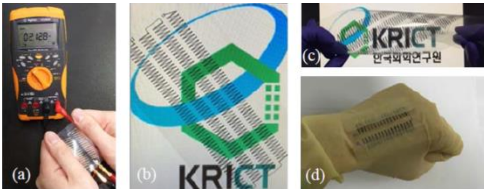

Figure 1: (a) Generation of electricity by grabbing both sides of the thermoelectric array at room temperature; (b), (c) images of the flexible and twistable thermoelectric generator comprising 240 legs arranged in four rows, and (d) demonstration of the thermoelectric generator embedded in a glove for the generation of electricity by human body heat.

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OA10.2

Photoinduced p- to n-type switching in thermoelectric polymer-carbon nanotube composites

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Abstract

Nanocomposites of conjugated polymers and carbon nanotubes are promising materials for large-area thermoelectric generators that operate at room temperature. They combine the high electrical conductivity of nanotubes with the low thermal conductivity and solution processability of polymers. While encouraging power factors have been achieved for composites with positive Seebeck coefficients (S>0, p-type) [1], air-stable organic n-type materials pose a real challenge. Here we report on composites of regio-regular poly(3-hexylthiophene-2,5-diyl) (rr-P3HT) and nitrogen-doped multi-walled carbon nanotubes (nCNTs), which can exhibit either S>0 or S<0. N-type behavior can be obtained by increasing the nCNT content of a p-type composite. However, we found a more powerful way by UV-irradiating a solution of p-type composite during deposition [2] (see Fig. 1). Using the developed method, we demonstrate a thermoelectric module, where both types of legs are deposited from the same solution and whose design takes full advantage of flexible substrates.

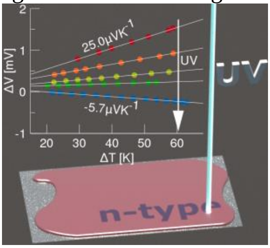

Figure 1: Seebeck voltage versus temperature difference for a P3HT/CNT composite as a function of UV irradiation.

References:

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OA10.3

Thermoelectric properties of PEDOT nanocomposites with electrochemically tuned oxidation state

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Abstract

Room temperature thermoelectric application of conjugated polymer poly(3,4-dioxyethylenthiofene) (PEDOT) has recently gained a lot of attention due to its peculiar features such as low cost, safety and possibility to easily process it, which makes it an interesting alternative to tellurides commonly used in this field [1]. In spite of these advantages, nowadays the main drawback of PEDOT is its low thermoelectric efficiency that has still to be successfully addressed. Two interesting paths have been explored: the first involves the development of PEDOT based nanocomposites [2], including nanostructured material into the polymer, in order to generate nanometric size related effects (e.g. energy filtering). The second one deals with the optimization of the oxidation state of the polymer, since it sets its electronic properties [3]. Considering both strategies, we prepared PEDOT nanocomposites, embedding inorganic nanoparticles (INPs) of Mn_3O_4 and CuO (Figure 1) in different concentration, and achieved a fine tuning of the oxidation state through an electrochemical path. This combined strategy allowed to analyse the dependence of the electric and thermoelectric properties on the applied electrochemical potential (Figure 2). Results will be discussed, showing the correlation between the two transport coefficients and the nanocomposite oxidation state.

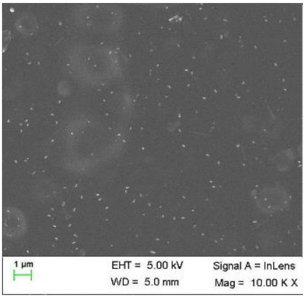

Figure 1: SEM image of PEDOT CuO nanocomposite (NP density of 10^{13}cm^{-3}), showing proper dispersion of INPs (white spots).

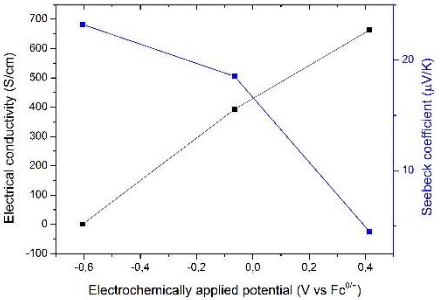

Figure 2: PEDOT:Tos conductivity and Seebeck coefficient as a function of its electrochemically set oxidation level.

References:

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OA10.4

Conducting polymers and hybrids films as thermoelectric materials

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Abstract

The classical inorganic thermoelectric materials exhibit good thermoelectric efficiency in terms of figure of merit ZT ($ZT=S^2\sigma T/\kappa$) where S, σ and κ are the Seebeck coefficient, the electrical and thermal conductivities, respectively. Most of them become from tellurium derivates such as Bi_2Te_3, Sb_2Te_3, PbSeTe or PbTe. However, even with their relative high thermoelectric efficiency, this kind of materials present several drawbacks when it comes to the fabrication of thermoelectric generators, such as scarcity of raw materials, high cost of production, and toxicity. Recently, organic semiconductors such as conducting polymers have become very important in the development of new thermoelectric materials, since these materials can solve the problems associated to the cost and the toxicity, because they are cheap and non-toxic. However, conducting polymers are not very efficient compared with classical inorganic thermoelectric materials. For this reason in this work we provide several routs to increase the thermoelectric efficiency, such as: chemical and electrochemical de/doping [1] [2] [3] and synthesis of hybrids materials using conducting polymers and inorganic thermoelectric materials (Tellurium). With these tools it is possible to increase the Power Factor ($PF = S^2\sigma$) until values around 300 μW/m K^2.

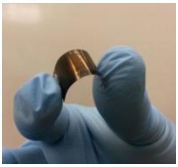

Figure 1: PEDOT-Te film.

References:

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OA10.5

Materials for roll-to-roll printed organic TEGs: Why ZT is not the most important factor

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Abstract

While material scientists in thermoelectrics traditionally focus on improving ZT, for the production of a working TE-Module many more factors come into play. This is especially true for organic thermoelectrics, were traditional module assembly methods cannot be applied. However, organic materials allow for extremely cost-effective production methods like printing. In order to make use of these new production techniques, the thermoelectric materials need to fulfill particular requirements, which research has not taken into account yet. We will show an innovative interplay of material design and production technology on the basis of roll-to-roll printed organic TEGs manufactured by otego[1].

From an application point of view, more, or at least equally important parameters in comparison to ZT are 1) processablility from solution, 2) air stability, 3) cost and 4) scalability. To prove this point, we will present a roll-to-roll printed, organic TEG. Although this TEG is based on commercially available PEDOT:PSS with ZT=0.003, it is already able to power a wireless sensor-node which transmits temperature measurements via Bluetooth.

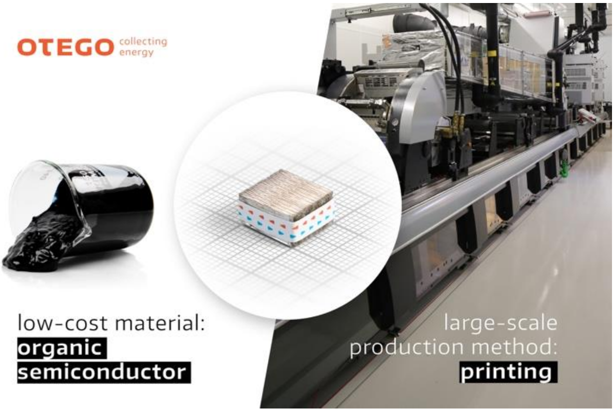

Figure 1: The interplay of a printable organic semiconductor and a scalable production method allows for the production of cost-effective TEGs.

References:

[1] www.otego.de/en

A11. New materials

OA11.1

Prospects of development in thermoelectricity: flexible composites, nanostructures and hybrid devices

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Abstract

While thermoelectricity strives to become a viable renewable energy source for wide-scale applications, a debate still divides the academic community regarding its energy conversion efficiency.[1] In this presentation, we take a look at some unconventional thermoelectric materials, such as doped polymers, or carbon based composites, which could soon enable a significant performance improvement. On this occasion, we also discuss some ideas developed in our own group, such as the versatile oxide based thermoelectric pastes,[2,3] or the supported thin layer approach.[4] The prospects of the mentioned materials for commercial implementation are underlined, while the advantages of such flexible, environmentally friendly composites are also revealed. Moreover, the general idea of combining several renewable energy sources into better performing hybrid devices is further promoted (see Fig. 1). Although momentarily still overlooked, such interdisciplinary research might hold the key to a broad introduction of sustainable energy facilities,[1] bringing Anastas' and Warner's 12 principles of green chemistry closer to realization.

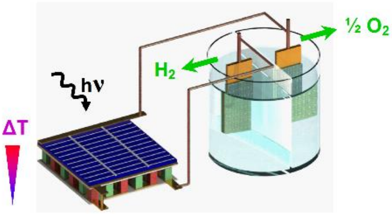

Figure 1: Artistic depiction of a hybrid device, which would combine thermoelectricity, photovoltaics and photoelectrocatalysis for a higher energy conversion efficiency.

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OA11.2

Magnetic-field enhanced thermoelectric coefficient in ferrofluids

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Abstract

Thermogalvanic conversion is currently attracting much attention as an alternative path to produce electricity from low-grade waste heat [1]. To enhance the thermogalvanic cell performance, improvements are made, in particular, through electrode materials, redox-couples and electrolyte types. Recently, it has been implied that in charged colloidal suspensions, such as ferrofluids (i.e., suspensions of magnetic nanoparticles (NPs)), the Seebeck voltage induced by the thermodiffusion of colloidal particles can further enhance the overall thermoelectric effect [2]. Moreover, it has been shown that the thermodiffusion effect of NP can be greatly increased by the application of a magnetic field [3]. Here we present the Seebeck coefficient (Se) measurements of two ferrofluids: DiMethyl SulfOxide based ferrofluids (DMSO-FF) with ferrocene/ferrocenium redox couple [4] and water based ferrofluids (H_2O-FF) with ferricyanide/ferrocyanide redox couple. In both systems, the Seebeck coefficient was measured as a function of magnetic field and the NP concentration. The magnetic field ranging between 0 and 0.5 T was applied either in parallel or perpendicular to the temperature gradient. It has been found that the application of magnetic field increases the Seebeck coefficient by as much as 25 % as expected from in-field thermodiffusion measurements performed on these ferrofluids. The observed phenomena are analysed in terms of competing thermogalvanic (redox couple) and thermodiffusion (NP) effects. Further insight into achieving higher thermoelectric conversion efficiency by tuning the solvent and NP properties is also presented.

References:

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OA11.3

New chalcogenides materials in Ba-T-Se systems

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Abstract

Many intermetallic compounds containing chalcogens have already been discovered from a structural point of view but for most of them no physical properties have been reported. Moreover, a literature survey tends to indicate that a large number of unknown phases are expected to be discovered with a systematic approach since many of these systems have not been thoroughly examined. In conclusion, clearly, chalcogenides phases have the potential to bring diverse structures and properties, and their further study is of great importance.

For example, chromium selenides based compounds have shown the potential of this family of compounds for thermoelectric applications. It is for instance the case of the new ternary $Ba_xCr_5Se_8$, in which the cations sit within the infinite channels formed by the $[Cr_5Se_8]^-$ anionic sub-network. The complex ordering of the cations lead to an extremely small thermal conductivity of less than 1 W/(mK), that together with a large Seebeck coefficient, produces thermoelectric figure of merit above of 0.1 at 900K. This example validates the fact that, indeed, attractive properties can be unveiled.

In this contribution, the first result of our systematic exploration will show that in certain systems, physical properties are promising and that the richness of these systems probably still hides some interesting materials. In addition to the known phases, new ternary intermediate phases have been isolated. We will present here the crystal structures refinements, based on transmission electron microscopy and X-ray diffraction data, as long with physical properties obtained by means of magnetic and transport properties measurements.

OA11.4

p, n control in thermoelectric borides and sulfides

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Abstract

Developing good p- and n- type pair thermoelectric materials is an important and often difficult aspect for moving forward thermoelectric application. I will present recent advancements we have made on this for high temperature borides and low to mid temperature sulphides. Excellent (|α|>200 μV/K) p-type or n-type characteristics could be controlled in YAl_xB_{14} by varying occupancy of the Al site (Fig. 1) [1]. This is p, n control with same crystal structure (i.e. good matching) and no necessity for doping of foreign elements (i.e. no migration problems). The discovery is surprising, since in metal borides, the metal site occupancies are typically with small homogeneity region. Theoretical investigations reveal the stable configuration of the atomic sites and density of states variation behind the thermoelectric properties. I will present recent further development we have carried out on the aluminoborides. Regarding sulfides, we have previously discovered high power factors at 300 K, for carrier-doped $CuFeS_2$. We have proposed that magnetic semiconductors can have enhanced thermoelectric properties [2]. This is an n-type material and we have recently found a new p-type sulphide with good properties and will present this also.

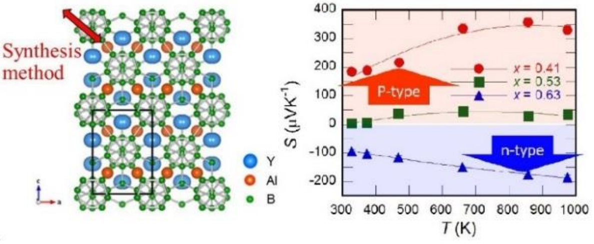

Figure 1: View of crystal structure and Seebeck coefficients of YAl_xB_{14} [1].

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OA11.5

Development of thermoelectric generator based on ionic liquids for high temperature applications

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Abstract

Current, Seebeck-coefficients (SE) and maximal power output (Pmax) of thermoelectric generators using ionic liquids (ILs) were measured to determine the optimal temperature window for their use as in a range between 100-250oC. The thermoelectric current extraction was identified to be a key factor based on dissolving redox-couples (I2/I-) that are added to the IL and the charge transition from the IL and the electrode. The experiments are carried out in a thermoelectric cell, where the IL is sandwiched between two electrodes [1]. Experimentally we determinate an increase of electrical power of more than 35 times while keeping the temperature difference of the two electrodes constant at 20 K and increasing the temperature of the hot electrode T(hot) from 30°C to 165°C whereby the heat-flow increases only 3.5 times.

Despite a decrease of Seebeck-coefficient by heating up the TEG the current increases continuously at increasing T(hot). Apparently, heating overcomes the activation energy for both, the bulk conductivity and the carrier extraction from the liquid and the solid electrodes. Saturation of the effect was not reached in the currently used generator with temperatures up to 165oC, using silicone as packaging material for the generator. A new TEG concept (compatible for T(hot), up to 250 °C) was developed and the thermo-electrical properties (SE, I, Pmax) of different ionic liquids were determined in this temperature range. The challenges and the potential of ionic liquids for thermoelectric applications in high temperature range, e.g. in the automotive industry, was discussed.

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A12. Nanomaterials

OA12.1

Thermoelectric properties of electrodeposited $Bi_{0.5}Sb_{1.5}Te_3$ nanowires in polycarbonate membranes

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Aiming to improve their transport properties, Dresselhaus et al. [1] have theoretically demonstrated that the use of low-dimensional systems can reduce its lattice thermal conductivity. Since 2000's the electrodeposition of nanowires in ion track-etched polycarbonate membranes (PCM) used as template has become one of promising and competitive processes due to its low-cost and simplicity [2]. It appears that pore diameter, potential of deposition and concentration of the bath are considered as important factors to be adjusted in order to obtain the desired composition, crystalline structure and morphology of the nanowires [3].

Nanowires (NWs), p-type bismuth-antimony-tellurium-based, were electrodeposited for different deposition potentials. Calibrated TEM-EDX analyses and XRD patterns showed a transition from Te-rich to $Bi_{0.5}Sb_{1.5}Te_3$ nanowires between 0 and -100mV associated to increasing content of antimony with the deposition potential. High-resolution transmission electron microscopy revealed polycrystalline NWs and smooth morphology along the length of NW. Specific experimental setup was used in order to measure the Seebeck coefficient and the output power of a nanowire bundle across of the membrane thickness. It appears that an optimal chemical composition $Bi_{0.4}Sb_{1.4}Te_{3.2}$ was detected exhibiting maximum values at 300 K of 140 µV/K for Seebeck coefficient and of 4.8 nW/cm^2 for output power factor. These results were associated with electrical properties of individual NWs performed trough 4-probe device in PPMS system in the temperature range 10K-400 K.

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OA12.2

Nanostructured $Yb_xCo_4Sb_{12}$ skutterudites

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Abstract

$Yb_{0.2}Co_4Sb_{12}$ displays the best figure of merit (ZT = 1.2 at 800 K) among single filled $A_xCo_4Sb_{12}$ (A = alkaline earth, rare earth). Since its lattice thermal conductivity is still high (λ_L = 2.8 W m^{-1} K^{-1} at 300K), further improvements of the figure of merit should be gained by scattering heat carrying phonons at the grain boundaries upon grain size reduction to nanometric sizes. Prior to nanostructuration, we re-examined the $Yb_xCo_4Sb_{12}$ series ($0 \leq x \leq 0.5$) synthesized at 800 °C, a temperature which allows a larger Yb solubility limit (x_{lim}) to be reached [1]. x_{lim} = 0.4 rather than x_{lim} = 0.25 is indeed obtained and the best ZT = 1.3 at 700 K is found for x = 0.25 (not for x = 0.20). $Yb_xCo_4Sb_{12}$ (x = 0.20, 0.25) compacts with exceptionally small grain sizes in the 90 – 120 nm range (Fig. 1) were synthesized by high energy milling and spark plasma sintering. A mechanism to reach these small grain sizes will be discussed in relationship to XRD, SEM and TEM data. This very fine microstructure leads to a reduced lattice thermal conductivity (λ_L = 1.4 W m^{-1} K^{-1} at 300K) and an improved ZT = 1.4 at 700 K.

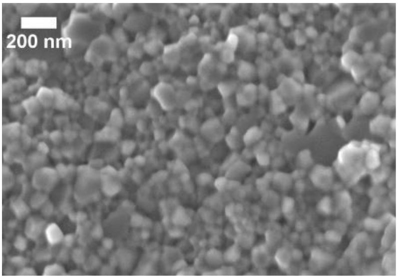

Figure 1: SEM picture of nanostructured $Yb_{0.2}Co_4Sb_{12}$

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OA12.3

Production of thermoelectric thin film to energy harvesting using Ion Beam Deposition technique

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Abstract

Thermoelectric (TE) device appear as an alternative solution to one of the major problems in this XXIth century concerning the energy crisis and environment deterioration. This technology have the capability in converting waste heat into the electricity thus contributing to a sustainability system [1]. TE alloys exhibit interesting properties to use in TE energy conversion such as: zero emissions, vast scalability, low maintenance, and long operating lifetimes. However, nowadays the TE devices are still the limited application mainly because of its low energy-conversion efficiency and corresponding high material cost. Recent investigations have shown that nanostructuring these materials can enhances the thermoelectric figure of merit (ZT) due the phonon scattering at nanodomains. For a long time the ZT has been limit to 1 in the most common TE materials. Here, ZT is defined as $ZT=(S^2\sigma/\kappa)T$, where S, σ, κ and T are the Seebeck Coefficient, electrical conductivity, thermoelectric conductivity and absolute temperature, respectively [1]. Thus, increasing the ZT through nanoscale reduction, it may increase the energy-conversion efficiency. The main goals of the present work are the production of efficient n-type Bi_2Te_3 and p-type Sb_2Te_3 thin films with nanometre thickness in order to be below the phonon mean free path of these materials. The films were deposited by Ion Beam Deposition in different substrates with thickness ranging from 40 nm up to 150 nm. The aims are to growth TE thin films in Si substrates and in flexible substrates such as PET and Kapton to support low temperatures working operation (T<200ºC). In addition, the influence of post-deposition annealing in structure, electrical and thermoelectric properties in these materials are analysed and discussed [2].

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OA12.4

Towards efficient thermoelectric performance in silicon by point- and extended-defects

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Abstract

Silicon is a remarkably useful element. Its abundance, low cost and low toxicity, combined with vast practical know-how means it is a leading material on which to base technologies. However for good reason, certain applications have under-utilised Si, with thermoelectrics (TE) being one example. Compared to other materials, highly-doped Si has desirably large Seebeck coefficient and high electrical conductivity, but these are negated by high thermal conductivity, meaning that TE performance is relatively poor for bulk Si, about 100-fold worse than for popular TE materials.

This paper will progress some of the methods currently being explored to reduce the Si thermal conductivity, highlighting the significant engineering challenges involved, particularly as solutions until now have involved substantial alteration of the Si crystal structure, such as the introduction of porosity or the formation of nanowires or nanostructures. We will describe a range of successful alternative processes – such as so-called *vacancy-engineering* [1] – which, via ion implantation and rapid-thermal annealing, leaves the Si structure almost indistinguishable from bulk Si. This novel approach shows that the introduction of large concentrations of lattice vacancies in silicon creates more than a 25-fold reduction in thermal conductivity, while electrical conductivity and Seebeck coefficient are largely maintained. This results in thermoelectric performance comparable to silicon nanowires, but in a more robust material that is straight-forward to fabricate [1]. Other novel strategies for Si thermoelectrics being explored by our group – such as *dislocation-engineering* [2] – will also be discussed, as will our recent work in up-scaling these methods to first, thin-films [3], and ultimately to bulk materials.

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OA12.5

LPCVD in-situ doped silicon for thermoelectric applications

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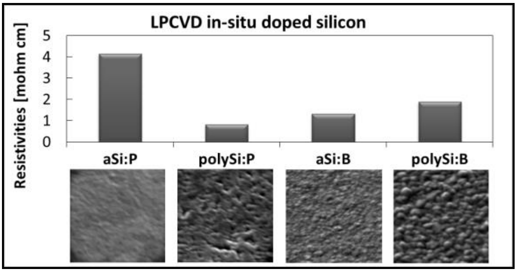
Abstract

Polysilicon materials doped via ion implantation are conventional CMOS compatible materials, which can be used for thermoelectric applications. The long anneals after ion implantation provoke a high thermal budget. In order to reduce the thermal budget, in-situ doped materials with rapid thermal anneal were investigated. The residual stress is released and the throughput is enhanced with this process integration. The aim of this study is to investigate Si-based in-situ doped materials and to determine the influence of the process parameters on physical, chemical and thermoelectric properties.

Processes and characterizations were carried out in a state-of-the-art cleanroom (ISO 6 class 1000) on industry standard tools. Thin films with a typical thickness of 250nm were deposited. The process characterization was carried out on 300mm unpatterned wafers using spectroscopic ellipsometry, sheet resistance, scanning electron microscopy, X-ray diffraction and time-of-flight secondary ion mass spectrometry. Figure 1 shows the resistivities and scanning electron microscopy results for the different processes with rapid thermal anneal. The thermoelectric properties were determined on 150mm patterned wafers. The investigations will show a first LPCVD in-situ doped silicon process screening.

The materials will be used within the ECSEL project Admont for CMOS compatible applications. Some of these applications are thermoelectric infrared sensors and thermoelectric generators via energy harvesting.



OA12.6

The role of functional interfaces to enhance figure of merit in Skutterudite Nanocomposites

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Abstract

High improvements have been achieved in thermoelectricity field in the last years, mainly through two different approaches: the nanostructuration and the use of complex materials. The main goal in this new kind of materials is the decoupling of electrical and thermal conductivity, being essential to enhance the thermoelectric figure of merit[1]. Within this framework, an important goal was achieved through a new method to obtain doped-Skutterudite nanocomposites with the combination of high energy milling in air and spark plasma sintering (SPS) (Fig. 1a). The effect of the functional interfaces between the conductor material (Te doped-$CoSb_3$) and the oxide inclusions was studied, corroborating the importance of these interfaces, which act as effective phonon scattering and trapping centers, thus, reducing the thermal conductivity. With this low value of the thermal conductivity by nanocomposite effect and low electrical resistivity by doping, high figure of merit of 1.3 at 790 K for $CoSb_{2.85}Te_{0.15}$ nanocomposite was achieved (Fig. 1b).

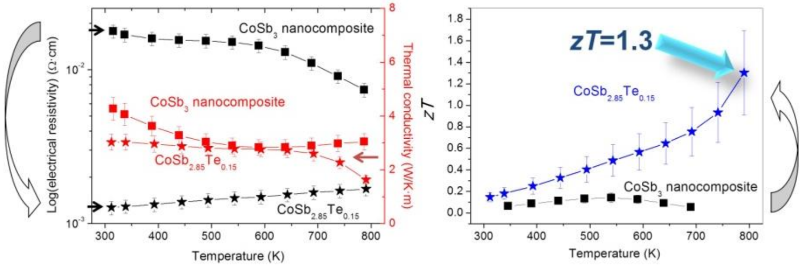

Figure 1: (a) Comparison between Log (electrical resistivity) and thermal conductivity of undoped $CoSb_3$ nanocomposite and Te-doped $CoSb_3$ nanocomposite;.(b) *zT* measurements for both nanocomposite samples. The decrease of the electrical resistivity by doping while maintaining the thermal conductivity by the effect of functional interfaces increase *zT* by a factor of 10.

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B1. Measuring techniques

OB1.1

Metrology of thermoelectric properties of materials, precision and performance improvement methods

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Abstract

The errors in determination of thermoelectric figure of merit Z with the use of known methods and equipment can reach 20-25%, which is an impediment to solving material science problems of Z increase.

The paper presents the results of using computer simulation methods for determination of the most important reasons giving rise to errors. First, they are governed by the technique itself of finding Z. It is established that when making a selection of techniques preference should be mostly given to absolute method. Second, when using the absolute method the most essential reasons for the origin of errors are primarily caused by deviations from the uniformity of temperature and electric fields in a sample due to inferior quality of electric and thermal contacts adjoining the sample, radiation and other heat losses from the sample surface and local distortions of temperature fields because of heat removal with measuring thermocouples.

Techniques for measuring Z, σ, α, κ have been developed, beginning with creation of correct geometry samples, attachment to them of special conducting elements with low values of contact and thermal resistances, application of thermal switches eliminating heat removal from the samples with measuring thermocouples, and ending with gradient screens with reflectors minimizing heat transfer due to radiation along the sample surface.

Measuring procedure includes special method of electric conductivity measurement reducing the influence of the Peltier effect by creating at the sample ends of equal temperatures using a special heater that compensates the action of the Peltier effect.

The measurements themselves and processing of their results are computer-aided in order to eliminate the effect of human factors on measurement process.

Measurement procedure also employs additional sample heat-ups in going from one measured temperature to the other by passing an electric current of special shape through the sample.

The measurement procedure and equipment are calibrated.

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OB1.2

Precise measurement on thermoelectric device performance by using active temperature control on a heater in the heat source

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Abstract

The thermoelectric performance of the device can be measured using a heat source and a heat sink. Conventionally, a block, located between the heat source and the device, with known geometry with temperature sensors in it was used to determine heat flux flowing from the heat source to the device. In this case, heat loss through the block cannot be avoidable, which could affect measurement accuracy. Here, we have developed the measurement setup which utilized two heaters in the heat source to accurately measure heat flux through the thermoelectric device. A heater, *e.g.*, control heater, controls temperature of the other heater, *e.g.*, main heater, which is located right on the top of the device. In this way, heat generated in the main heater can only dissipate through the device. Also, we suggest an apparatus to implement uniform pressure on the device, which is critical in thermal contact between the device and the heat source/heat sink. The measurement setup was located in a vacuum chamber surrounded by radiation shields so that convectional and radiational heat losses were minimized. With this setup, we present data of both the power generation and refrigeration purpose of thermoelectric devices. This measurement scheme should be useful for those of who needs accurate measurement on performance of a thermoelectric device.

OB1.3

Measurement of thermal conductivity with thermoelectric modules

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Abstract

Thermoelectric devices can be used as coolers, heaters, power generators and heat flux sensors. In this work we present a new application: thermal conductivity sensors for disc shaped samples. The method involves a simple setup where a squared thermoelectric module with similar size to that of the disc sample is attached to a copper block, acting as a heat sink, at the bottom side, and the disc sample is attached to the top side (see Fig. 1).

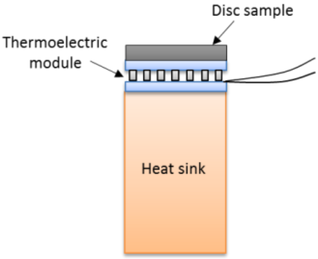

Figure 1: Setup used for the measurement of thermal conductivity of disc samples with a thermoelectric module.

Impedance spectroscopy measurements are performed under this setup at room conditions. From these measurements different parameters can be calculated which relate to the thermal conductivity of the sample. The relationship with the thermal conductivity was evaluated employing reference materials and the repeatability and accuracy was estimated.

OB1.4

Measuring the efficiency of thermoelectric generators: accuracy and methods for heat flow determination

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Abstract

Thermoelectric (TE) materials are designed to convert heat into electrical energy, with no moving parts involved, completely silent and very reliably with proved operation times over decades in space applications. In order to apply thermoelectric generators (TEG) successively to terrestrial waste heat applications, high temperature TEG modules are currently developed worldwide by many research groups and industrial players.

Hence, precise metrology for TEG builds the base for a reliable assessment on the development progress and gives crucial input information to system design and on the applicability of TEG modules in terms of stability and effective performance. According to results of an international round robin (RR) campaign on TEG characterization up to temperatures of 470 K the deviation of the module efficiency was determined to be higher than 15 %, while the discrepancy of the thermal characterization exceeded occasionally even 30 % for the conducted heat flow measurements. Since these deviations are too high for an industrial benchmark and deficient for many scientific investigations and technological developments, tests have been conducted to quantify the achievable accuracy of the commonly employed reference principle for heat flow determination. Based on experimental data and FEM simulations the reference principle turned out to be limited to a heat flow uncertainty of approximately 20 % under best measurement conditions, whereas non-uniform heat flow distributions and parasitic heat losses entailed increased uncertainties of up to 34 %, which is in good agreement to the outcome of the RR test. Furthermore, a method for absolute heat flow determination, which is formally known as the guarded hot plate method (GHP), was developed and investigated thoroughly for the achievable accuracy. Results obtained from finite element modelling assisted parametric studies on the GHP-apparatus demonstrate the enhanced accuracy and give proof of the effectiveness of active thermal guarding for thermal TEG characterisation. Between room temperature and 1020 K the resulting uncertainty for heat flow determination was proofed on different samples to be below 3 %. Variances of the measured electrical power output of Bi_2Te_3-based TEG revealed an expanded uncertainty for the efficiency of 4.5 % for temperatures up to 470 K. Thus, the GHP method represents a superior approach for precise and traceable metrology for high temperature TEG, which exceeds the accuracy of the reference principle at least fourfold.

B2. Optimizing the figure of merit

OB2.1

Phonon filtering in silicon: the combined effect of internal surfaces and voids

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Abstract

The lattice thermal conductivity of a crystalline material is significantly reduced by the introduction of morphological defects such as dislocations, internal surfaces, precipitates, nanovoids, and other extended (2D and 3D) defects which affect the phonon mean free path. Since performing thermoelectric materials require efficient phonon scatterers marginally impacting on the electrical conductivity, it is not surprising that over the last few years a large number of papers had appeared proposing sophisticated theoretical approaches to the analysis of phonon scattering. Specifically, the analysis of the reduction of thermal conductivity due to grain boundaries and porosity has motivated a revision of the standard kinetic model. A frequency-dependent phonon mean free path (mfp) was proposed, overcoming the standard grey model. It was actually advanced that, paradoxically enough, about 60% of the total heat flowing in silicon is carried by phonons with a mfp longer than the grain size.

We will discuss the dependency of the thermal conductivity on the size, shape, and density of morphological defects (MDs). Two interlaced fundamental issues are aimed at, namely (1) whether the grey model may actually be used to explain the reduced thermal conductivity observed in defective crystalline solids and its temperature dependency; and (2) how heat may be possibly carried through internal surfaces by phonons with wavelengths larger than the crystalline domain. To this end, a combined approach is followed. Single-crystalline and polycrystalline silicon films, either porous or non-porous, were investigated so to compute their thermal conductivity by non-equilibrium molecular dynamics simulations. Results are compared with literature data on polycrystalline silicon films. The co-presence of more MDs allowed estimating their interplay, possibly shedding some light on the mechanism of phonon filtering at internal surfaces.

OB2.2

Reducing the lattice thermal conductivity by driving PbTe and its alloys to the verge of the ferroelectric phase transition

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Abstract

There has been an increased interest in exploring methods to reduce lattice thermal conductivity that do not rely on the concept of nanostructuring. Recent investigations have indicated a link between a low thermal conductivity and proximity to a structural phase transition, for example, in PbTe [1,2] and SnSe [3]. Building on this idea, we predict from first principles that driving PbTe near the transition from rocksalt to rhombohedral structures will significantly reduce the thermal conductivity [4]. We illustrate this concept by applying biaxial tensile (001) strain to both PbTe and its alloy with rocksalt PbSe, and also by alloying PbTe with rhombohedral GeTe. We find that the considerably softened zone centre optical modes lead to increased acoustic-optical phonon coupling, which significantly decreases phonon lifetimes and thermal conductivity.

We further generalise this concept by investigating the thermal conductivity of both rocksalt and rhombohedral (Pb,Ge)Te alloys. We predict that (Pb,Ge)Te alloys driven near the ferroelectric phase transition will have considerably reduced thermal conductivities in comparison to both PbTe and GeTe. We also find that the thermal conductivity changes continuously between rocksalt and rhombohedral structures, and reaches a minimum near the point of transition. This proposed concept may open new opportunities for the development of more efficient thermoelectric materials.

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OB2.3

High thermoelectric and electronic performance in graphene nanoribbons by isotope and vacancy engineering

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Abstract

In spite of naturally poor thermoelectric ability of graphene, it has been shown that various strategies of nanostructuring may be used to achieve very high thermoelectric performance.[1,2] However, the approaches to enhancing the thermoelectric figure of merit are usually based on the reduction of phonon thermal conductance and generally accompanied by an undesirable degradation of the electrical conductance.[3,4]

Since electronic properties are among the most intriguing ones of graphene, it is naturally targeted to achieve an enhancement of thermoelectric performance without degrading electronic transport. For this aim, we propose here a graphene structure as sketched in Fig. 1(a), made of a ^{12}C nanoribbon with the presence of a fraction of ^{14}C isotopes or/and vacancies at positions (along the width) $m = 3i$, where the electron density is very small. By means of atomistic simulation, we show that the electrical conductance is fully persevered while the phonon conductance is strongly reduced (Fig. 1(b)). The maximum of ZT reaches about 0.49 for the structure of width $M = 5$ and length $L_A = 64$ nm with only ^{14}C isotope doping and is even as high as 0.96 with the addition of vacancies at positions $3i$. The red curve in Fig. 1(c) shows that $ZT > 3$ can be achieved at room temperature in long devices of length $L_A > 700$ nm.

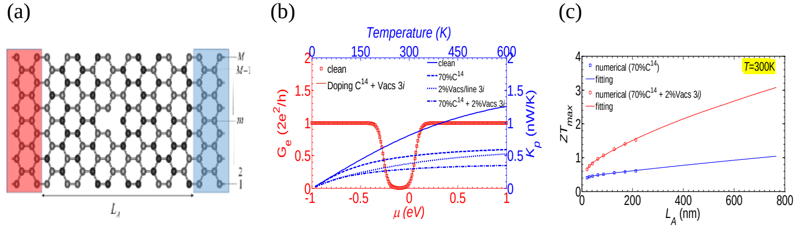

Figure 1: (a) Schematic of an armchair graphene ribbon (^{12}C) in the presence of ^{14}C isotopes and a single vacancy at $m = 6$. (b) Electrical (300K) and Phonon conductance without (clean structure) and with isotopes and vacancies. (c) Maximum value of ZT as a function of the device length L_A.

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OB2.4

Enhanced thermoelectric properties of spark plasma sintered p-type $Si_{0.8}Ge_{0.2}$ bulk alloys

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Abstract

It has been shown recently that SiGe-based thermoelectric materials prepared by mechanical alloying followed by different consolidation method demonstrate a large enhancement in figure-of-merit (ZT). We report on thermoelectric properties of p-type boron doped nanostructured bulk $Si_{0.8}Ge_{0.2}$ synthesized via spark plasma technique. Characterization of thermoelectric properties of the samples revealed that the enhancement of ZT is due mainly to the nanostructuring-induced reduction in the thermal conductivity. Thermal conductivity of the studied p-type SiGe alloys sintered at different conditions, industrial radioisotope material (RTG) [1] and n-type bulk nanostructured sample [2] sintered at temperatures from 1050 to 1100 K is shown in Fig.1. Power factor of the studied material was also slightly enhanced due to energy filtering of hot carriers at the interface.

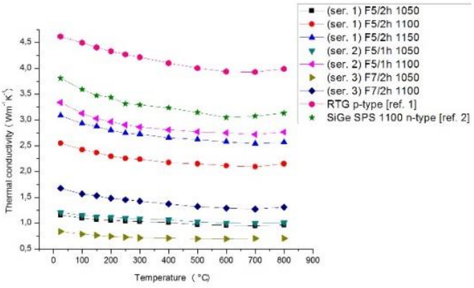

Figure 1: Thermal conductivity of p-type SiGe nanostructured bulk alloys sintered at different conditions

References:

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OB2.5

Nanostructured Bi_2Te_3 compounds prepared by arc-melting technique

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Abstract

Bi_2Te_3 alloys present the best thermoelectric performance for room temperature applications. We show that it can be readily prepared in nanostructured form by arc-melting synthesis, a rapid and straightforward preparation technique [1]. It yields mechanically robust pellets of highly oriented polycrystals. This material has been characterized by neutron powder diffraction (NPD), scanning electron microscopy (SEM) and electronic and thermal transport measurements. A microscopic analysis from NPD data demonstrates a near-perfect stoichiometry of Bi_2Te_3, and a fair amount of anharmonicity of the chemical bonds. The as-grown material presents a metallic behavior, showing a record-low resistivity at 320 K of 2 μΩ m, which is advantageous for its performance as thermoelectric material. SEM analysis shows a stacking of nanosized sheets, each of them presumably single-crystalline, with large surfaces perpendicular to the c crystallographic axis. This nanostructuration notably affects the thermoelectric properties, involving many surface boundaries that are responsible for large phonon scattering factors, resulting in a thermal conductivity as low as 1.2 $Wm^{-1}K^{-1}$ around room temperature.

In n-type $Bi_2(Te_{1-x}Se_x)_3$ solid-solutions thermal conductivity is further reduced to 0.8 $Wm^{-1}K^{-1}$ around room temperature. Se doping increases absolute Seebeck coefficient values up to 80 μVK^{-1}. Both nanostructuration and doping contribute to a higher thermoelectric efficiency.

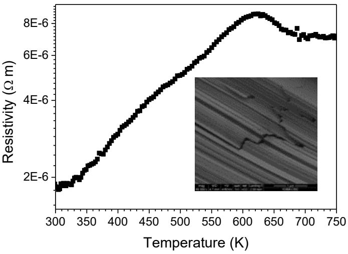

Figure 1: Bi_2Te_3 with very low resistivity. Inset: arc-melting produces nanolaminated pellets

References:

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B3. Theory and Modelling

OB3.1

Calculating the power factor of nano-composite materials from fully quantum-mechanical large-scale simulations

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Abstract

Nanostructuring of materials is commonly put forward as a means of improving thermoelectric efficiency above their bulk values. Such structures either act to scatter phonons, create quantum confinement effects or filter carrier energies to maximize the power factor [1]. Thus, their fundamental mechanism of enhancement is often quantum mechanical and non-equilibrium in nature. In addition, their nanoscale feature sizes lie in the regime where transport is neither totally diffusive, nor ballistic. Despite the fact that advanced simulation packages exist for phonon transport in these materials (mostly based on molecular dynamics), no such framework exists for electronic transport. In this work we present a non-equilibrium Green's function (NEGF) based simulation framework which captures all effects for electronic transport, from quantum mechanical to semiclassical, and from ballistic to diffusive, all within the same theoretical framework, and is tailored for 1D and 2D nanostructured geometries.

Such a solver allows for the inclusion of nanostructures of many different shapes and types, whether superlattices, nanovoids or more complex structures, and calculation of the energies of carriers, the Seebeck coefficient, charge densities and current anywhere within the channel. The ability to attain such thorough spatially resolved data from a non-equilibrium, two-dimensional, quantum mechanical channel allows for great insights into the nature of thermoelectric power factor enhancement in such systems.

Using this simulator, we will present example studies for the thermoelectric power factor in different geometries: superlattices [2], channels with nano-inclusions and other nano-engineered structures. We illustrate visualizations of the nature of carrier energy flow in such structures and discuss strategies for optimal power factor enhancement.

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OB3.2

Promising thermoelectric properties of the hypothetical binary ME_3 compounds

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A large number of $FeGa_3$-type [1] ME_3 compounds (Fig.1 left, M = group 7-9 transition metal and E = Ga, In) are of interest due their thermoelectric properties. ME_3 compounds of group 7 and 9 transition metals are metallic whereas those with group 8 metals are semiconducting. The latter show large thermopower and their thermal conductivity can be significantly decreased by peculiar substitution (e.g., In by Sn or Zn in $RuIn_3$ [2]). With earlier Group 4 and 5 metals, ME_3 compounds crystallise in a different atomic arrangement, namely in the $TiAl_3$-type structure (Fig.1, right) [3]. Surprisingly, no ME_3 compounds have been reported so far with transition metals of group 6. Density functional theory calculations that we performed show indeed that the most reliable structure of these hypothetical compounds should be the $FeGa_3$-type one. Their structural and electronic properties were analysed and their transport properties were computed using a semi-classical approach [4]. Pertinent results of this *in silico* study will be presented, and a special attention will be paid to the most promising thermoelectric candidates.

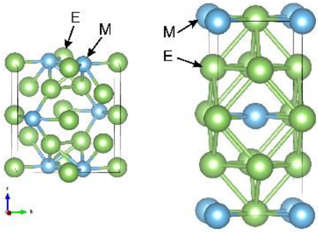

Figure 1. Crystal structures of the $FeGa_3$ (left) and $TiAl_3$ type (right).

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OB3.3

Effect of alloying and doping on electronic structure and crystal stability in tetrahedrites and tennantites from KKR-CPA method

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Abstract

Copper-based minerals as tetrahedrites $(Cu,M)_{12}Sb_4S_{13}$ or tennantites $(Cu,M)_{12}As_4S_{13}$, where M denotes transition metal element, exhibit propensity to energy gap opening in the electronic density of states (DOS) [1]. Besides, their complex crystal structure (space group *I*-43m) containing 58 atoms distributed over 5 inequivalent crystallographic sites, strongly governs their particular phonon properties (see eg. [2]) that are responsible for their very low thermal conductivity. All these favourable properties make these materials highly attracting for thermoelectric conversion and offer possibility of selective substitution on Cu sites (eg. Fe, Co or Zn), Sb site (eg. Te or As) or even S sites (eg. Se), which results in effective tuning of electronic transport properties as well as lattice dynamics behaviours. Here, we present results of electronic band structure calculations, focusing mostly on DOS features near the Fermi level, when substituting and/or doping the ideal systems $Cu_{12}Sb_4S_{13}$ [3] and $Cu_{12}As_4S_{13}$. The Korringa-Kohn-Rostoker method with the coherent potential approximation (KKR-CPA) was employed to account for chemical disorder and allowing not only to study electronic DOS and energy bands characteristics, but also energetic aspects such as the site preference of dopants and crystal stability.

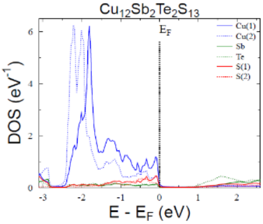

Figure: Site-decomposed density of states in $Cu_{12}Sb_2Te_2S_{13}$.

References:

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OB3.4

Examining the effectiveness of energy-filtering in 1D vs. 2D structures using quantum mechanical transport simulations

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Abstract

The energy filtering of carriers has been proposed as a promising means of improving the power factor, and thus, enhancing the ZT, figure of merit, of thermoelectric materials. In this talk we will review recent work, based on large-scale simulations using the fully quantum mechanical, non-equilibrium Green's functions (NEGF) method with electron-phonon scattering, which explores the relative potential for power factor enhancement in one-dimensional (1D) vs. two-dimensional (2D) channels.

We will demonstrate that the van Hove singularity in 1D channels (which has been suggested by Hicks and Dresselhaus[1] to provide larger Seebeck coefficients) makes more effective use of the energy filtering mechanism[2] as well, whether with a single filtering barrier structure or with many (i.e. a superlattice). In the most extreme case the relative advantage of 1D in utilizing energy filtering can be up to a factor of 3 compared to filtering in 2D channels. We show how the van Hove singularity of the 1D density of states plays in forcing carriers to flow at lower energies as well as producing a shorter energy relaxation length and discuss how these features allow 1D structures to receive a greater benefit from filtering.

We will also discuss the scenario where the thermal conductivity of the barrier material is less than that of the bulk and the direct effect that has on the power factor. Again we find that, although the power factor in 1D and 2D is benefited from variations in the thermal conductivity along the channel, the 1D channel sees 50% more benefit.

Our results demonstrate the higher potential of 1D materials in utilizing energy filtering, and could be particularly helpful in the design of low- dimensional nano-composite thermoelectrics.

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OB3.5

Optimization design of thermoelectric power generation for Maximum W per $: the competitive relation between high figure of merit and high-performance heat exchanger

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Abstract

Maximizing the factor of cost performance (i.e. W per $) is very important for the optimization design of thermoelectric power generation (TEG) system, especially for large-scale industrial application [1, 2]. The costs and performances of TE materials together with heat exchangers at cold and hot sides are some of the main factors that can influence the output power and cost dramatically. In this study, a fully developed analytical TEG model is built, in which the temperature depended performances such as Seebeck coefficient, electrical conductivity and thermal conductivity of TE materials, and the junction temperatures of p-type and n-type TE elements at hot side (T_{1p}, T_{1n}) and cold side (T_{2p}, T_{2n}) as well as the geometry of TE elements are concerned. This model predicts a significant difference of junction temperatures between p-type and n-type TE materials (Fig. 1(a)), and can predict maximum output power $w_{\max}$ with optimized load resistance (Fig. 1(b)) and geometry (A_p/A_n, L_p/L_n) of TE elements. It is found that some TE materials with relative lower ZT combined with better heat exchangers are competitive with some high-performance TE materials.

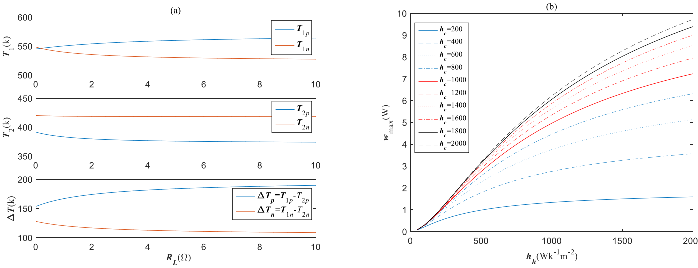

Figure 1: (a)hot side (T_{1p}, T_{1n}) and cold side (T_{2p}, T_{2n}) temperatures of p-type (Zn4Sb3) and n-type ($Mg_2Si_{1\_x}Sn_x$) TE elements versus load resistance, with h_h=h_c=1000wk^{-1}m^{-2}; (b)Maximum output power $w_{\max}$ with optimized load resistance versus hot side heat transfer coefficient h_h for different cold side heat transfer coefficient h_c. Plate TEG size 4cm×4cm, uni-couple number 160, fill factor F=0.8, A_p=A_n, L_p=L_n=1mm, hot and cold side fluid temperatures 650k, 293k .

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OB3.6

Electronic and thermoelectric properties of impurity doped Mg_2Si incorporating Mg-related defects

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Abstract

Thermoelectric silicide materials have recently been receiving increasing attention because of their important role in sustainable energy technologies. Mg_2Si, a narrow band gap semiconductor, is a promising candidate for mid-temperature (600–900 K) thermoelectric applications, e.g., reuse of discarded heat of vehicles.

Theoretical [1] and experimental [2] studies have previously proposed that Mg-related defects play a crucial role in carrier transport in Mg_2Si. Therefore, it is of paramount importance to achieve a thorough understanding of the influence of Mg defects on the electronic and carrier transport properties of Mg_2Si in order to enable the design of high-performance Mg_2Si-based materials.

Mg_2Si has the antifluorite crystal structure as shown in Fig. 1. The figure depicts two types of defects: an extra Mg atom inserted into the center of the cell (center), and simultaneously incorporated an extra interstitial Mg atom along with a vacancy of a regular Mg atom (on the right). We performed a pseudo-potential first-principles calculation in order to find the optimal cell structures. The results of our calculation show that the defects illustrated in Fig. 1 alter the carrier concentration as follows: the interstitial Mg acts as an *n*-type dopant; on the other hand, the vacancy generates holes. This alteration to the carrier concentration, induced by unintentional doping due to the defects, can compensate for intentional doping due to the added impurity atoms. In conclusion, we have examined the electronic states of Mg_2Si incorporating the defects as well as *p*-type impurity dopants and we discuss the influence of these defects on the carrier transport properties of the systems using a KKR-CPA method.

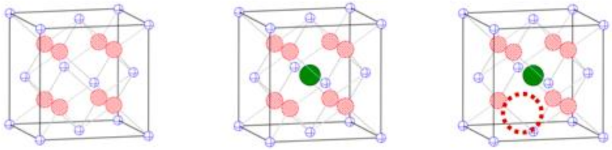

Figure 1: Mg_2Si crystals having no defects (perfect crystal) (left), the interstitial Mg atom (center), and the interstitial Mg atom plus the vacancy (right). Small and large symbols represent Si and Mg atoms, respectively.

References:

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C1. Modules and thermoelectric generators

OC1.1

Year four on Mars: An update on the multi-mission radioisotope thermoelectric generator powering the curiosity rover

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Abstract

The Multi-Mission Radioisotope Thermoelectric Generator (MMRTG) powering the Mars Science Laboratory (MSL) mission was developed by the United States Department of Energy (DOE) for the National Aeronautics and Space Administration (NASA) and fueled on October 28, 2008. It has been operating, fueled, for approximately 8 years and has been on Mars for approximately the last 4 years; MSL was launched on November 26, 2011. The Curiosity rover was landed on August 12, 2012 and the MMRTG was producing nearly 114W at that time [1]. Since then power output of the MMRTG has decreased as expected. This paper updates previous reports [2] on the MMRTG's performance throughout the rover's primary mission and the first extended mission as well as discuss related events and phenomena that affected the MMRTG's performance.

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OC1.2

Relationship between flow rate of counter-flowing thermal fluids and thermoelectric performance

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Abstract

Thermoelectric (TE) performance of a three-dimensional (3D) TE module is examined by exposing it between two streams of counter-flowing thermal fluids in which the temperature-dependent properties are ignored. The thermal fluids have the fixed inlet temperature, 500 K and 300 K for hot and cold fluids, respectively, and flow in the opposite direction using a sequential varied rate of hot fluid and a constant flow rate of cold fluid, and then generate temperature difference on the hot and cold surface of TE module. TE performance caused by different relative flow rates of thermal fluids are numerically analyzed by using finite-volume method on 3D meshed physical models, as shown in **Figure 1**, and then compare with the previous performance of using the constant temperature boundary [1]. The results show that TE performance is increased with the flow rate of hot fluid and reach a stable value after a transition from a beginning moment to a stable flow, and a suitable relative flow rate between counter-flowing thermal fluids exists to achieve a stable performance quickly. Further, 3D contours of fluid pressure, temperature, enthalpy, electromotive force, current density and heat flux are exhibited in order to clarify the influence of flow rate of counter-flowing fluids on TE generation.

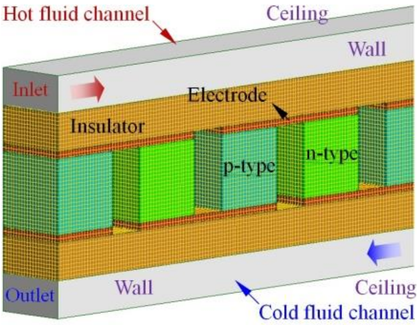

Figure 1: 3D physical model of TE module.

References:

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OC1.3

Recent developments in high performance thermoelectric modules for waste heat harvesting

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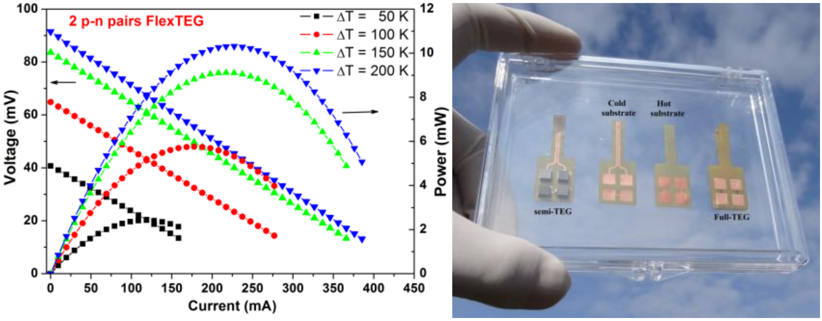
Abstract

In this work, various types of TE modules have been developed using all oxide materials, intermetallic compounds, and their segmentation. An all oxide 8 couples module comprising of doped-$Ca_3Co_4O_{9+}$ as *p*-leg and Al-doped ZnO as *n*-leg exhibits a maximum power density of 329 mW/cm^2 at $\Delta T = 700$ K. By using segmentation of misfit-layered cobaltite $Ca_3Co_4O_{9+}$ and half-Heusler $Ti_{0.3}Zr_{0.35}Hf_{0.35}CoSb_{0.8}Sn_{0.2}$ as *p*-leg and Al-doped ZnO as *n*-leg, the power density at $\Delta T = 700$ K achieved ~650 mW/cm^2, which is about two times higher than that of an all oxide module [1]. Long-term stability test at the hot side temperature of 800 °C in air revealed that the all oxide module is more stable than the segmented one, which showed a degradation rate of 4% for over 300 h. A novel TE module on a flexible substrate has also been demonstrated using Bi_2Te_3 materials, as shown in Fig. 1 is an example. Some results of our newly achieved module with 11% energy conversion efficiency using intermetallic compounds will be also presented.



(a) (b)

Figure 1: Power generation characteristics at various temperature gradients (a) and photo of a typical flexible TE module (b).

References:

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OC1.4

Towards cost effective and efficient energy generating skutterudite thermoelectric modules and the use of computational modelling to predict their properties

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Abstract

Skutterudite based thermoelectric materials have the potential to be a commercially viable energy harvesting system for waste heat recovery in the 300 °C to 600 °C temperature range, based on their good mechanical and thermoelectric properties and their composition of relatively abundant elements. Simplifications to the fabrication process are also important in driving down costs. Here we present modules which have been fabricated using low cost techniques such as electroplating of the metalisation layer and basic encapsulation methods. We report excellent power outputs and efficiencies, indicating that the module performance can be maintained using these fabrication techniques. In addition, a computer model has been developed to predict the module properties based on simple input parameters which have been experimentally obtained. The model can be used to investigate different hot-side/cold-side temperatures and load resistances, as well as show the optimisation of the module through alterations to the aspect ratio of the legs.

OC1.5

Heat exchanger performance impacts on optimum cost conditions in thermoelectric energy recovery designs

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Abstract

Cost is just as important as power density or efficiency for the adoption of waste heat recovery thermoelectric generators (TEG). Prior work [1] has shown that system designs that minimize cost (e.g., the $/W value) can be close to the designs that maximize system efficiency or power density, however, it is important to understand the relationship between those designs to optimize TEG performance-cost compromises. Expanding on recent work [1, 2, 3] the impact of heat exchanger conditions on optimum TEG fill factors and cost scaling of a thermoelectric energy recovery generator (TERG) with a detailed treatment of the hot side exhaust heat exchanger has been investigated. The effects of heat lost to the environment and updated relationships between hot-side and cold-side conductances [4] that maximize power output are considered. Optimum fill factors to minimize TERG energy recovery system costs are strongly dependent on heat leakage fraction, σ, exhaust mass flow rate, hot-side heat exchanger effectiveness, heat exchanger UAh, and heat flux. These relationships are examined for gas-flow and liquid-flow conditions to show the inherent design complexities. Heat exchanger costs often dominate the TERG cost equation and it is critical to fully understand the tradeoff between heat exchanger performance, optimum TERG fill factors, and cost to establish potentially optimum design points within the cost-performance design space. This work explores design relationships within the cost-efficiency-power density design space, identifying preferred TERG design regimes and compromises, for a typical TERG application. The interplay between optimum TERG fill factors and heat exchanger design can impact system footprint, volume, and mass in weight-sensitive applications. Design emphasis acknowledging the interdependence of optimum TERG fill factors and heat exchanger performance has significant implications on TERG system designs and their operation. This effort provides a focus for future TERG system research and development efforts.

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OC1.6

Thermal and electrical characterization of silicon nanowires forests for thermoelectric generation

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Abstract

A strong reduction of thermal conductivity in silicon nanowires (SiNWs), with respect to the bulk value, has been demonstrated in the last few years on devices consisting of a single, or very few nanostructures. This offers interesting opportunities for the exploitation of silicon as a thermoelectric material. Our experimental work focuses on the development of techniques for the fabrication of devices based on a large number of interconnected SiNWs[1], to be used for thermoelectric purposes. In particular, SiNW forests, made up of more than 10^7 nanowires/mm^2 oriented perpendicularly to a silicon substrate, with a diameter of about 80 nm and lengths of several tens of micrometers, are fabricated by means of highly directional vertical etching, based on metal assisted catalysis (metal assisted chemical etching). The SEM image on the left of Fig. 1 shows a nanowire forest, achieved by etching a Si wafer in an aqueous solution of silver nitrate and hydrofluoric acid (16:5:60 in volume) for 180 minutes. Nanowires can be doped both *n* type or *p* type, by exploiting conventional silicon doping processes. We developed a simple technique, based on chemical electrodeposition, for the selective growth of copper on the nanowire top ends. Our technique allows the reliable fabrication of a common contact on the top of the silicon nanowire forests. The SEM image on the right of Fig. 1 shows a nanowire forest with a Cu layer grown at the top. This layer provides a good thermal and electrical top contact; the bottom contact is provided by the silicon substrate (see the sketches in Fig. 1). Electrical and thermal characterization of *n* and *p* doped SiNW forests, with different doping levels, will be presented and discussed. The inset of Fig. 1 compares *I*-*V* characteristics of *n* doped and heavily *n* doped (n+) forests.

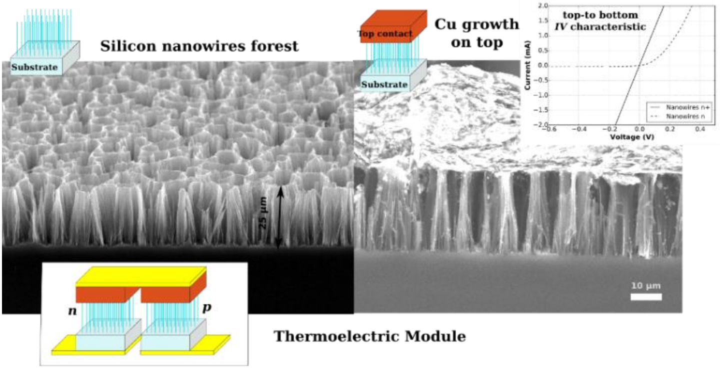

Figure 1

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OC1.7

Thermoelectric properties of doped *n*-$Mg_2Si_{0.4}Sn_{0.6}$ and *p*-$MnSi_{1.81}$ and their processing into thin-Thermoelectric Chips

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Abstract

We report on the powder metallurgical preparation and thermoelectric properties of doped Mn-silicide and Mg-silicide-stannide and their further processing into thermoelectric chips 5 mm x 5 mm x 500 µm. High-energy ball-milling under Ar-atmosphere is used for the preparation of the starting powders. The synthesis and compaction into silicide wafers (diameter 2 cm – 4.5 cm, thickness ~ 5 mm) are performed in one single step by Spark Plasma Sintering (SPS). The figure of merit zT of the *n*-type $Mg_2Si_{0.4}Sn_{0.6}$ and the *p*-type $MnSi_{1.81}$ reaches a peak value of at least 1.2 and ~ 0.6, respectively. Moreover, for $Mg_2Si_{0.4}Sn_{0.6}$, a $zT \geq 1$ is attained in a broad temperature range (from 250 °C to 570 °C). The wafers are ground and polished coplanar for a further contacting with metallic foils in a second SPS process. The thermoelectric chips are diced from the pre-contacted silicides. The processing into TE-chips is not a trivial task since both thermoelectric materials are very brittle. Electroerosion and slurry multi-wire dicing were used to overcome this difficulty.

The choice of the metallic foil for the electrical contacting is a challenge. The foils should just slightly react with the silicide material in order to produce a thin reaction-products layer (< 20 µm). The foils should possess similar thermal expansion coefficient to the silicide material in order to produce a thermo-mechanical stable construction. The foil should also act as a diffusion barrier against the solder during the brazing process. Moreover, for broad applications, the foil should have a low price. The demand of TE-material in a TE-Module can be ~ 10-fold reduced by using TE-Chips instead of massive TE-legs with typical size 3 mm × 3 mm × 5 mm.

OC1.8

Design and microfabrication of highly doped silicon-germanium thermoelectric modules for 500°C operation

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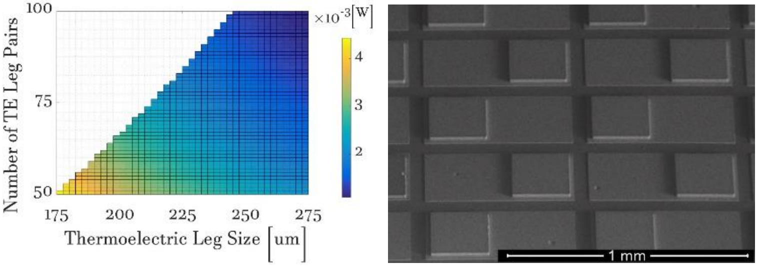
Abstract

The main commercial microelectronic semiconductors such as Si, Ge and $Si_{1-x}Ge_x$ reveal their optimum thermoelectric efficiency at high temperature (~1000 °C). However, in Si-like alloys ($0 < x < 0.5$), the doping level dependency of the thermoelectric figure of merit, zT, allows to translate the peak of the latter towards lower temperatures [3].

Thereby, 23 µm thick (including 3µm linearly graded buffer) $Si_{0.7}Ge_{0.3}$ layers were grown by chemical vapour deposition (CVD) on top of silicon on insulator wafers. With the aim of shifting the thermoelectric performance peak towards 500 °C, both p- and n-type were doped, respectively with boron and phosphorous, at $1x10^{19}cm^{-3}$.

The optimal number and dimension of the 20 µm long thermoelectric legs have then been investigated assuming a 1 cm^2 module, with hot side fixed at 500 °C, under the hypothesis [2] of constant heat flow ($Q_h = 5$ W) and considering the effects of air thermal conduction and convection within the device. Additional restrictions on temperature gradient across the module ($\Delta T < 25$ °C), internal resistance ($R_{in} < 5\ \Omega$) and output voltage ($V_{out} > 0.1$ V) resulted in the power output diagram presented in Fig.1a. From the microfabricated thermoelectric module (128 legs of 200 µm width), Fig.1b, under the above mentioned conditions, a power output of 2.8 mW/cm^2 is expected together with a Seebeck voltage output per degree Kelvin of 35 mV/K. The experimental results from the fabricated module will be presented at the conference.



(a) (b)

Figure 1: a) Module power output. b) SEM image of the microfabricated thermoelectric legs.

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OC1.9

Bi_2Te_3-based micro thermoelectric cooler fabrication by electrochemical deposition

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Abstract

To enable further miniaturization and closer integration of photonic integrated circuits, driven by the continuously growing network traffic, local heat management on the chip component scale is required [1]. A cost-efficient and highly scalable synthesis method, that is compatible with existing IC processing techniques, is the electrochemical deposition. In this work we present a new fabrication process for micro thermoelectric coolers using a laser lithographic process combined with electrochemical deposition of thermoelectric p- and n-type materials. By optimizing the pulsed electrochemical deposition of ternary n-type $Bi_2(Te_xSe_{1-x})_3$ and p-type $(Bi_xSb_{1-x})_2Te_3$ materials, compact and smooth films with thermoelectric properties close to the bulk counterpart can be achieved after appropriate annealing [2,3]. We investigated the influence of the deposition parameters on the film composition and crystal structure as well as the thermoelectric properties for thick films and confined structures. Especially the influence of the structure size on the film morphology was investigated to achieve smooth and compact films. The developed process enables the fabrication of thermoelectric coolers with single thermoelectric legs with a lateral resolution down to 20×20 μm² and a film thickness from 1 to 100 μm. The distance between the legs can be as low as 3 μm. For further optimization of the micro thermoelectric cooler we investigated the influence of different contact materials on the contact resistance to improve the efficiency of the device.

The support by the European Union's Horizon 2020 programme via TIPS (grant agreement No 644453) is acknowledged.

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OC1.10

SiGe thermoelectric far-infrared sensors

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Thermoelectric sensors of far-infrared radiation may lead to the low-cost fabrication of arrays for applications in the home-appliances and automotive industry [1]. We are investigating sensors where hot and cold junctions are located in a suspended membrane due to their potential for miniaturization and easier fabrication process [2]. Our improved sensors are fabricated on a single-crystalline SiGe membrane supported by a silicon substrate. SiGe layers were deposited by molecular-beam epitaxy on oriented SOI wafers. Ti/Au contacts were deposited and patterned to form an array of SiGe/Au thermopiles. Silicon was selectively etched below the hot junctions to form suspended membranes. Hot junctions were covered with polymers or nano-particles as radiation-absorbing materials (Fig. 1). Illumination with infrared radiation heats up quickly the hot junctions on the suspended membranes due to its low thermal capacity, whereas the cold junctions remain at a lower temperature due to the larger thermal capacity of the silicon substrate. This original design allows for a simple fabrication process which is potentially compatible with standard CMOS technology. Electrical measurements under infrared irradiation of a concept-demonstration device produced encouraging results. We intend to use these devices as a test-bench to improve thermoelectric materials by incorporating a variety of nanostructures in the layer such as modulation-doped quantum wells and quantum dots.

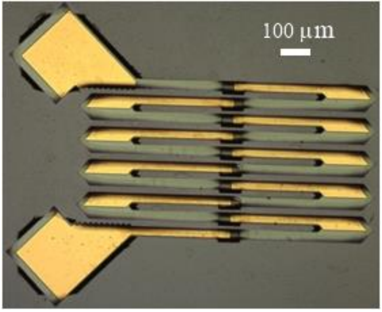

Figure 1: SiGe thermoelectric far-infrared sensor composed by 10 junctions in series.

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OC1.11

µTEGs with copper and tellurium as p-type materials

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Abstract

Recently we presented a fabrication process for micro thermoelectric generators (*µ*TEGs) based on multi-step photoresist lamination and sequential electrodeposition of *p*- and *n*-type thermoelectric legs enabled by selective sealing and unsealing of pre-structured cavities on a substrate [1]. The process requires a minimal amount of clean room processing, reducing the production cost in contrast to other state-of-the-art processes. The key step requires two selectively dissolvable photoresists which can be precisely applied by an industrial pick and placer system.

During the last month the process underwent significant changes and improvements ranging from an alternative photoresist to be used for sealing cavities to a change in *p*-type material as well as material for the upper contact. The modified new process will be presented along with a comparison of two different obtainable *µ*TEGs, Bi_2Te_3/Cu and Bi_2Te_3/Te. Thermoelectric and power measurements were carried out and will be compared, hinting a direction for further development.

The targeted applications for small energy supplier are mostly autonomous wireless systems (e.g. for automotive industry) and in our special case the energy supply of a neuroprobe for brain function monitoring and malfunction treatment (e.g. stimulation in case of epilepsy).

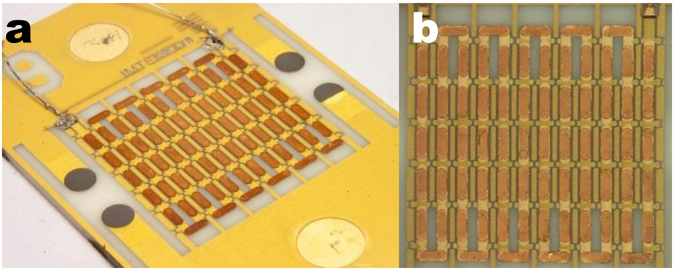

Figure 1: a) Bi_2Te_3/Cu *µ*TEG with 71 thermocouples (TCs) on Al_2O_3 substrate;
b) 71 TCs Bi_2Te_3/Te *µ*TEG with Au upper contact instead of Cu

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OC1.12

Enhanced platforms for Si NWs based thermoelectric generators

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Abstract

This work reports the advancements attained in the development of micromachined platforms to create all-silicon thermoelectric generators using Si NW arrays as active material [1]. Changes introduced in design and fabrication sequence have allowed to surmount critical issues limiting the process yield. Compact dielectric membrane supports for the metallic thermocouple parts (Fig. 1a) were introduced to avoid missalignment and provide a regular opening for backside DRIE. Membrane holes are aligned with fast etching planes, while the trench walls that will allocate the Si NWs are <111> aligned, and remain unaffected by the short KOH step (20 min.) used to release the membrane. Despite the hole/membrane area ratio reduction introduced to limit generator internal resistance the measured thermal conductances (Fig. 1b) are simmilar to that obtained for previous membrane designs [2]. Generator internal resistance is further reduced by improving the Si/metal contact resistance through boron implantation and thermal treatment.

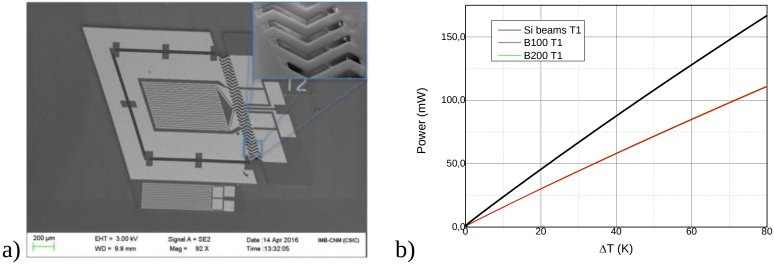

Figure 1: a) A single trench suspended platform with a membrane support for the metal interconnections (see the inset) obtained after anisotropic wet removal of the silicon underneath. **b)** Comparison of the platform-rim thermal conductance for 200µm bulk Si beam supports: 1.99 mW/K and 100µm and 200µm Si_3N_4 membrane: 1.26 mW/K.

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OC1.13

Dispenser printed flexible and full organic thermoelectric generators

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Abstract

The dispenser printing technology can be used for the manufacturing of thermoelectric generators (TEGs). It enables printing with barely any material losses, the absence of masks and the material can be directly applied in a desired form on a wide range of substrates.

For the manufacturing of flexible TEGs we use as substrates like Kapton or non-wovens. In contrast to the state-of-the-art-materials like bismuth tellurides which are brittle and stiff after printing, conductive polymers have the advantage to be elastic on substrates like Kapton and non-wovens. With these TEGs it is possible to convert waste heat from exhaust pipes or body-heat from T-Shirts into usable electrical energy.

As a promising organic p-type material, PEDOT:PSS doped with a co-solvent like dimethylsulfoxide (DMSO), is essential for this kind of application. The thermoelectric properties and as well as the ability to print make it the best choice for a flexible TEG. Apart from this p-type material we use a self-synthesized and further improved polymer , the n-type material poly[Kx(Ni-ett)], which currently exhibits the highest power-factor amongst n-type materials [1]. It is also known that poly[Kx(Ni-ett)] is insoluble and is therefore difficult to process. We achieved a dispenser printability of this n-type polymer. After drying, the poly[Kx(Ni-ett)] remains flexible which is a pivotal requirement for the application on a bendable substrate.

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OC1.14

Conditions to achieve the real maximum power point in thermoelectric generator systems

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Abstract

The majority of thermoelectric generators (TEGs) are characterized using setups that maintain a constant temperature gradient across the device. However, when switching from open- to short-circuit conditions, the Peltier effect influences greatly the thermal conductivity of the thermoelectric (TE) module and hence the temperature gradient across the device. A “constant temperature” parameter characterization maintains a constant gradient across the device but, at the same time, it disregards the variation of the system input thermal power that occurs to compensate for the Peltier effect. In actual TEG applications, the heat source available for TEG integration has limited heat flux and it does not provide a constant temperature if the operating conditions of the module change. This article provides a “constant heat” parameter characterization of a TEG corresponding to the conditions found in TEG integrated applications.

Moreover, it is generally known that a TE module operates at its maximum power point (MPP) when the voltage is set to half of the open-circuit voltage according to the maximum power transfer theorem. However, this relationship is not sufficient condition to operate the TEG system at the MPP. Voltage varies approximately linearly with temperature, whereas power varies as the square of the voltage. Hence, a slight reduction in the operating current yields a higher voltage and hence the peak power realizable is at a voltage slightly higher than the value predicted by the maximum power transfer theorem. This article proves experimentally that the “real” MPP in a TEG system is reached with additional conditions to the ones set by the maximum power transfer theorem. The experimental results are acquired from a hot gas system that is able to reproduce the actual conditions of a TEG integrated application with constant heat flux.

OC1.15

Testing and evaluation of electrical contact resistance for thermoelectric legs

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Abstract

For thermoelectric modules a low resistivity of the thermoelectric legs is essential for a good module efficiency. The total electrical resistance of a module, where the legs are normally connected in series, is the sum of the resistances of all single legs plus the sum of the single contact resistances. Therefore the contact resistance must be as low as possible and must be considered in module fabrication.
This work presents a study of the contact resistance and resistivity for single legs of Mg2SiSn, Zn4Sb3 and ZnSb that are connected with the contacts with different methods. The results are compared with standard commercial modules.
The measurements were performed with the Potential Seebeck Microprobe, using a special sample holder where an electrical AC current can be applied to the sample. A probe moves in microsteps along a leg including the contacts. The potential between one end and the probe tip can be measured, that is related to the electrical conductivity at the samples position. A gap in the measured potential is proportional to the contact resistance, so that it can directly be determined, when knowing the area and current (see Fig. 1).
The total resistance or impedance of the legs is measured as well with impedance spectroscopy to have a comparison for the resistivity of the leg material. With this systematic study the soldering or contacting process can be optimised.

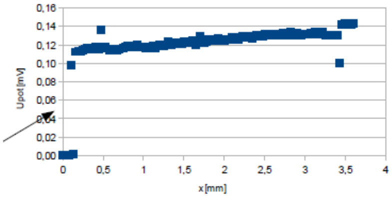

Figure 1: Electrical potential at a Zn_4Sb_3 leg including contact. The gap at the arrow indicates the contact resistance, the slope of the line is proportional to the electrical conductivity.

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C2. Applications (general, automotive, industrial)

OC2.1

Thermoelectric energy harvesting system for aluminium electrolysis industry: system design, manufacturing and test in industrial environment

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Abstract

Primary aluminium production industry represents an interesting target for thermal energy harvesting due to the high quality waste heat over 300°C [1]. This paper describes a thermoelectric generation system developed to harvest waste heat released on the surface of Hall-Héroult Electrolytic cells. The optimisation of the thermal and mechanical sizing has been investigated to get the highest performances. Such thermoelectric system is able to generate 200 W/m² electric power during nominal operating conditions without affecting the production process.

A first demonstrator and its clamping system has been developed and fabricated following the thermal and mechanical specifications. This demonstrator has been successfully tested in an industrial environment. The potential usage of this free energy generated by the thermoelectric device will be further discussed.

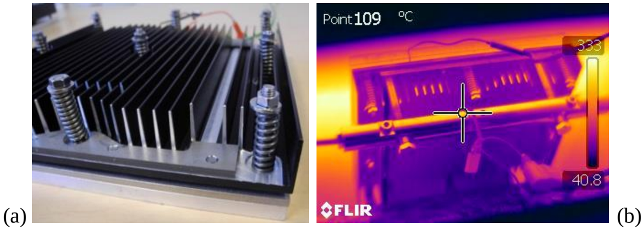

Figure 1: Thermoelectric energy harvesting system (a) and IR image during test in industrial environment (b)

References:

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OC2.2

Computational and experimental evaluation of solar cell thermoelectric hybridization: a multi-parametric approach

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It is well known that the major constrain to the photovoltaic (PV) efficiency, especially in single-junction solar cell, comes from the spontaneous generation of unused heat within the device. Therefore, in principle thermoelectric generators (TEGs) may be used to recover and convert part of this heat into electricity. Recently, both theoretical and experimental works were published on Hybrid Thermoelectric-Photovoltaic (HTEPV) systems [1]. Although some of them reported large efficiency improvements, they mostly focused on the coupling between commercial TEGs not optimized to be hybridized in HTEPVs. Furthermore, the experimental procedures have been often affected by very optimistic estimates of the cold side temperature that may lead to severe overestimations of the HTEPV efficiency [2, 3].
In this communication we propose a multi-parametric model developed to find the HTEPV parameters needed for a beneficial coupling between PV and TEG devices. Starting from modeling the PV part, we computed the PV and the HTEPV efficiencies as a function of the energy gap of the absorber material and of the device temperature. The model, which was experimentally validated, showed that hybridization leads to an increase in efficiency only when the energy gap of the absorber material and the PV backside temperature are sufficiently large. This sets in turn quantitative constraints on the TEG and HTEPV designs that are not usually met by standard (commercial) TEGs. The actual implications of such results in the experimental assessment of HTEPV generators will be discussed.

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OC2.3

Cooling performance of a thermoelectric façade prototype

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Abstract

This paper will present the results of monitoring a prototype for residential buildings called Thermoelectric Unit System (TUS) [1]. Although there are works on this technology (see e.g. [2]), the two main contributions of this work are: 1) it has been designed in a School of Architecture to try to develop a prototype that can reach the real market and 2) it is a significant improvement over a previous prototype designed and built by researchers [3].

Compared with a conventional air-conditioning system, this TUS system is a pre-commercial design, so that, in investment costs, a conventional air-conditioning system is economically cheaper than TUS system, but the paper will be focus on describe the data related with energy consumption and its heat transfer capacity.

Figures 1 and 2: Integration of the Peltier Cells in façade (left) and interior view (right) of the thermoelectric prototype.

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OC2.4

Application of silicide based, cost efficient thermoelectric generators for high temperature waste heat recovery

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Abstract

Although the development of thermoelectric materials and generators has been ongoing for many years, the transition from today’s prototype- and niche applications to future large scale markets, such as industrial waste heat recovery in the steel and glass industry, is the challenge ahead. RGS Development has decided to focus on development, production and market introduction of a cost efficient, silicide material based thermoelectric generator system that converts high temperature industrial waste heat into electricity. The aim is to provide a viable business case with negligible impact on the industrial production process itself.

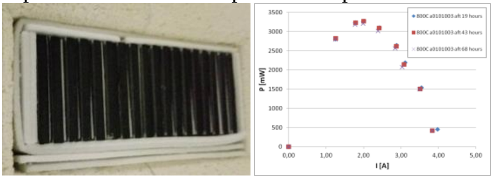

Figure: Left: 40×100 mm^2 thermoelectric module installed in a furnace wall; middle: power output curve; right: design of a 200 x 300 mm^2 thermoelectric generator.

Based upon its capability to produce silicide materials in wafer form on industrial scale, RGS Development has produced thermoelectric materials, made test modules (fig. left, middle) and designed large format thermoelectric generators (fig. right) that can be applied at high temperatures in situations that are typical for heavy industry waste heat recovery.

These materials and modules were successfully tested in furnace environments up to 1000°C, where TE module top temperatures in excess of 600°C were achieved and degradation tests up to 1000 hours were done.

Due to the advanced thermoelectric generator design, the TE panels can be applied efficiently in a variety of practical situations without the need for sophisticated system components such as external pressure devices or protective gas sealing. Consequently such TE panel design can be applied more cost efficient and flexible.

In parallel to the TE module and panel development program, Tata Steel and RGS Development are engaged in an industrial pilot project to test the thermoelectric system in a relevant application environment.

OC2.5

Computational and experimental study on thermoelectric generators using thermosyphons as heat exchangers

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Abstract

To improve the electric generation in thermoelectric applications it is key to maintain a high gradient of temperature between the hot and cold side of the thermoelectric modules. In order for the temperature to be as low as possible on the cold side, a thermosyphon heat exchanger with phase change has been developed. Its ability to efficiently distribute and transfer a heat flux from a small surface to a larger one, as well as its lack of moving parts, make the thermosyphon a proper option to combine it with a thermoelectric generator.

A computational model capable of predicting the behaviour of these kinds of heat exchangers together with a thermoelectric generator has been developed. Important aspects of the exchanger have been taken into account, such as: boiling and condensation phenomena or constriction thermal resistances.

The validation of the model has been accomplished with a prototype and a computational study has been performed, in which, several geometric parameters have been optimised to maximize the electric energy production. Furthermore, a comparison between a thermosyphon and a common finned heat sink has been carried out in order to show whether a thermosyphon outperforms the finned sink while used in thermoelectric applications.

The computational model here presented turns out to be a powerful tool that will be very useful to design thermoelectric generators that include thermosyphon heat exchangers with phase change on the cold side.

OC2.6

Optimal integration of cascade thermoelectric cooler into electronic housing

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Abstract

Integration of thermoelectric cooler (TEC) into electronic housing is a real issue due to specific constraints imposed on the TEC parameters under such application. The TEC dimensions must be small enough to fit internal sizes of standard electronic housing. Another problem originates from the fact that these objects are usually used as components of a man-portable device with autonomous power supply. This means that the TEC must be optimized to achieving necessary cooling with minimal input power which is proportional to the heat load at the TEC cold side. Hence, to optimize the TEC design for minimal power consumption, it is necessary to make accurate estimation of the heat load on the TEC inside of electronic housing.

The case of heat transfer in a closed environment with tight geometry is complicated for analytical study. All three mechanisms - convection, radiation and conduction are generally involved. The contribution of each one is dependent on many factors including the TEC and header dimensions, emissivity of the substrate and that of a header interior, the nature and pressure of a filling gas, and the material and dimensions of the wires attached to the cooled substrate.

In this study, the experimental approach to the definition of the heat load on the TEC inside electronic housing is proposed. The method is based on application of a TEC with calibrated dependence of temperature difference on applied heat load. Standard two-stage Thermion's TEC with identical top and bottom substrate dimensions is used for this purpose. The heat gains from the header body are defined by direct measurement of temperature difference generated by this specimen inside the header. Studied was TO8 header which is widely used for incorporating thermoelectrically cooled temperature sensitive optoelectronic components. Defined are heat gains in gas atmosphere and in vacuum as a function of residual pressure. The data are represented in a form of a specific heat load per 1 K of temperature difference related to the unit of the TEC top surface. Obtained results provide a reliable basis for optimal integration of a TEC into housing. The data are used for design of the 2- and 3-stage TECs optimized for receiving temperature difference over 100 K with minimal power consumption.

OC2.7

Autonomous temperature monitoring: application of thermal harvesting to food control

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Abstract

Temperature control in foodservice industry is mandatory both to prevent food borne illness and to ensure food quality. To this aim, thermal harvesters may enable the use of wireless sensors even when the appliance is supposed to operate off-grid. We present the design, the implementation and the characterization of such an autarkic device that uses ultra-low power RF data transmission units, suitable to be powered by an all-silicon thermoelectric generator (TEG) to log oil temperature readings in a industrial fryer.

TEG power source made use of a platform of silicon nanowires obtained with IC-compatible technologies. For the sake of comparison, also a conventional, commercial thermoelectric module based on bulk Bi2Te3 legs was used. A heat sink was designed and to maintain a constant temperature difference of at least 50 K across the TEG in steady air. TEG collected heat from the hot wall of the fryer chimney at temperatures between 280 and 320 °C. The 434MHz RF module with pulse-based transmission, provided with a microcontroller from MSP430 family and coupled with a temperature monitor (a J-type thermocouple) was in charge of reading and transmitting the temperature data to a remote logging unit (Figure 1b). No rechargeable battery was used. We verified that the device was capable of sending out readings at a rate better than 0.5 Hz, with an initial lagging period shorter than 5 seconds. Results demonstrated the actual usability of thermoelectric harvesters as a power supply of industrial appliances to monitor and control food quality, enforcing EC policy in this area.

This work was partially supported by FP7-NMP-2013-SMALL-7, SiNERGY (Silicon Friendly Materials and Device Solutions for Microenergy Applications) Project, Contract n. 604169.

OC2.8

Experimental application of distributed maximum power point tracking to a thermoelectric system for hot gas

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Abstract

Several thermoelectric systems are nowadays being developed and commercialised for a wide range of automotive and industrial applications. Most of these systems aim at recovering heat from exhaust gas and convert it to usable electrical power. Reliable and efficient operation of these systems results from the robust integration of thermo-mechanical and electrical design. This work focuses on the electronics required to maximise the electrical power generated by the thermoelectric generators for any thermal situation. Dc-dc converters controlled by maximum power point tracking algorithms are employed for this task.

Thermoelectric generators are not always guaranteed to be working at the same temperature difference due to their location on the heat exchanger or to uneven gas flow. In this situation it is advisable to connect thermoelectric devices in arrays, each connected to a separate converter. This work presents a quadruple boost converter controlled by a single microcontroller, thus effectively forming a distributed maximum power point tracking system. This system is used to optimise the efficiency of a thermoelectric power generator that extracts heat from hot gas. Experimental results are provided to demonstrate the effectiveness of this solution and to compare its performance to other currently accepted tracking methods.

OC2.9

Thermoelectric energy recuperation for aviation jet engines – Module design and installation

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Abstract

The reduction of fuel consumption of future aircrafts represents a major challenge on the way to environmentally friendly and cost efficient air transport systems. Among discussed approaches a conversion of engine heat into electrical energy is considered as a highly promising attempt to move closer to specified goals of ACARE and Flightpath 2050. Thermoelectric generators (TEG) can offer a robust and direct recuperation of lost heat from an aircraft engine. Although lower in today’s achievable efficiencies, they do avoid additional complex thermodynamic cycles with moving parts (e.g. ORC). However the integration and determination of the effective performance of TEG in the application environment of jet engines has not been focus of any detailed research yet. Germanys fifth Aeronautical Research Program (LuFo-V) gives the framework for the “TERA” project (Thermoelectric Energy Recuperation for Aviation), which focuses on a holistic reflection of possibilities and challenges for the adoption of a TEG to aircraft systems.

In a previous publication [1] the general potential of thermoelectric modules applied on the exhaust nozzle of a jet engine has been outlined. This paper focusses on the design of the thermoelectric modules for given thermal boundary conditions and the resulting performance for different flight phases of a reference mission. With respect to a maximization of the power density, pellet lengths are optimized for given operation conditions. It is shown, that a significant share of the overall temperature difference between the hot core stream and the cold bypass flow of the jet engine is lost at the convective heat resistance towards the nozzle material. In order to reduce the convective heat resistance a new module design concept has been explored. Removal of one base plate of the module and direct immersion of coated pellets in the air stream is proofed to lower weight and to enhance power output simultaneously. Together with a conservative approach of materials performance (ZTmax ~ 1.2) these measures yield power densities comparable to the electric machinery and its periphery used for the electric energy supply on aircraft – making it an option for an additional or alternative energy source for both today’s and tomorrow’s on-board electrical nets.

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C2.10

A compact thermoelectric air cooler for vehicles

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Abstract

Global warming continues to challenge all countries around the world in terms of environment. Unfortunately, a conventional air cooler is difficult to apply to environmentally friendly vehicles. The conventional air cooler uses the refrigerant, while a thermoelectric (TE) module is powered by DC electricity without the refrigerant. For weight lightening of vehicles, the size and weight of air cooler should be small and light. The only commercially available miniature-sized air cooler today is the TE cooler [1].

The purpose of this study is to design and fabricate a compact thermoelectric air cooler (CTAC). Most vehicles are equipped with heating, ventilating and air conditioning (HVAC) system. However, passenger in the back seat of the car can’t feel cool as soon as they get into the car. Therefore, it is necessary to install the secondary air cooler at the top of the back seat. The CTAC is suited for the secondary air cooler due to the limited space between the roof and cabin of the car.

A proper TE module is chosen by analyzing maximum input current (Imax), amount of heat absorption (QC) and temperature difference (∆T) between cold side and hot side of the TE module. The evaluation system developed previously consists of vacuum chamber with water cooler and metal block. The characteristics of the TE module are measured in a vacuum to minimize heat loss.

The CTAC with the proper TE modules is composed of heat sinks, fans and flow channel. The 5mm height heat sinks are designed owing to height limit 15mm. The TE modules are used to increase cooling rate continuously. The CTAC is tested in insulating chamber with an inner volume of 250mm×250mm×250mm, the same size as an average human head. Thermocouples were installed for measuring temperature at the center of the chamber and the cold side of the TE module.

The CTAC can be switched to a heating system with a polarity reversal of the direct current that supplies the power. The CTAC is used to heat up the air inside chamber before evaluating the cooling performance of the CTAC. After the temperature inside the chamber sets 45℃ as the typical temperature inside the car in a hot summer day, time to be cooled down to 26℃ is measured. The results showed that it took 200 seconds to reach the target temperature. It is found that the CTAC could make passenger in the back seat of the car feel cool within 4 minutes.

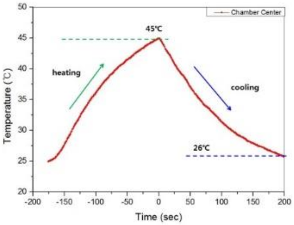

Figure 1: Performance of the compact thermoelectric air cooler in heating and cooling.

References:

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OC2.11

V_2O_5 thin films seebeck coefficient optimization and application in flexible and transparent temperature sensor

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Abstract

This work reports the optimization of V_2O_5 Seebeck coefficient to obtain high sensitivity and transparent temperature sensors.

The influence of film thickness, annealing temperature and time were studied, being the Seebeck coefficient of -690µV/K optimized for films thickness around 75nm, deposited on glass and annealed during 1h at 773K, in air. Likewise V_2O_5 films were deposited on polyimide substrates that require lower annealing temperature, 573K for 3h, to maintain the flexibility and integrity of the substrate but the optimized films still exhibit high Seebeck coefficient, -591µV/K (Figure 1)

The films deposited on polymeric substrates were used in a novel thermal sensor that combines high sensitivity, flexibility and transparency, which is advantageous for specific applications. Also, the materials used are harmless and abundant in nature.

The fabricated sensor was tested to evaluate the temperature variation on the surface of a microfluidic channel (500µm) made of PDMS (polydimethylsiloxane), while having hot water flowing through it. The response time was below 1 second and the recovery time around 5 seconds (Figure 2).

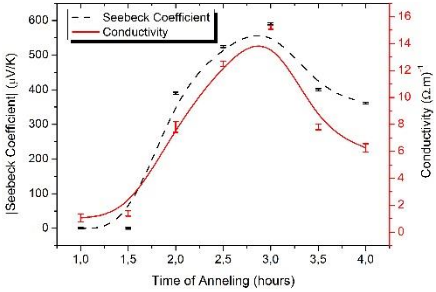

Figure 1: Seebeck coefficient and conductivity of V_2O_5 film deposited on Kapton, as a function of the annealing time, at 573K.

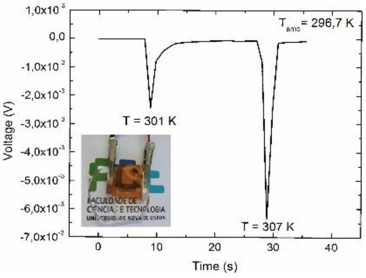

Figure 2: Continuous voltage response when water flows inside the 500µm channel of the PDMS.

OC2.12

Waste heat recovery at scale: a system approach to bring a sizeable re-use of high temperature industrial waste heat to reality

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Abstract

The industry is continuously looking for feasible and viable means to harvest the enormous potential of high temperature waste heat. Nevertheless, these reservoirs have remained virtually untapped, partially due to the disadvantages and limitation of conventional technologies – like organic ranking cycle (ORC), and partially due to the immaturity of new technologies– like thermoelectric generation (TEG). Whereas over the past years much efforts and attention has gone and still goes to the development of thermoelectric materials, it is time to use a systems approach to bring the TEG technologies to realize practical and scalable implementation. In addition to the many approaches of exhaust waste heat recovery, RGS Development has added a systems approach for harvesting radiation heat through an integrated supported panel without any complicating system components. This approach is realized by taking coherent directions with respect to: materials, module architecture, systems design, mass manufacturing, ease of installation, and either minimum or positive impact on the primary product manufacturing process. When compared with the references as for exhaust waste heat in industry or automotive from the perspective of cost and scalability, such approach shows a leap forward on the way to broad adoption. It finally creates a realistic energy harvesting option for multiple heavy industries.

OC2.13

Maximizing efficiency under variable thermal load using temperature-controlled exhaust thermoelectric generators

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Abstract

The viability of automotive exhaust thermoelectric generators (TEGs) is highly dependent on the ability of these systems to operate efficiently over a broad range of engine loads. This is not straightforward task when the hot exhaust gases vary substantially in flow rate and temperature during real-world driving cycles. In conventional systems, a small sized, low thermal resistance TEG will operate well under medium engine loads but it will have to be protected against overheating under high loads. A big sized system will operate suitably at full engine load but it will suffer from thermal dilution under the medium-to-low engine loads typical of urban driving. The authors have been exploring a concept in which the temperature faced by the thermoelectric (TE) modules may be regulated nearly independently from the engine load. This is done with the help of a thermosiphon device which acts as a thermal buffer/interface between the hot exhaust gases and the hot face of the TE modules. The variation of engine load will affect mainly the active heat transfer area (the heat will be directed only to a fraction of the modules) while the hot face temperature of the active modules will be fairly constant. This seems highly convenient as it allows a variable load operation without having thermal dilution nor overheating risk, in a passive way, something that has not been achieved with conventional TEG prototypes. The present work details the heat transfer modelling across the whole system, integrating it with the modelling of the engine, driving cycle and TE. This is an improved version of a previously presented one [1], and is used to assess the performance of a passenger vehicle TEG during type-approval and real (recorded) driving cycles. The overall merit of using either thinner (power-oriented) or thicker (efficiency-oriented) TE modules is assessed. It was found that despite active thinner modules providing higher power than thicker ones, their use would normally lead to a lower net power output because a lower fraction of the modules would be active. Exceptions to this would happen when using small sized systems or high load driving cycles, where the higher thermal power consumption of thin modules would not be limitative.

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OC2.14

Thermoelectric triggering of a phase-change heat battery

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Abstract

The authors present the application of a peltier heat pump to cause nucleation in a supercooled phase change material (PCM) in the liquid state. The commercially available BiTe peltier module has a footprint of 15x15mm and contains 17 couples. In order to increase the cold-spot performance of the module the face in contact with the PCM is covered in a layer of pyrolytic graphite sheet with an in-plane thermal conductivity of 1600W/m.K. This is covered with an insulator with a circular aperature for exposure to the PCM. The Peltier module is attached to a copper plate that forms part of the heat exchanger system in the heat battery and which provides the reference against which the ΔT is established.

The application of PCMs to long-term heat storage is an emerging technology. When energy storage is required over a known temperature range it is possible to store sensible and latent heat, significantly increasing released energy density over existing systems. Current PCM heat storage systems release latent heat as they make the transition from liquid to solid. This constrains the energy stored to its freezing point. When PCMs are supercooled in the liquid phase they retain their latent heat until the phase change is initiated. In the application presented, a Peltier module is used to locally cool a small amount of PCM in contact with the exposed module surface to cause spontaneous nucleation, thereby initiating the energy release from the whole heat battery. By cooling a small volume of material the energy available for heating purposes is greater than would be the case for auto-nucleation because of the decreased sensible heat reduction needed. Multiple trigger units can be employed to accelerate the energy release from the heat battery.

The performance of the peltier module and its coefficient of performance are presented when cooling different materials. The power requirements to achieve the required temperature for nucleation to occur are also presented.

OC2.15

Effectiveness of thermoelectric generators mounted into exhaust tract of internal combustion engine

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Abstract

In the present study, the complex efficiency of internal combustion engine (IC-engine) exhaust gas waste heat utilization by means of the thermoelectric generators (TEG) mounting into an exhaust tract is studied.

The results of mathematical simulation of the TEG, including the gas flow inside the heat-exchange unit flow channel and the heat exchange through thermoelectric modules, the calculation of the basic performance characteristics of the TEG (electric power, efficiency, weight and etc.), as well as an overall estimation of the efficiency of IC-engine with TEG considering the influence of the generator aerodynamic resistance on the IC-engine power loss are represented.

In the current work modeling combines previously presented TEG analytical model [1] and computational fluid dynamics model, used to refine the heat exchanger emission coefficients for the certain operating conditions.

The experimental studies of the TEG parameters and the integrated quality factors for the developed mathematical model verification and the TEG performance characteristics determination are conducted.

The comparison of the effectiveness of various design techniques of heat exchange intensification is performed based on the gas dynamic resistance coefficients ratio ξ/ξ_0 and the dimensionless criteria ratio N_u/N_{u0}. As a result, conclusions about the applicability of the heat exchange intensification techniques for thermoelectric generators of various purposes are formed, and the complex efficiency of TEG application for the internal combustion engine exhaust gas waste heat utilization is assessed.

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Poster Contributions

A1. Skutterudites

PA1.1

Transport and thermoelectric properties of *p*-type double-filled $R_{1-z}R'_zFe_{4-x}Co_xSb_{12}$ (R or R': Pr, Nd, Yb) skutterudites

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Abstract

Filled skutterudites are regarded as potential candidates for thermoelectric power generation applications at intermediate temperatures [1,2]. *n*-Type filled skutterudites have high thermoelectric performances, but *p*-type filled skutterudites have relatively low thermoelectric performances [3]. Therefore, *p*-type skutterudites need to enhance the thermoelectric properties for thermoelectric modules with *pn* couples. In the present study, *p*-type double-filled $R_{1-z}R'_zFe_{4-x}Co_xSb_{12}$ (R or R': Pr, Nd, Yb, z = 0.25, 0.75, and x = 0, 0.5, 1.0) skutterudites were synthesized by encapsulated melting and annealing, and consolidated with hot pressing. The effects of double filling and charge compensation on the microstructure, the electronic transport, and the thermoelectric properties of the skutterudites were examined. A small amount of $FeSb_2$ phase was formed for all specimens, but the $FeSb_2$ phase formation was suppressed by Co substitution for Fe. The electrical conductivity of all specimens slightly decreased with increasing temperature, showing degenerate semiconductor characteristics. The Hall and the Seebeck coefficients of all specimens showed positive signs, indicating that the major carriers were holes (*p*-type conductions). The Seebeck coefficients of Co-substituted specimens increased due to the decrease in the carrier concentration while the electrical conductivities and the thermal conductivities decreased. The dimensionless figure of merit, $ZT = 0.81$ was obtained for $Nd_{0.75}Yb_{0.25}Fe_3Cob_{12}$ at 723 K, and $ZT = 0.83$ was attained for $Pr_{0.75}Nd_{0.25}Fe_4Sb_{12}$ at 823 K. The maximum $ZT = 0.85$ was achieved for $Pr_{0.75}Yb_{0.25}Fe_{3.5}Co_{0.5}Sb_{12}$ at 723 K.

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PA1.2

Thermoelectric properties of $(La/Ce)_{1-z}(Pr/Nd)_zFe_{4-x}Co_xSb_{12}$ skutterudites

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Abstract

Skutterudites have been widely investigated as promising materials for thermoelectric power generation at temperatures from 500 K to 900 K [1]. Skutterudite structure has two large voids per unit cell that can be occupied by filler atoms, which play two important roles. First, the fillers donate electrons to the host compound to tune the electrical property and second, the vibration of fillers in the voids leads to phonon scatterings and substantially reduces the lattice thermal conductivity [2]. Each filler atom has a specific atomic mass and a unique resonant frequency [3]. Thus, double or multiple filling can cause more phonon scattering, resulting in the improvement of thermoelectric performance with lower lattice thermal conductivity. In this study, *p*-type $(La/Ce)_{1-z}(Pr/Nd)_zFe_{4-x}Co_xSb_{12}$ ($z = 0.25, 0.75$ and $x = 0, 0.25$) skutterudites prepared by encapsulated melting and hot pressing. The effects of double filling and charge compensation on the thermoelectric properties were examined. The electrical conductivity decreased with increasing temperature, implying a degenerate semiconductor behaviour, and also decreased with La/Pr and Co contents. The Seebeck coefficient increased with increasing La and Pr contents and Co content due to decrease in the carrier concentration. Also, The Seebeck coefficient increased with increasing temperature and reached to a maximum value at 823 K. The thermal conductivity increased at temperatures above 623 K due to bipolar conduction. The lattice thermal conductivity decreased with increasing Pr and Nd contents. The dimensionless figure of merit, $ZT = 0.83$ was obtained at 823 K for $La_{0.75}Pr_{0.25}Fe_4Sb_{12}$, $ZT = 0.82$ was attained at 823 K for $La_{0.75}Nd_{0.25}Fe_4Sb_{12}$, and $ZT = 0.84$ was achieved at 823 K for $Ce_{0.25}Pr_{0.75}Fe_4Sb_{12}$. Also, for Co-substituted specimens, $ZT = 0.81$ was attained at 723 K for $La_{0.75}Pr_{0.25}Fe_{3.75}Co_{0.25}Sb_{12}$, $ZT = 0.78$ was obtained at 723 K for $La_{0.25}Nd_{0.75}Fe_{3.75}Co_{0.25}Sb_{12}$, and $ZT = 0.80$ was achieved at 823 K for $Ce_{0.25}Pr_{0.75}Fe_{3.75}Co_{0.25}Sb_{12}$.

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PA1.3

Glass coating/$CoSb_3$ interface: characterization by transmission electron microscopy

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Abstract

Doped cobalt triantimonides are used as components of thermoelectric devices at temperature range about 400–600˚C. The main difficulty of the $CoSb_3$ application is the degradation of its thermoelectric properties as a result of antimony sublimation and material oxidation at elevated temperatures. To prevent these processes protective coatings are foreseen. The objective of this work was to characterize the glass coating/$CoSb_3$ interface and to determine its influence on the $CoSb_3$ stability at elevated temperatures. To determine oxidation resistance, coated samples were oxidized at 600˚C in air and examined by SEM/EDS, TEM/EDS, STEM-EDS and SAED electron diffraction. The results of the study showed that effective protection for $CoSb_3$ against oxidation at 600˚C in air was possible only if:

no crystallization near glass/substrate interface occurred;

porosity at the glass coating/$CoSb_3$ interface was as small as possible;

adhesion was ensured by both chemical and mechanical bonding.

The glass coating was an effective barrier for oxygen diffusion into the material and for antimony sublimation, therefore chemical and phase composition of the substrate was not affected by the oxidation (Fig.1).

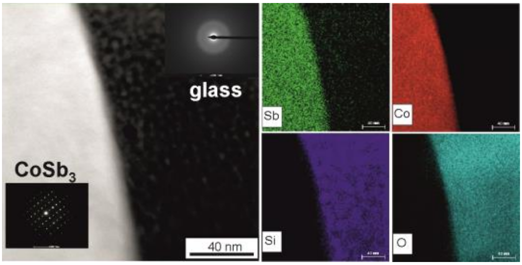

Figure 1: STEM-HAADF image of glass coating/ $CoSb_3$ interface with EDS maps of selected chemical elements and two diffraction patterns (insets) form amorphous and crystalline regions.

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PA1.4

High-temperature degradation study of $Fe_{4-x}Co_xSb_{12}$ filled skutterudites

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Abstract

Thermodynamic instability of $Fe_{4-x}Co_xSb_{12}$-based skutterudites substantially limits their applicability in thermoelectric converters. In this report we present a detailed study of phase degradation of filled $Fe_{4-x}Co_xSb_{12}$ upon high-temperature processing. DSC studies revealed a weak endothermic (within 240 – 480°C) and two strong exothermic (at ~500°C and ~580°C) events occurring upon heating of $Ce_yFe_{4-x}Co_xSb_{12}$, which can be ascribed to volatilization of Sb and irreversible formation of $Fe_{1-x}Co_xSb_2$, as confirmed by *in-situ* high-temperature PXRD (Fig.1). Except for temperature, the spark-plasma-sintering parameters had little effect on skutterudite decomposition. The latter remained virtually intact at sintering temperatures below 500°C. We shall further discuss transport properties measurements, which underline that abundant impurity phases are detrimental to the thermoelectric performances of filled $Fe_{4-x}Co_xSb_{12}$.

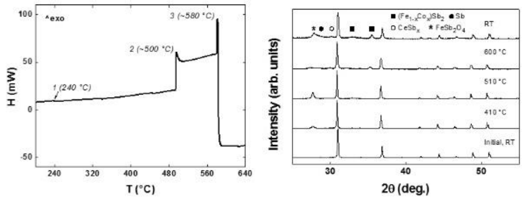

Figure 1: Heat flow and *in-situ* high-temperature PXRD for $Ce_yFe_{4-x}Co_xSb_{12}$.

PA1.5

Towards band gap engineering in skutterudites: the role of X_4 rings geometry in $CoSb_3$-$RhSb_3$ system

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Abstract

During the very first theoretical investigation [1-2] of the electronic structure of skutterudites it was found that the value of calculated band gap E_g is strongly dependent on positional parameters of the pnictogen in the unit cell. According to Jung *et al.* [3] even small changes in the geometry of X_4 ring have strong influence on the energy of molecular orbitals and in result lead to broadening of the band gap due to hybridization of *p* states.

In the present work experimental results confirming the theoretically predicted relation between bonds properties in Sb_4 rings and band gap E_g are presented for solid solutions of $Co_{1-x}Rh_xSb_3$ ($x = 0$ to 1) and other systems. Crystal structure parameters determined from XRD data and band gap values estimated from electrical conductivity [4] are interpreted in the context of DFT analysis of influence of X-X bonds lengths on the electronic band structure.

The results show very complex behaviour and sensitivity of states lying close to the band gap due to Sb_4 ring geometrical parameters. New concepts of band gap engineering for skutterudites by selective doping or applying high pressure are discussed.

Acknowledgements

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A4. Tellurides

PA4.1

Nanostructuring effects on the thermoelectric properties of n-type $(Bi_{0.95}Sb_{0.05})_2(Te_{0.95}Se_{0.05})_3$

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Abstract

Nanostructuring has proven to be an efficient way to enhance the performance of state-of-the-art or advanced thermoelectric materials. Many techniques to produce nanoparticles and nanostructured materials have been explored in the literature.

We propose here to check the thermoelectric properties of n-type $(Bi_{0.95}Sb_{0.05})_2(Te_{0.95}Se_{0.05})_3$ composites made simply by a mixture of nano-sized particles produced by the original way of laser fragmentation in a liquid medium with micron-sized particles of the same composition. Nanoparticles of n-type $(Bi_{0.95}Sb_{0.05})_2(Te_{0.95}Se_{0.05})_3$ have been prepared by pulsed laser fragmentation in water from micron-sized particles of same composition. Different amounts of nanoparticles ranging from to 2 to 20% in weight have then been gently mixed to micron-sized powders. Sintering of the resulting mixtures was carried by cold pressing to avoid any grain growth. Reference samples containing none or only nanoparticles were also prepared.

Microstructural investigations of the resulting ingots have been performed by scanning electron microscopy and powder x-ray diffraction. The transport properties, i.e. the electrical resistivity, the thermopower, Hall coefficient, and the thermal conductivity have been measured between 2-300 K on the various samples. Influence of the weight content of nanoparticles and microstructure will be discussed as well as anisotropy effects measured at room temperature. Beneficial effect on the thermal conductivity has particularly been observed.

PA4.2

Influence of synthesis processes on the thermoelectric properties of SnTe

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Abstract

Recently SnTe has attracted attention in thermoelectricity as a lead-free analogue of PbTe with a similar valence band structure [1-3]. However, pristine SnTe is a poor thermoelectric material because of its very high hole concentration arising from intrinsic Sn vacancies in the lattice [4,5], which give rise to low Seebeck coefficient and high electrical and thermal conductivity. In this study, we demonstrate how the hole concentration can be controlled in SnTe-based material by varying the synthesis process. In particular, we show that self-compensation can effectively reduce the concentration of Sn vacancies and decrease the hole carrier density. For example, a 3 mol % self-compensation of Sn results in a 50% improvement in the figure of merit *ZT* that reaches 0.6 at 800 K.

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PA4.3

Enhanced thermoelectric properties in Bi-Sb-Te based composites with Y_2O_3 nanoparticles

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Abstract

Thermoelectric materials (TE) have the capability of direct conversion of waste heat energy into electricity via Seebeck effect, or active cooling via Peltier effect [1]. Recently, incorporation of ceramic nanoparticles(NPs) in the bulk thermoelectric matrix is one of the new strategies to boost Seebeck coefficient via energy filtering effect (EFE) with simultaneous decrease in thermal conductivity via scattering mechanism at newly formed interfaces [2].

In this research, p-type BiSbTe/Y_2O_3 nanocomposites (NC) have been fabricated by mechanical milling and spark plasma sintering. The existence of the Y_2O_3 nanoinclusions are confirmed by x-ray diffraction and TEM-SAED analysis. The hardness of the NCs are significantly improved than pure BiSbTe bulks due to the grain boundary hardening. The temperature dependence of thermoelectric properties are severely affected by the dispersion of Y_2O_3 NPs in BiSbTe matrix. The thermoelectric figure of merit, ZT is remarkably improved in BiSbTe/Y_2O_3 NCs due to significant increase in Seebeck coefficient via EFE, and dramatic decrease in thermal conductivity via carrier scattering mechanism.

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PA4.4

Enhancing the figure of merit of GeTe-based thermoelectric materials

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Abstract

The alloys $(GeTe)_x(AgSbTe_2)_{1-x}$ (commonly known as TAGS) are among the best high-temperature thermoelectric materials, largely due to their low thermal conductivity. Here we focus on TAGS-85, which is reported to have a transition from a rhombohedral phase to a cubic phase above ~200 °C. We have found a way to stabilize both of these polymorphs at room temperature by careful adjustment of the synthesis conditions. We study the structural properties of both rhombohedral and cubic TAGS-85 as a function of thermal cycling and reveal a much more complex behavior than previously reported, involving transformations to novel layered structures. The thermoelectric properties of both polymorphs will be discussed with respect to their electrical conductivity, Seebeck coefficient and thermal conductivity.

PA4.5

Thermoelectric Properties of iodine-doped β-As_2Te_3

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Abstract

The β-As_2Te_3 compound is isostructural to the well-known Bi_2Te_3-based thermoelectric materials used in solid-state cooling applications. It was recently shown that this compound displays interesting thermoelectric properties around 400 K when appropriately alloyed with Sn or Bi [1-3]. Since a large number of isovalent and aliovalent substitutions can be envisaged in β-As_2Te_3, it is highly desirable to investigate in detail the influence of other “dopants” on its thermoelectric properties to see if further improvement can be obtained in this new family of compound.

Here, we report on the synthesis, physico-chemical characterizations and thermoelectric properties (5-400 K) of β-$As_{2-x}I_xTe_3$ compounds. The electrical and thermal properties were measured on samples cut parallel and perpendicular to the pressing direction to probe the anisotropy. Alloying with iodine does not change the *p*-type nature of the samples but results in higher electrical resistivity values leading to less favorable thermoelectric properties.

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PA4.6

Thermoelectric characterization of compounds with the composition $(Ge_{1-x}Sn_x)_yBi_2Te_{y+3}$

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Abstract

Germanium antimony tellurides (GST) are well-known phase change materials and have more recently been investigated as thermoelectric materials with ZT values of up to 1.5.[1] Concerning crystal structures and typical phase transitions, germanium bismuth tellurides $Ge_xBi_2Te_{x+3}$ (GBT) represent a comparable class of materials. Some of these pseudo-binary compounds crystallize in a cubic rocksalt-type at high temperature in which the vacancy concentration on the cation position depends on the ration of GeTe to Bi_2Te_3. Upon quenching, this high temperature phase transforms to a metastable pseudocubic structure. [2] Its disordered domain structure was elucidated by transmission electron microscopy. The stable modification of GBT at room temperature, however, exhibits a layered structure in which the vacancies form van-der-Waals gaps between rocksalt-type slabs whose thickness depends on the composition.

The electrical conductivity of quenched compounds with $7 \leq y \leq 17$ increases from ~150 to ~400 S cm^{-1} (at 500 °C) with increasing GeTe concentration. Upon the same compositional variation, the Seebeck coefficient increases from ~150 to ~270 μVK^{-1} (at 450°C). This results in an increase of the ZT_{max} value from ~0.18 for samples with the composition $Ge_9Bi_2Te_{12}$ to ~1 for $Ge_{17}Bi_2Te_{20}$.

Partial substitution of Ge by Sn leads to materials $(Ge_{1-x}Sn_x)_yBi_2Te_{y+3}$. These exhibit even higher electrical conductivities, e.g. for $(Ge_{1-x}Sn_x)_7Bi_2Te_{12}$ whose electrical conductivity increases by 100-300 % (for x = 0.25 and 0.75, respectively) compared to pristine GBT. This is accompanied by higher thermal conductivity. For certain combinations of substitution x and content y of (Ge,Sn)Te, the thermoelectric properties at low temperatures can be improved. Substituting e.g. 25 % of the Ge in $Ge_{12}Bi_2Te_{15}$ by Sn lowers the maximal ZT values but significantly enhances those at low to intermediate temperatures compared to the corresponding pristine GBT. ZT values remain almost constant over a wide temperature range.

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PA4.7

Unravelling the domain structures in GeTe and $LaAlO_3$

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Abstract

Alloys based on GeTe, such as GeSbAgTe (TAGS) and GeSbTe (GST) are intensively studied to optimize their thermoelectric properties. Here we unravel the extensively twinned herringbone structure observed in these alloys. Since the observed domain boundaries may act as a scattering mechanism for phonons, knowledge of the microstructure is essential for thermoelectric applications [1]. We resolve the current controversy in the literature concerning this 3D structure [2,3], using electron microscopy to properly identify both the domain boundaries and the local rhombohedral distortions. The structure arises due to the phase transformation from cubic to rhombohedral symmetry, where twins are formed to reduce global shape change without introducing local stress. From the simple model we developed, we conclude that the commonly observed structure is the only stress-free domain configuration. Because our model does not assume material-specific parameters, it is argued to be valid for a wide range of materials: GeTe alloys, but also perovskites such as $LaAlO_3$.

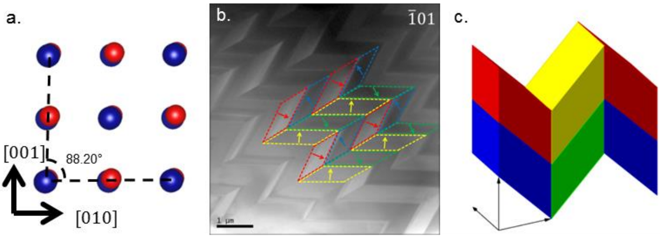

Figure 1: a.) Rhombohedral distortion of the rock-salt GeTe reduces the pseudocubic angle from 90° to 88.20°, 'stretching' the unit cell along one <111> axis. All four <111> distortions are expected to occur equally to obtain a stress-free structure. b.) A bright-field TEM image of GeTe, with the projection of their distortion vector. c.) Modeled domain structure (arrows indicate pseudocubic axes) of GeTe. This mixed {010}/{011} twin boundary system is the most commonly observed structure, and from modelling is the only stress-free domain tiling.

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PA4.8

Optimization of ball milling parameters for production of high efficient p-type Bi_2Te_3 thermoelectric materials

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Abstract

In order to overcome the issues like depletion of fossil fuels, energy crisis and global warming, much effort has been devoted to developing new alternative technologies. Thermoelectric materials (TE) can convert waste heat to electrical energy or electrical to heat in an eco-friendly manner [1]. The TE performance is directly influenced by the preparation technologies. Hence, we are focused on the optimization of the ball milling parameters such as the ball to powder ratio, rotation per min (RPM) and ball size [2]. As-milled powders were consolidated using spark plasma sintering. The crystal structure and microstructure of the powders and their bulk samples were systematically analyzed. The particle size distribution and oxygen content of the as-milled powders were analyzed using particle size analyzer and ONH determinator respectively. The micro Vickers hardness of the bulk samples were measured using Vickers indentation method. The maximum Vickers hardness was obtained due to a high density of fine grains. The thermoelectric properties with temperature were analyzed using TEP-1000 thermoelectric measurement system. The results indicate that the Seebeck coefficient and electrical transport properties exhibited nearly same. However, the thermal conductivity varied with ball milling conditions, as a result, high figure of merit (ZT) was achieved for 20:1 with 1100 rpm.

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A5. Bismuth and related materials
&
A8. Silicides

PA5-8.1

Influence of CuI doping on the thermoelectric effect of Bi_2Te_3

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Abstract

Bulk-bismuth telluride (Bi_2Te) and its alloys are the best room-temperature thermoelectric material found to date. Different approaches have been tried in order to enhance the thermoelectric properties of Bi_2Te. Doping is a commonly used way to improve the thermoelectric properties of Bi_2Te_3-based materials. Here, bismuth telluride (Bi_2Te_3) samples doped with copper iodide (CuI) have been successfully prepared in the series compounds of $(CuI)_xBi_2Te_3$ ($0 \leq x \leq 0.1$) by the conventional solid state reaction. Electron and thermal transport properties, i.e., electrical conductivity, carrier concentration, Hall mobility, Seebeck coefficient, thermal conductivity, of CuI-doped Bi_2Te_3 are measured at the temperature range of 250–600 K to clarify the influence of doping upon the thermoelectric performance of Bi_2Te_3. The microstructure and morphologies of CuI-doped Bi_2Te_3 were investigated by powder X-ray diffraction and high resolution transmission electron microscopy. The electrical conductivity increases with increasing CuI contents. This value is much higher than that of Bi_2Te_3 doped with Cu prepared with the same experimental condition. All the CuI doped samples exhibit n-type conduction. High resolution TEM images of both samples reveal that all systems contain compositional fluctuations at the nanoscopic level and are nanostructured. Inserting additional CuI is very effective in improving electrical conductivity and Seebeck coefficient, and suppressing thermal conductivity, thus enhancing ZT.

PA5-8.2

Thermoelectric properties of Iodine-doped $Bi_2Te_{3-y}Se_y$ solid solutions prepared by mechanical alloying and hot pressing

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Abstract

Bi_2Te_3 compound with rhombohedral structure is the most superior thermoelectric material for use in the room temperature range [1]. Typically, Bi_2Te_3 is used to make solid solutions to *p*-type $(Bi,Sb)_2Te_3$ or *n*-type $Bi_2(Te,Se)_3$. Because Bi_2Se_3 has the same crystal structure and similar electronic structure to Bi_2Te_3, they can form complete solid solutions of $Bi_2Te_{3-y}Se_y$. The Se atom occupies the Te site and thereby, the strengthened alloy scattering for electrons and phonons can reduce the carrier mobility and the lattice thermal conductivity [2, 3]. Thus, the donor doping is necessary to increase the carrier concentration, which leads to the increase in the electrical conductivity. In this study, $Bi_2Te_{3-y}Se_y$ and I-doped $Bi_2Te_{3-y}Se_y$ solid solutions ($y = 0$ to 0.6) were prepared by mechanical alloying and consolidated by hot pressing. The effects of the Se substitution and the I doping on the crystal lattice, the change transport and the thermoelectric properties were examined. All specimens exhibited *n*-type conductions in the measuring temperature range from 323 K to 523 K, and their electrical conductivity decreased slightly with increasing temperature, indicating degenerate semiconductor behaviors. The electrical conductivity decreased with increasing Se substitution while it increased by I doping, which was in contrast with the Seebeck coefficient. The electronic and the lattice thermal conductivities decreased with increasing Se substitution and decreasing I doping due to the decreased carrier concentration and the increased alloy scattering. The maximum figure of merit $ZT_{max} = 0.76$ was obtained at 473 K for undoped $Bi_2Te_{2.55}Se_{0.45}$ while $ZT_{max} = 0.84$ was attained at 473 K for iodine-doped $Bi_2Te_{2.4}Se_{0.6}{:}I_{0.005}$.

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PA5-8.3

Mechanical and thermoelectric properties of $Bi_{2-x}Sb_xTe_3$ prepared by encapsulated melting and hot pressing

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Abstract

Bi_2Te_3 and Sb_2Te_3 have a layered structure in the order $-Te^1$-Bi(or Sb)-Te^2-Bi(or Sb)-Te^1-, and a cleavage plane is easily formed along the basal plane perpendicular to the *c*-axis due to the weak van der Waals bonding between Te^1-Te^1 [1]. Although single crystals prepared by the unidirectional crystal growth methods such as zone melting, Bridgman, and Czochralski methods have excellent thermoelectric performance along the *a*-axis, the crystal growth technique is time and energy consuming and exhibits poor mechanical properties along a cleavage plane [2]. In this study, $Bi_{2-x}Sb_xTe_3$ ($x = 1.4$ to 1.7) solid solutions were synthesized by encapsulated melting and consolidated by hot pressing. Microstructure, mechanical properties and thermoelectric properties were evaluated for hot-pressed specimens. X-ray diffraction peaks shifted to lower angles with increasing Sb content, which confirmed that Sb successfully substituted for Bi, and thus formed solid solutions. The pole figures of all hot-pressed specimens indicated randomly oriented texture, and their calculated orientation factors ranged from 0.003 to 0.115. The electrical conductivity increased with increasing Sb content while the Seebeck coefficient decreased, which was due to the increase in the carrier concentration. The maximum ZT = 1.14 was obtained at 323K for the $Bi_{0.4}Sb_{1.6}Te_3$ hot-pressed at 698 K.

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PA5-8.4

Development of forming process and electrical characterization of electrodes for Mg_2Si

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Abstract

Increasing energy prices and strict fuel consumption regulations in the EU are prompting the automotive industry to improve fuel consumption urgently. Installation of thermoelectric generator (TEG) systems in vehicles is one possible solution for reusing discarded heat to supply electricity and conserve fuel. Mg_2Si is suitable for on-board TEG systems, as this material is non-toxic, lightweight, and its constituent elements are abundantly available. Long-term usage of TEG for applications at elevated operational temperatures (~ 900 K) requires better fabrication techniques for manufacturing Mg_2Si TE chips, including forming electrodes with sufficient durability at those temperatures.

In this study, we address the deterioration of TE chips fabricated using the mono-bloc sintering technique that sinters Mg_2Si at high temperatures while simultaneously forming electrodes. To study the deterioration mechanism, we performed exposure test for pure and Al-doped samples maintained for 30–500 h in an air atmosphere or Ar gas at 873 K. We found deposition of MgO and degradation of all samples regardless of the atmospheric conditions. This suggests poor sintering as the cause of degradation. Therefore, we introduced a modified screen-printing technique to form metal electrodes terminating in the already-sintered Mg_2Si. For fabrication, we used Ni paste mixed with Mg_2Si powder as an electrode to improve adhesion to the Mg_2Si matrix. We exposure tested in the above atmosphere at 873 K and then observed the samples under an optical microscope. Fig. 1 shows sufficient adhesion of electrodes to the matrix for up to 500 h of testing, without any decomposition. Furthermore, contact resistance at the interfacial junction of the electrode with the Mg_2Si was approximately 10^{-9} Ωm^2, which meets the 10^{-9} -10^{-10} Ωm^2 standard for practical use. We evaluated the output power of our samples at various temperature differences from $\Delta T=573$ to 773 K (Fig. 2). The results indicate that screen-printing improves the output power (maximum 157 mW at $\Delta T=500$ K), compared to that of monoblock sintering (110 mW). In conclusion, the screen-printing method introduced here can produce TE chips with good interfacial junctions to the Mg_2Si, has a better output performance, and improved durability.

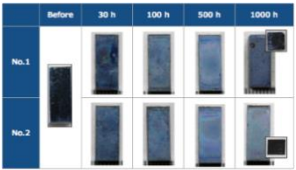

Figure 1: Screen printing samples after exposure test in the atmosphere at 873 K.

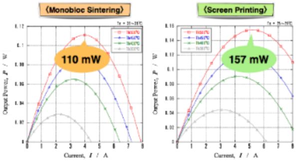

Figure2: Output power of monobloc sintered and screen printed samples at $\Delta T=573$ to 773 K.

PA5-8.5

Synthesis and thermoelectric properties of composite $Mg_2Si_{0.4-x}Sn_{0.6}Bi_x$ with addition of Yb or SiC nanoparticles

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Abstract

Thermoelectric generators (TEGs) allow for the direct conversion of thermal energy to useful electrical energy by using solid state, emission- and maintenance-free devices. By harvesting waste heat, TEGs can improve the energy efficiency of automotive, industrial and domestic processes and thereby help save fuel and cut emissions. The materials of the solid solution system $Mg_2(Si,Sn)$ possess favourable thermoelectric properties in the important temperature range of 300 °C to 600 °C. Additionally, the starting materials are available in high purity at low cost, the constituent elements are abundant in nature and non-hazardous to human health and the environment. $Mg_2(Si,Sn)$ thermoelectrics are therefore among the most promising materials for a wide-scale industrial production and application.

We report on the powder metallurgical synthesis, microstructure and thermoelectric properties of composite $Mg_2Si_{0.4-x}Sn_{0.6}Bi_x$ with addition of Yb or SiC nanoparticles and an optimized Bi doping level. An Mg-Yb pre-alloy and commercially available SiC nanoparticles are used. Powder mixtures are produced by vibratory disc milling or high energy ball milling under Ar-atmosphere. The samples are synthesized and compacted in a single step by Spark Plasma Sintering (SPS). The density of the compacted pellets is higher than 96 % of the crystallographic density. The figure of merit zT reaches a peak value of at least 1,2. A $zT \geq 1$ is attained in a broad temperature range (from 250 °C to 570 °C). Powder XRD, SEM and TEM investigations show that the samples consist of a fine-grained single phase matrix with embedded Yb-rich or SiC particles and homogeneously distributed Bi dopant. Depending on the local availability, Yb forms particles by reaction with either Si and Fe impurities from the milling jar or Sn and Bi. The distribution of Yb between solid solution in the matrix and the particles depends on the SPS parameters. Despite the marginally higher absolute value of $\Delta_f G^0$ of Yb_2O_3 (|-575,6| kJ/mol per O) compared to MgO (|-569,3| kJ/mol per O), no formation of Yb_2O_3 is observed.

PA5-8.6

Powder size and annealing effects on $Bi_2Te_{3-x}Se_x$ alloys fabricated by hot-extrusion technique

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Abstract

Thermoelectric (TE) materials and devices have been investigated over the past several decades for the applications in TE energy conversion. Up to date, Bi-Te based alloys have exhibited the best TE properties around room temperature. Well known sintering methods for Bi-Te alloys have been based on hot-pressing, spark plasma sintering (SPS) or hot-extrusion processes [1]. Among them, we fabricate $Bi_2Te_{3-x}Se_x$ (BTS) alloys using hot-extrusion which is considered as a way to improve the mechanical strength, thermoelectric performance, and to create highly oriented texture [2]. Also, we study the effects of BTS powder size and annealing on their TE properties. As a preliminary result, a BTS alloy fabricated with powders (75~180μm) and annealed at 500°C showed a maximum figure of merit (Z) of 3.17 (10^{-3}/K) at 300K.

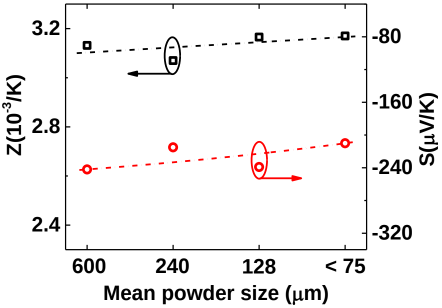

Figure 1: Z and Seebeck coefficients of BTS made using powder with different sizes

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PA5-8.7

Flash sintering of magnesium silicide stannide

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Abstract

Several methods are used to produce magnesium group IV compounds, typically the two step route: powder synthesis followed by densification process. Powder metallurgy is commonly used in industry for its ability to handle large amounts of powders. The main drawback are low densities and porosity, which are deleterious for mechanical properties. The thermal and pressure assisted hot pressing method is also a well-developed technique, requiring processing times from minutes to hours. In the last ten years the development of field assisted sintering technologies, in particular Spark Plasma Sintering, has lead to a reduction of processing times and a better control of microstructure. For TE materials their low electrical resistivity allows part of the SPS current to flow through the sample giving rise to a hybrid current-pressure assisted sintering. It has recently been demonstrated that flash sintering can sinter nanograins of zirconia in 5s at 850 °C, when conventional furnace processing needs hours at 1450°C. The lower resistivity and sintering temperature of the silicides should allow the flash sintering of TE material, as it was demonstrated for ZrB_2 [1]. This study analysed the feasibility of flash-sintering magnesium silicide stannide (MSS) using a Spark Plasma Sintering furnace and then compared the materials to samples sintered using conventional-SPS processing from powder and from a green pellet using optimal conditions. An $Mg_{2.1}Si_{0.487}Sn_{0.5}Sb_{0.013}$ (MSS) green compact was sandwiched between two graphite punches without a die. The direct heating was so efficient that a heating rate of ~1000 °C/min was achieved and the sample was fully sintered in less than 45 sec. Due to the strong local Joule heating at the contacts of the particles, the onset of flash-sintering temperature was 170 to 350 °C lower than that in convectional SPS. It was possible to produce a dense sample within a sintering windows of 6 sec. The process was controllable and repeatable. SEM images and XRD evidenced a phase separation in flash sintered samples, mainly related to local surface melting and subsequent cooling, producing a mixture of phases. The electrical resistivity of the flash sintered samples decreased. This could be related to a different oxide distribution, which allowed the formation of an oxide free network available for charge carriers. A final ZT of 0.7 at 400 °C was measured for flashed sintered sample, seven times higher than CSPS sample. The above results indicate that flash sintering could open a new way for quick production of large quantity of high quality nanostructure and/or textured thermoelectric material with low electrical resistivity.

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PA5-8.8

High Thermoelectric Figure of Merit in n-type Bi-Te alloys at Low Temperatures

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Abstract

Bi_2Te_3 and its solid solution alloys are the best commercial thermoelectric materials with the highest figure of merit(ZT). Recently, a significant ZT value improvement has been achieved by nano-engineering approaches [1,2]. ZT improvement is the result of decreasing lattice thermal conductivity due to the phonon scattering by boundaries and structural defects. However, these results are limited to p-type Bi-Te based materials. In this study, we report the high thermoelectric figure of merit in n-type Bi-Te alloys at low temperatures. Bi-Te alloys with high ZT values were prepared by hot-pressing method and its carrier concentration and anisotropic properties were optimized by chemical composition and crystalline alignment using slip-casting under a high magnetic field. A maximum ZT value of 1.05 was obtained at 250K.

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PA5-8.9

Industrially scalable production of micro thermoelectric generators (µTEG) through Screen Printing

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Abstract

Escalating demands for energy consumption in last decades and the consequent scarcity of natural resources exploited so far, led us closer to a global energy crisis [1]. It is crucial to achieve a sustainable production, educate the population for energy saving needs and improve the recovery methods developed so far. Heat loss is an inevitable process and the ability to re-use it would bring many potential applications for powering devices and reduce the energy costs in industrial processes or building maintenance. Thermoelectric phenomena [2], which involve the conversion between temperature differences and electric current, can play an important role in the energy harvesting paradigm.

The goal of this work is to conceive a flexible and fully screen printed thermoelectric generator prototype for energy harvesting, based on Bi_2Te_3 materials, which has been endorsed as a prime thermoelectric material, with a unique set of characteristics that currently make it the most suitable to fabricate devices, with the best performance values for near-room temperature applications.

Screen printing3 is an economically viable production technique which has been widely used to print flexible electronic devices, however there is a lack of specific works on the field of thermoelectrics, with the current challenge being the creation of a printable paste4 without loss of thermoelectric properties.

Up to this moment, the Bi_2Te_3 sintering process was optimized, from Bi and Te powders, using a compressing method to facilitate the atomic diffusion followed by an annealing at 720ºC for 5 hours on an inert atmosphere. The obtained samples achieved $S \sim -160\,\mu V \cdot K^{-1}$ and $\rho \sim 0.02\,\Omega\, m^{-1}$. Towards the screen printing method, they were submitted to a Ball Milling process to reduce the mean particle size down to $50\mu m$. Several polymers have also been tested in order to achieve the desired paste and will be discussed during this work.

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PA5-8.10

$Bi_{0.5}Sb_{1.5}Te_3$ thin films with bulk-like thermoelectric properties on glass and flexible substrates

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Abstract

Localized cooling in micro- and nano-electronics as well as energy autonomy in applications such as wireless sensor networks and wearable electronics could be well served by thin film thermoelectric devices fabricated on solid and/or flexible substrates. $Bi_{0.5}Sb_{1.5}Te_3$ is considered to be a state-of-the-art p-type thermoelectric material, at temperatures near room temperature, due to its high power factor and ZT value. Nevertheless, the deposition of $Bi_{0.5}Sb_{1.5}Te_3$ thin films with bulk-like thermoelectric properties remains a great challenge.

We have grown p-type $Bi_{0.5}Sb_{1.5}Te_3$ thin films onto different types of substrates such as fused silica and Kapton using pulsed laser deposition and home-made targets. The films were grown at room temperature and then were subjected to a post-deposition ex-situ annealing process.

In this poster presentation, we will present our recent results on Seebeck coefficient, electrical resistivity and Hall carrier concentration as a function of temperature (200-390K). We will discuss how the thermoelectric properties of the obtained films are affected by the substrate type and stoichiometry. Also, we will address the effect of post-annealing treatment on the structural and thermoelectric properties. The power factor values of our post-annealed films are similar to those of the best bulk materials.

PA5-8.11

Thermoelectric properties of Cu/In doped Bi_2Te_3 based alloys prepared by zone melting

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Abstract

Bi_2Te_3 based alloys are regarded as the best thermoelectric materials near room temperature [1,2]. Depending on composition and temperature, Bi_2Te_3 features *p*-type or *n*-type transport behavior. Compared with *p*-type, *n*-type materials exhibit significantly lower zT values. In the present work we report our recent work on *n*-type Bi_2Te_3 based alloys, aiming for enhanced properties via multi-doping and nanostructuring. The effects of doping with Cu and In on the thermoelectric properties of *n*-type Bi_2Te_3 based alloys prepared by zone melting have been investigated. With a small amount of Cu/In doping of 0.05 at% to Bi_2Te_3 of *p*-type transport behaviour at room temperature and the *p-n* transition at ~150 ℃ are found. With a further increase of the doping level of 0.1at% Cu and adding up to 3at% In, *n*-type transport behaviour is determined from room temperature to 300 ℃. Doping with Cu and In and further alloying with Se to Bi_2Te_3 have been investigated, and enhanced zT values of up to 1.35 at 60 ℃ are obtained. This is on the one hand due to an increase of the Seebeck coefficient and on the other hand due to the reduction of thermal conductivity, which results from the suppression of bipolar conduction and the formation of nanoscale precipitations.

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PA5-8.12

Nanotwin engineering by Ag doping in bismuth telluride-based thermoelectric materials

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Abstract

We report the enhanced thermoelectric properties of the Ag-doped $Bi_{0.5}Sb_{1.5}Te_3$ compounds synthesized by engineering atomic scale dislocations. Nanotwin engineering by Ag doping in $Bi_{0.5}Sb_{1.5}Te_3$ system is introduced as a new approach to simultaneously optimize the electrical properties and lattice thermal conductivity. The highest figure of merit, *zT*, of the nanostructured $Bi_{0.5}Sb_{1.5}Te_3$ bulk sample reaches 1.36 at 373 K due to the twin effects. Thermoelectric transport measurements were compared with microstructure studies and theoretical modelling. Herein, newly suggested twin structures will be demonstrated by tuning the formation energy of nanotwins which are developed with Ag doping,[1] and are found to be in good agreement with experiments. In the twin models suggested by the computational calculations, the twin boundaries were stabilized in Te(1)-Te(1) layers,[2] and while the twin is formed by Ag interstitial in Bi-Te system, the additional substructure such as Bi_2 metal block can be generated.[3]

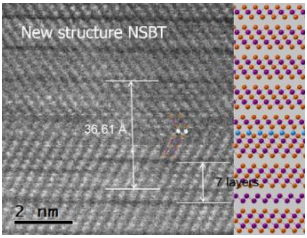

Figure 1: Cross-sectional HR-STEM image of 0.08 wt. % Ag-doped sample, NSBT(the six quintuple layer of BT (= Bi_2Te_3) and one triple layer ($BiTe_2$)) with Bi bilayer

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A7. Oxides

PA7.1

Electrical and thermal transport properties of crystallographic shear-plane transition metal oxides

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Abstract

Oxides form a prospective class of thermoelectric materials. Most complex metal oxides are electrical insulators. However, the presence of mixed valence states, due to a partial reduction of metal ions (e.g. W^{5+}, Mo^{5+} Ti^{3+}), and the accompanying crystallographic shear planes, lead to the appearance of free carriers and therefore quasi-metallic electrical conductivity. Consequently, the studies of oxide materials for potential use in thermoelectric are rapidly progressing. The known high-temperature synthesis methods reveal difficulties in controlling the reaction progress at elevated temperatures and the homogeneity of the final product. The SPS studies of reaction mechanisms reveal that the formation of phases follows a diffusion-controlled reaction between the reaction components induced by dc current [1].

We report the SPS-assisted investigation of a part M – O (M – Ti, Mo, W) binary systems in regions TiO_2 – TiO [1, 2] and MO_3 – MO_2 (M – Mo, W) [3-5] phases, which were used as a starting components in the preparations. The influence of the time, temperature, heating rate on the formation oxide products was studied. Besides the known phases, two new binary phases were synthesized. All materials were characterized by a powder XRD, DTA / TG, metallography, and TEM. The electrical and thermal transport properties of the obtained materials have been investigated.

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PA7.2

Thermoelectric properties of B_2O_3 doped $Ga_2O_3(ZnO)_m$ homologous compound

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Abstract

$Ga_2O_3(ZnO)_m$ (m = integer) homologous compounds are naturally occurring nanostructured compounds [1,2]. The ability of these nanostructured interfaces to scatter phonons effectively and therefore promote a low thermal conductivity makes the $Ga_2O_3(ZnO)_m$ homologous compounds suitable for high temperature thermoelectric applications [2]. However, it is difficult to produce high density $Ga_2O_3(ZnO)_9$ ceramics [3]. In this study, by using B_2O_3 and controlling the calcination and sintering time and temperature, we have produced high density $Ga_2O_3(ZnO)_9$ ceramics via the conventional solid-state reaction technique.
Structural characterisation of the samples was carried out by both X-ray diffraction and electron diffraction techniques. Study revealed that the samples had *cmcm* symmetry with $a_0 = 3.2$, $b_0 = 19.67$ and $c_0 = 33.5$ Å. SEM observations showed plate shaped grains within the microstructure and confirmed that the formation of homologous structure at 1100°C and above. Microstructural analysis by HRTEM and aberration corrected STEM-HAADF revealed the correct lattice site positions for Zn and Ga and nano size twinned structure promoting a low thermal conductivity of ~1.6 to 1.4 W/Km in the temperature range of 300 to 900 K. In the optimised samples a power factor of 9.0×10^{-5} W/mK^2 was obtained at 900 K. This is an improvement with regards the highest values reported value for un-doped $Ga_2O_3(ZnO)_9$ [3]. The air sintered ceramics showed a promising ZT of 0.055 at 900 K.

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PA7.3

Technological options to tune electrical conductivity of titanium suboxide – an experimental approach

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Abstract

Titanium suboxide is a group of defined Ti-O compounds the so called Magneli-phases with the general formula Ti_nO_{2n-1}. The ratio of Ti-O determines the electrical conductivity, which ranges over more than five orders of magnitude. The Seebeck-coefficient varies as well and can reach reasonable high values. The thermal conductivity, what is the third property of relevance to thermoelectric behaviour, is found in the range between 1-3 W/mK. This property spectra is certainly of interest for thermoelectric materials. According to theoretical considerations [1] single Magneli phases are limited to low thermoelectric performance. Despite of this the effect of phase mix may cause advantageous solid state electronic modification which could improve the thermoelectric performance drastically. This paper experimentally approaches in gaining knowledge about relationship of defined and controllable Magneli-phase mixes with concern to thermoelectric properties of titanium suboxide. New experimental results demonstrate that the properties can be shifted within the thermoelectric property spectra. The control of Magneli-phase mixes is achieved by simple technological procedures what would allow industrial manufacture in the future.

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PA7.4

Improving $Ca_3Co_4O_9$ performances through a new sintering method

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Abstract

High thermoelectric performances have been reached in $Ca_3Co_4O_9$ ceramic material through a modified solid state route. Samples were prepared using the classical solid state synthesis method with the addition of different K_2CO_3 amounts (0, 5, and 10 wt.%). It provides a very flexible, economic and easy processing route which allows microstructural control and improves the sintering procedure. K_2CO_3, with ~898ºC melting point produces a liquid phase during sintering procedure (at 900ºC), which is vanished during the process. Electrical resistivity was decreased by enhanced grains connectivity and sizes, while a significant increase in Seebeck coefficient at high temperatures has been produced. The best PF values at 800°C have been obtained in 5 wt.% K_2CO_3 samples (0.43 mW/K^2m), which are much higher than the obtained in bulk sintered materials, and around the best measured in high density ones.

PA7.5

Towards higher zT in metal oxides: playing with the “x” in WO_{3-x} compounds

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Abstract

In addition to reasonable efficiencies, thermoelectric materials are asked to be cheap, non-toxic and thermally stable in order to fulfil the required environmental criteria. Metal oxides possess most of these requirements, therefore they are considered highly interesting candidates for applications. Among others, metal oxides with adaptive structures, like Magnéli phases, have shown their potential [1] thanks to the possibility of tuning their electronic properties without affecting their intrinsic low thermal conductivity. The conduction mechanism of the Magnéli phases within the W-O system vary with the extent of reduction. A promising stoichiometry belonging to the W_nO_{3n-1} family ($WO_{2.90}$), was previously identified and characterized by our working group.[2] This composition has been taken as starting point for an optimization process intended to obtain higher zT values through the manipulation of the charge carrier density. We used a controlled oxidation of the reference composition ($WO_{2.90+x}$) to decrease the charge carrier concentration and hence obtain better thermoelectric properties. A complete thermoelectric characterization of the prepared samples has been carried out up to 1200 K, showing an effective increase of zT upon increasing the oxygen content.

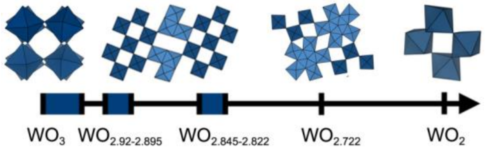

Figure 1: Crystal structure of the quasi ternary system $WO_3 – WO_2$.

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PA7.6

Microstructure and thermoelectric properties of n-type doped $CaMnO_{3-\delta}$

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Abstract

Self-sustaining smart sensors use low-maintenance energy harvesting from solar radiation, vibration and waste heat for energy supply. Low temperature gradients of 10 K to 20 K can be sufficient to produce useable amounts of electric energy with ceramics based thermoelectric generators [1]. The power output depends among other factors on the thermoelectric performance of the ceramic material.

The perovskite $CaMnO_{3-\delta}$ is an n-type conducting ceramic with interesting thermoelectric properties. We have studied the effects of ceramic microstructure on the thermoelectric performance of this material. Nano-sized $CaMnO_{3-\delta}$ powders were synthesized using different soft-chemistry routes. Compared to samples prepared by the conventional mixed-oxide route, the ceramics sintered from nano-sized powders exhibit better homogeneity and full densification at lower sintering temperatures. The effects of aliovalent doping with Gd, W, Bi and Yb/Gd were investigated and the variation of microstructure and thermoelectric performance as function of doping concentration is presented. Increased dopant concentrations affect the grain size and reduce the tendency of crack formation. Different sintering techniques were applied to vary the grain size of the ceramics. Moreover, thermoelectric properties of composites from $CaMnO_{3-\delta}$ and secondary phase particles were studied. The effects of powder synthesis, microstructure and doping level on the electric and thermophysical properties of $CaMnO_{3-\delta}$ will be discussed and the potential use of $CaMnO_{3-\delta}$ in transversal thermoelectric generators will be highlighted.

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PA7.7

Thermoelectric properties of $Fe_2(Ti_{1-x}Nb_x)O_5$ ceramics

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Abstract

Cost-effective and nontoxic thermoelectric materials are required for the practical application of thermoelectricity. Pseudobrookite Fe_2TiO_5 contains elements that are rich on Earth and can be easily synthesized from ilmenite ores in a large scale. It has an orthorhombic structure (space group Cmcm) with Fe and Ti in the 4c and 8f octahedral sites. Studies on pseudobrookite has been focused on its crystal structure [1], anisotropy spin glass behavior [2,3], anisotropy thermal expansion [4], dielectric properties [5], electrical transport properties [6], etc. In this study, for the first time, we explored the thermoelectric performance of $Fe_2(Ti_{1-x}Nb_x)O_5$ (x = 0, 0.005, 0.01, 0.02, 0.1) synthesized by conventional solid-state reaction. Pure pseudobrookite is obtained in the samples with $0 \leq x \leq 0.01$, indicating a low solubility of Nb in the crystal structure. All compositions show n-type semiconductor behavior. The electrical resistivity and absolute values of Seebeck coefficient decrease with increasing x until $x = 0.01$. Extremely low thermal conductivity has been observed in all compositions, ranging from 0.95 W/m/K to 1.5 W/m/K. A ZT value of 0.006 has been obtained in $Fe_2(Ti_{1-x}Nb_x)O_5$ with $x = 0.02$ at 1000 K.

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PA7.8

Thermoelectric properties of sol-gel derived Gd-doped $Sr_3Ti_2O_7$ sintered by SPS

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Abstract

One of the new energies challenges is to harvest the loss of thermal energy; this can be done by thermoelectric materials which have the possibility to transform the heat into electricity. Nowadays, the best thermoelectric materials belong to the family of BiTe or SbTe alloys. Nevertheless, their efficiency is limited at low temperature and they suffer from oxidation under high temperature conditions. Thermoelectric oxides have been intensively investigated in order to improve their properties since they are cheap, less toxic and have high temperature durability, like in the layered cobaltite for the p-type [1-2]. For the n-type, Ruddlesden-Popper (RP) doped materials seem to be promising for thermoelectric applications. The RP materials are described by an $A_{x+1}B_xO_{3x+1}$ (x=1, 2…, ∞) structures (Fig. 1). In the RP phase, $Sr_3Ti_2O_7$ appears to be sticking the best to thermoelectric criteria [3]. Nevertheless, performances need to be improved in comparison of layered cobaltite. Among the different possible strategies, the nanostructuration is a key parameter which will block the phonon scattering by developing grain boundaries. This project deals with the development of nanostructured thermoelectric materials by using a combination of a soft chemistry route and a flash sintering technique (spark plasma sintering techniques). The key issue to overcome is maintening the nanometric dimension during the sintering process. We present here the results in terms of synthesis, particles morphology, SPS sintering and thermoelectric properties.

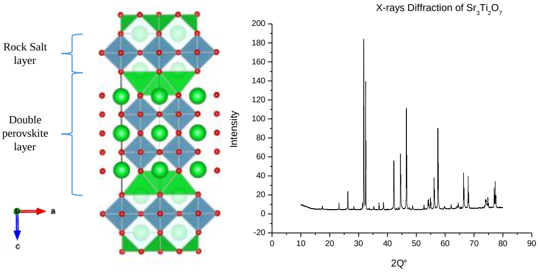

Figure 1: Crystal structures and XRD pattern of $Sr_3Ti_2O_7$

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PA7.9

Thermoelectric properties of $Ba_2Co_9O_{14}$ layered cobalt oxide

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Abstract

Conventional thermoelectric layered cobalt oxides present CdI_2-type CoO_2 layers separated by Na atoms (Na_xCoO_2) or two rocksalt layers ($[Sr_2O_2]_qCoO_2$), three rocksalt layers ($Ca_3Co_4O_9$) or four rocksalt layers ($Bi_2Sr_2Co_2O_y$) [1]. More recently, a new family of layered cobalt oxides has been described [2]: these compounds belong to a $Ba_{n+1}Co_nO_{3n+3}(Co_8O_8)$ family composed by alternating CdI_2 based layers (Co_8O_8) with n (111) perovskite blocks ($Ba_{n+1}Co_nO_{3n+3}$). The terms $n = 1$ ($Ba_2Co_9O_{14}$) have been synthesized as single crystal and ceramic [2,3]. The main differences with thermoelectric layered cobalt oxides are the presence of cobalt in tetrahedral environment and the lower cobalt valence in the CdI_2 layers (Co(II) and Co(III) rather than Co(III) and Co(IV) in conventional layered cobalt oxides) [2, 3]. These compounds have first been studied for their magnetic properties and the spin states of the cobalt cations [2-4]. Nowadays, $Ba_2Co_9O_{14}$ is also considered as a promising material for SOFC electrodes due to mixed ionic and electronic conductivity [5-7]. The aim of this study is to investigate the high temperature thermoelectric properties of $Ba_2Co_9O_{14}$ compound ceramics.

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PA7.10

Spin Seebeck effect in Y-hexagonal ferrite thin films

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Abstract

Spin Seebeck effect (SSE) is a combination of two phenomena - the generation of a spin current by a temperature gradient applied across a ferro(ferri)magnetic material (FM), and a conversion of the spin current to electrical current by means of the inverse spin Hall effect (ISHE) [1]. Most of the SSE experiments employed $Y_3Fe_5O_{12}$ garnet as FM, because of its low damping constant, *i.e.* slow decay of spin waves, since this decay was expected to restrict the active thickness of the FM layer. However, SSE with comparable magnitude was also observed in materials with higher damping constant, on the other hand a positive correlation of SSE with magnetization was evidenced [2]. Considering this correlation, we have investigated Y-hexaferrite $Ba_2Zn_2Fe_{12}O_{22}$ as the FM material for SSE, since its mass magnetization at room temperature M = 42.0 emu/g is significantly higher than M = 27.6 emu/g of $Y_3Fe_5O_{12}$. Y-hexaferrite thin films were prepared by spin-coating method using M-hexaferrite of a non-magnetic stoichiometry $BaCo_4Ti_4Fe_4O_{19}$ as a seeding layer. The spin Seebeck and magnetization dependences on magnetic field for a selected thin film with 650 nm thickness of Y-hexaferrite and 50 nm of a seeding layer are displayed in Fig. 1. Whereas the shape of a magnetization curve resembles typical behaviour of Y-hexaferrite as a soft magnet, the hysteresis of SSE is much broader. We tentatively explain this difference by a formation of a layer of hard magnet $CoFe_2O_4$ at a boundary between M- and Y-hexaferrite. The sample magnetization could be explained as a volume weighted sum of magnetizations of Y-hexaferrite and $CoFe_2O_4$, but the influence of $CoFe_2O_4$ on SSE is relatively bigger.

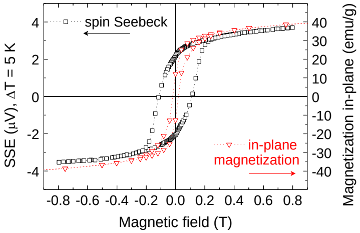

Figure 1: Spin Seebeck effect and in-plane magnetization *vs.* magnetic field.

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PA7.11

Nanostructure effect on thermoelectric properties of amorphous-InGaZnO thin film

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Abstract

Amorphous-InGaZnO (*a*-IGZO) is a widely studied for applications in flexible and transparent transistor devices due to its characteristic such as transparency and low temperature fabrication process. Our group has investigated the thermoelectric properties of *a*-InGaZnO thin films by optimizing the carrier concentration[1]. However, the obtained thermoelectric properties were not enough to meet the practical application request.

In this report, we fabricated nanostructures in *a*-IGZO thin film using a biological nanofabrication process to improve the thermoelectric properties. Nanostructures consisted of various nanoparticles (CoO_x, Au_2S and PtS) were fabricated on a glass substrate using a biological nanofabrication process, the BNP[2]. The separation distance was controlled about 50 nm. *a*-IGZO thin films with thickness of 20 nm were deposited on the substrate using RF magnetron sputtering. Thermoelectric properties were measured using the thermal transport option for physical property measurement system (PPMS, Quantum Design, Inc.).

It was shown that the electrical conductivity slightly increased and the Seebeck coefficient decreased, which should be attributed to the introduced dispersed nanoparticles arrays. The power factor of nanoparticle-embedded *a*-IGZO thin film was about 1.6 times larger than that of *a*-IGZO thin film at 300 K.

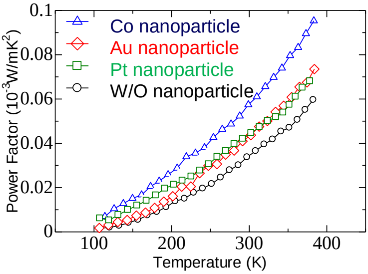

Figure 1: temperature dependence of the power factor of nanoparticles embedded thin film and w/o nanoparticles

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PA7.12

Thermoelectrical properties of single phase cuprous oxides from annealed Cu thin films

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Abstract

P-type copper oxides (CO) have been used in several thin film (TF) device applications, such as solar cells, transistors and gas sensors. The electronic and optical properties of these oxides strongly depend on the production technique as it influences the obtained phases: cuprous oxide (Cu_2O) or cupric oxide (CuO) (the most common ones). In this work, Cu-TF deposited by thermal evaporation (at room temperature, RT), with thicknesses between 40-160nm, were annealed in the temperature range of 225-375ºC, between 1 to 4h, in order to study the influence of this annealing step on the thermoelectric, electrical, optical, morphological and structural properties of the CO films.

The results show that Cu_2O phase is formed above 225°C, and CuO needs higher annealing temperatures to be formed, however, both the film thickness and the annealing time have a strong influence on the CO phase, since it depends on the necessary time to perform a complete film oxidation.

The Seebeck coefficient (S), measured at RT, is always positive, which confirms the p-type behaviour, and reaches 1.2mV/K, which is above the state of art for these materials [1], [2]. The optimized Power Factor (PF) is 2.8 $\mu Wm^{-1}K^{-2}$, corresponding to a 55nm deposited Cu film, annealed at 225°C during 4 hours, with S = 0.98mV/K, $\sigma = 2.9\ (\Omega.m)^{-1}$ and visible transmittance above 50%.

A semi-transparent material with these properties can be used as an electrical trigger activated by human touch (due to its high temperature sensitivity) and therefore a proof of concept has been made.

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PA7.13

Anomalous Photo-Thermoelectric Effects of Platinum-Loaded Tungsten Trioxide

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Abstract

Anomalous photo-thermoelectric effects (a photoconductive effect (photoconductivity, σ_{photo}) and a photo-Seebeck effect (photo-Seebeck coefficient, S_{photo})) could be observed in response to the visible-light irradiation of platinum-loaded tungsten trioxide (Pt/WO_3) in the absence of oxygen after a photochromic reaction, converting WO_3 to protonated WO_3 (H_xWO_{3-y}). Under visible-light irradiation, both σ_{photo} and the absolute value of S_{photo} increased. After the irradiation, both values decreased, that is, σ and the absolute value of S were smaller than σ_{photo} and the absolute value of S_{photo}, respectively (Figure 1). These effects are likely to be due to the photoinduced charge carriers and the accumulated electrons in Pt contributing to the increase in σ_{photo}. In addition, electrons are extracted from the W^{5+} state, decreasing the number of W^{5+} in H_xWO_{3-y} and thus contributing to the increase in S_{photo}. After light irradiation, the accumulated electrons in Pt returned to the energetically favorable W^{5+} state, and Pt/H_xWO_{3-y} returned to the initial state. Then both σ and S decreased. We suggested that the observed phenomena are caused by the accumulation of electrons in Pt, which is different from the previous explanation of two-carrier contribution to the transport properties for the anomalous phenomena demonstrated in past studies [1,2].

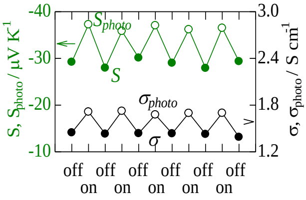

Figure 1: Detection of photoconductivity (σ_{photo}) and photo-Seebeck effect (S_{photo}) under N_2 flow with HCHO by on-and-off alternation of visible-light irradiation (>500 nm) of Pt/WO_3 that had previously undergone UV light irradiation (300−400 nm, N_2 with HCHO atmosphere).

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PA7.14

Thermoelectric property of layered rhodium oxide, $Bi_2Sr_2Rh_2O_x$

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Abstract

$Bi_2Sr_2Co_2O_x$ (BSCO) has a stacked structure composed of a CoO_2 layer and a $Br_2Sr_2O_4$ block layer alternately along *c*-axis, and thus shows electrical anisotropy [1]. Therefore, the fabrication of highly oriented ceramics with a large electrical conductivity (σ) along *a*(*b*)-axis would be a key factor for the thermoelectric (TE) application using such a layered cobalt oxide. Compared with Co 3*d* orbitals, Rh 4*d* orbitals is more widely spread spatially. Hence, electron correlation of Rh oxide is weaker than Co oxide, which contributes to increased mobility of charge carriers [2]. Also, Rh ions favor low spin states because of their large crystal field splitting (ΔP1 eV). On the basis of these theories, it is possible that layered Rh oxide consist of Rh^{3+} and Rh^{4+} ions ($Rh^{3+}/Rh^{4+}=1/1$) shows high Seebeck coefficient (*S*) by analogy with BSCO having $Co^{3+}/Co^{4+}=1/1$ [3]. In this presentation, the TE property of $Bi_2Sr_2Rh_2O_x$ (BSRO) is discussed. BSRO powder was synthesized using a conventional solid-state reaction, and confirmed to have the single phase of BSRO by X-ray diffraction. An X-ray photoelectron spectroscopy indicated that the ratio of $Rh^{3+}/Rh^{4+}=1/1$. Figure 1 shows temperature dependence of *S* and σ. The maximum power factor was estimated to be 4.3×10^{-5} $Wm^{-1}K^{-2}$ at 700 ºC. Detailed experimental results including *ZT* and κ values measured by a Harman method will be discussed at the conference.

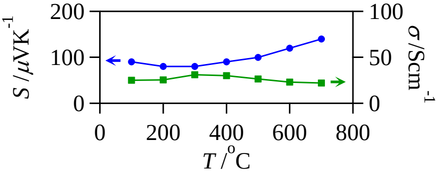

Figure 1: Temperature dependence of *S* and σ of BSRO.

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PA7.15

The tuning of BiCuSeO band structure by Nd doping

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Abstract

Oxide based thermoelectric materials have been attracted considerable attention over last few years. Thermoelectric oxides, composed of nontoxic, naturally abundant, light and cheap elements, are expected to play a vital role in extensive applications for waste heat recovery in an air atmosphere [1]. Recently, it has been reported that rare earth element (REE) substitution at the Bi^{3+} site can lead to p-type thermoelectric BiCuSeO with excellent performance [2]. Bulk samples of a $Bi_{1-x}Nd_xCuSeO$ (x = 0, 0.05, 0.10, 0.15) system were prepared by simple processing methods, which involved a two-step solid-state reaction, ball milling and spark plasma sintering (SPS). The commercial powders of Bi_2O_3, Cu, Bi, Se and Nd_2O_3 were mixed and cold pressed to pellets and then sealed to evacuated quartz tube, which was heated at 573 K for 8 h and then 973 K for 12 h. The reaction products were crushed into powders using a pestle and a mortar, followed by high-energy ball milling with ceramic balls in a planetary ball miller in vacuum at 400 rpm. Then the resultant powders were densified by SPS at 973 K for 5 min under a uniaxial pressure of 50 MPa. The synthesized samples were analyzed by a range of techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM). Results of these studies revealed that all specimens $Bi_{1-x}Nd_xCuSeO$ (x = 0, 0.05, 0.10, 0.15) consists of the single phase. Seebeck coefficient (S), electrical (σ) and thermal (k) conductivities were measured in a temperature range 293 – 923 K. Details of these measurements shall be given in the presentation.

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PA7.16

Effect of Sodium substitution on the thermoelectric properties of $Bi_2Sr_2Co_2O_x$ ceramics

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Abstract

$Bi_2Sr_{2-x}Na_xCo_2O_x$ polycristalline ceramics with x=0.0, 0.025, 0.050, 0.075, 0.10, 0.125, and 0.15 have been prepared using the classical solid state technique. SEM micrographs have shown that all the Na has been incorporated into the $Bi_2Sr_2Co_2O_x$ structure. It has been found that Na decreases porosity and improves grain growth. The lowest amount of porosity is observed in the highest Na containing samples (x=0.15). The temperature dependence of electrical resistivity, as a function of Na content, shows two kind of behaviors. For samples up to x=0.05 a semiconducting-like behavior ($d\rho/dT<0$) from room temperature to about 550 ºC and a slightly metallic-like one ($d\rho/dT>0$) at higher temperatures, has been found. For higher Na content, a slightly metallic-like behavior is observed. Moreover, when increasing Na content, a significant reduction on the resistivity values at room temperature is produced, in agreement with an increase of apparent density. On the other hand, Seebeck coefficient shows smaller variations than expected from the resistivity variations. Power Factor increases with Na content until 0.125, decreasing for further Na addition. These results indicate that small Na-substitution can be very useful in order to strongly reduce electrical resistivity and, as a consequence, raising the thermoelectric performances of these ceramic materials.

Acknowledgement

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PA7.17

Improvement of $Bi_2Sr_2Co_2O_x$ thermoelectric performances by K doping

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Abstract

$Bi_2Sr_{2-x}K_xCo_2O_x$ polycristalline ceramics with x=0.0, 0.025, 0.050, 0.075, 0.10, 0.125, and 0.15 have been prepared using the classical solid state technique. SEM micrographs have shown that all the K has been incorporated into the $Bi_2Sr_2Co_2O_x$ structure. It has been found that K drastically raises grain sizes. Electrical resistivity has been clearly modified by K doping, from a semiconducting-like behavior ($d\rho/dT<0$) for the undoped samples, to a metallic-like one ($d\rho/dT>0$) for all the K substituted samples. Moreover, K significantly decreases the resistivity values until 0.0125K, slightly increasing for higher content. On the other hand, Seebeck coefficient also decreases with K substitution. Power Factor increases with K content until 0.075, decreasing for further K addition.

These results indicate that small K-substitution can be very useful in order to strongly reduce electrical resistivity and, in spite of a Seebeck coefficient decrease, raising the thermoelectric performances of these ceramic materials.

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PA7.18

High thermoelectric performances obtained by laser technology

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Abstract

$Bi_2Sr_2Co_{1.8}O_x$ bulk polycrystalline ceramics were prepared by conventional sintering of powders and laser floating zone technique (LFZ). Microstructural analysis showed randomly oriented grains in the traditional sintered materials, while LFZ grown samples possessed well oriented crystals. Sintered materials present higher electrical resistivity due to their higher porosity and the random orientation of grains. As-grown and annealed laser-textured samples present a power factor of about, respectively, 2 and 5 times higher when compared with the classically sintered samples. The maximum power factor obtained at 650 ºC in the annealed laser-textured samples (~ 0.20 mW/K^2 m) is much higher than the best value obtained in sinter–forged textured materials at the same temperature.

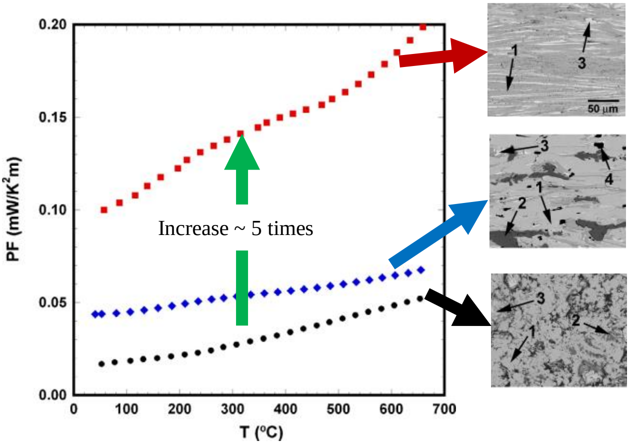

Figure 1: Temperature dependence of power factor for the different processed samples: ● sintered at 810 ºC for 24 h; ♦ laser-textured by the LFZ technique; ■ annealed laser-textured at 810 ºC for 24 h. On micrographs: #1 thermoelectric phase; #2 $Sr_3Co_4O_x$; #3 $Bi_{0.75}Sr_{0.22}O_y$; #4 CoO)

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PA7.19

Optimization of Solid-State-Reactions of Calcium Cobaltite $Ca_3Co_4O_9$

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Abstract

Conventional non-oxide thermoelectric materials are not stable in air at higher temperatures [1]. Oxide thermoelectric materials like calcium cobaltite are an interesting alternative for high temperature applications. The solid-state-reaction is well known for large scale powder synthesis of functional materials. The reaction kinetic of soli-state-reactions is mainly depended on the synthesis temperature, the dwell time and the reactivity of the raw materials. In different studies different synthesis conditions like synthesis temperature, dwell time, and particle size distribution of the raw materials were used for the preparation of calcium cobaltite powder [2-4]. To the author’s knowledge, a systematic study of the synthesis conditions of calcium cobaltite has not yet been published.

Therefore, the synthesis factors for calcium cobaltite (synthesis temperature, dwell time, and milling time) were studied with a statistical design of experiments (2^3) and optimized regarding the phase composition (XRD), bulk density and electrical properties. Beside thermal analysis (DTA and DTG) was used to determine the best synthesis temperature for calcium cobaltite.

It could be shown that a synthesis temperature close to a phase transition temperature of one of the educts enhances the reaction velocity. According to the design of experiments, 900 °C is the best temperature for the powder synthesis of calcium cobaltite. An interaction between synthesis temperature and dwell time was determined. Longer dwell times at lower temperatures (800 °C) lead to a higher calcium cobaltite output, whereas at higher temperatures (900 °C) the dwell time had no significant influence.

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PA7.20

Effect of Na substitution in directionally grown $Bi_2Sr_2Co_2O_x$ ceramics

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Abstract

$Bi_2Sr_{2-x}Na_xCo_2O_x$ polycrystalline ceramics with x=0.0, 0.025, 0.050, 0.075, 0.10, 0.125, and 0.15 have been prepared through the solid state method and directionally grown using the Laser Floating Zone (LFZ) technique. Microstructural studies have shown that Na has been incorporated into the $Bi_2Sr_2Co_2O_x$ structure, as no Na-based secondary phases appear. Moreover, all samples possess very low porosity and a good grain alignment along the growth direction. On the other hand, due to the incongruent melting of these materials, the samples are composed by several phases, besides the thermoelectric one. The electrical resistivity displays a semiconducting-like behavior ($d\rho/dT<0$) in the whole measured temperature range, for all samples. Furthermore, it decreases, especially at low temperatures, when Na is added, reaching the minimum values for the 0.15 Na doped samples. On the other hand, these samples also show the highest Seebeck coefficient and, as a consequence, their maximum Power Factor (~ 0.15 mW/K2m at 650 ºC) is more than three times higher than the obtained in undoped samples, and only around 30 % lower than the reported in single crystals.

These results indicate that adequate Na substitutions in LFZ textured materials can be very useful in order to strongly reduce electrical resistivity and raise Seebeck coefficient, leading to high thermoelectric performances.

Acknowledgement

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A9. Selenides and Sulfides

PA9.1

Thermoelectric properties of densified misfit-layered sulfides $[Ln_2S_2]_pNbS_2$ (Ln = Lanthanides)

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Abstract

Misfit-layered sulfides $[La_2S_2]_pNbS_2$ consist of an alternate stacking of a NaCl-type $[La_2S_2]$ block and a trigonal prism-type $[NbS_2]$ layer, parallel to *c*-axis [1]. The $[La_2S_2]$ block creates disorder and is responsible for phonon scattering, which reduces lattice thermal conductivity. Charge transfer from the $[La_2S_2]$ block to the $[NbS_2]$ layer behaves as a charge-carrier pathway can be controlled by a total substitution of La to other lanthanides. In a previous study, we reported substitution of La to other lanthanides and their thermoelectric (TE) properties [2]. However, as the samples had considerably lower densities relative to the theoretical ones, TE properties contained ambiguities, in particular the thermal conductivity values. We have succeeded in synthesizing $[Ln_2S_2]_pNbS_2$ (Ln = Lanthanides) samples with reasonably high densities by using spark plasma sintering. All samples were confirmed to be single-phase $[Ln_2S_2]_pNbS_2$ from X-ray diffraction patterns (Fig. 1), and show high relative densities (about 90%). The effect of lanthanides substitution on Seebeck coefficient, electrical conductivity and thermal conductivity with increasing atomic weight of lanthanides will be presented.

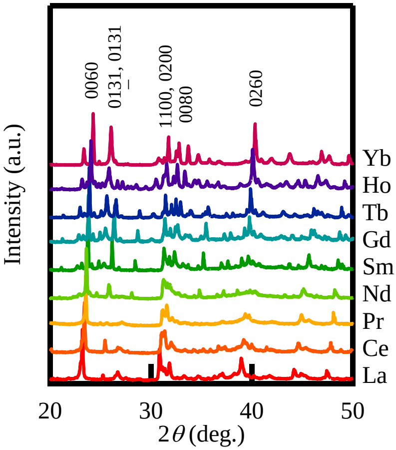

Figure 1: Powder X-ray diffraction patterns for $[Ln_2S_2]_pNbS_2$ (Ln = Lanthanides) samples.

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PA9.2

Thermoelectric properties of the homologous compounds $(PbSe)_5(Bi_2Se_3)_{3m}$ (m = 2 and 3)

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Abstract

Homologous compounds are interesting platform for designing novel thermoelectric materials. Such compounds form a series of crystal structure built from similar blocks whose number increases by regular increments. In particular, they allow an easy manipulation of the complexity of the crystal structure by simple variations in the chemical composition. Among them, the series $(PbSe)_5(Bi_2Se_3)_{3m}$ (m = 1, 2, 3) is particularly intriguing. Besides a topological insulating state discovered for m = 2 [1,2], the m = 1 compound has been recently shown to harbor extremely low thermal conductivity values and *n*-type semiconducting properties resulting in encouraging *ZT* values of 0.5 at 720 K [3]. Yet, the thermoelectric properties of the m = 2 and 3 remain so far unexplored. Here, we report on the synthesis, structural and chemical characterizations and thermoelectric properties measurements in a broad range of temperatures (2 – 700 K) of the m = 2 and 3 compounds. The transport properties were measured on samples cut parallel and perpendicular to the pressing direction to probe the anisotropy. All the compounds show *n*-type behavior with very low thermal conductivity values of the order of 0.5 W m^{-1} K^{-1} at 700 K. Both compounds are heavily doped resulting in moderate thermopower values.

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PA9.3

Oxidation studies of tetrahedrites

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Abstract

Tetrahedrites, with a $Cu_{10}M_2Sb_4S_{13}$ (M = Cu, Mn, Fe, Co, Ni, Zn) general formula, have recently been considered with good potential to be sustainable thermoelectric materials. Indeed, they are mainly formed by non-toxic elements, the raw material cost is low (7 $/kg) and can be prepared using cheap, rapid and scalable methods. However, more studies on aspects like corrosion resistance, oxidation at the working temperatures or electrical and thermal resistance of contacts are still needed.

Here we present studies of the $Cu_{12}Sb_{3.9}Bi_{0.1}S_{10}Se_3$ tetrahedrite oxidation and corrosion under selected conditions. To explore the possibility of tetrahedrite use in air atmosphere at medium temperatures oxidation studies were made between 230ºC and 375ºC. The evolution of the phases at the interior and surface of the material was followed using X-ray diffraction and SEM/EDS and the weight change controlled during 1500 hours. It was observed that the $Cu_{12}Sb_{3.9}Bi_{0.1}S_{10}Se_3$ tetrahedrite phase is stable below 300ºC, but does not exist above this temperature. All samples have oxides at the surface. The corrosion behaviour was assessed by electrochemical impedance spectroscopy and the results permitted to define corrosion behaviours that were dependent on the oxidation temperature.

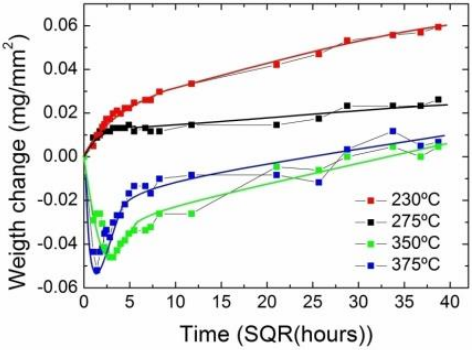

Figure 1: Weight change versus time (in square root of hours) for samples oxidized at the temperatures indicated in the figure.

PA9.4

Tetrahedrite synthesis by glass crystallization

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Abstract

The use of thermoelectric devices for waste heat recovery is frequently seen as part of a route for a more sustainable world. Tetrahedrites ($Cu_{12}Sb_4S_{13}$), have low-cost, earth-abundant and low toxic elements, like Cu and S, which make them good candidates to be used as thermoelectric materials. Unfortunately, tetrahedrites only have a p-type semiconductor behavior but they were recently considered as good candidates for mid-temperature thermoelectric applications. They are usually prepared by melting or reacting the elements under vacuum, followed by long term heat treatments, milling and SPS or hot press sintering, the full process being expensive and taking several days. Here an alternative rapid and low cost tetrahedrite preparation process is presented that is the synthesis from glass crystallization.

$Cu_{12}Sb_{3.6}Bi_{0.4}S_{10}Se_3$ nominal composition glasses prepared by melt spinning have a Tg ~ 120ºC, with a crystallization peak at ~ 190ºC. Samples treated just above this temperature show X-ray diffractograms typical of tetrahedrites, with only minor amounts of impurities. However, SEM and TEM observations point to the presence of Bi-rich sub-micro and nano precipitates. Treatments at higher temperatures lead to the appearance of the skinnerite phase. Electrical transport properties measurements indicate a maximum power factor at room temperature for the best tetrahedrite samples of ~400μW/K^{2}m, similar to what was observed on tetrahedrites obtained by other methods.

Acknowledgments

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PA9.5

Thermoelectric properties of some sulphides with mineral-related crystal structures

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Abstract

Due to their potential industrial application as thermoelectric materials the cheap and widespread natural and synthetically manufactured sulphur-containing minerals and mineral-related compounds are of particular interest. The most prominent representatives of such sulphides are chalcocite ($Cu_{2-x}S$) with dimensionless figure of merit (ZT) of 1.6 at 700 °C [1] and modified tetrahedrite ($Cu_{12-x}M_xSb_4S_{13}$) with ZT = 0.9 at 400° C [2]. With this respect the natural pyrite FeS_2 would be of special interest, taking into account its abundance and cheapness. However, this material shows very low $ZT_{\max}$ = 0.002 at 300 °C [3], mostly due to the bad electrical conductivity. Our current studies of natural pyrites from Navajún (Spain) and Cavnic (Romania) showed that their ZT-values are increased by a factor of 4 in comparison with synthetic materials. We explain this with the presence of a remarkable quantity of TiO_2 impurity (up to 0.5 wt. %) in the natural crystals.

The so called thiospinels have been an object of numerous studies due to their exciting magnetic properties. We synthesized for the first time $Ti_{0.8}In_{2.2}S_4$ (space group $Fd\bar{3}m$, a = 10.7779(2) Å). This thiospinel is found to be a typical metallic system with low $ZT_{\max}$ = 0.005 at 500 °C. On the other hand well known isostructural $Fe_{0.9}In_{2.1}S_4$ (a = 10.6006(2) Å) is shown to be an isolator below room temperature and a semiconductor above 400 °C. The $ZT_{\max}$ = 0.002 is observed at 300 °C for this material. Taking into account: i.) that the MIn_2S_4 (M = Mn-Cu) thiospinel series exist almost with all *d*-metals and ii.) their conductivity type varies from metallic to isolating, the thermoelectric properties can be accordingly tuned in the broad range.

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PA9.6

Tetrahedrite solvothermal synthesis for thermoelectric applications

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Abstract

A big challenge in the thermoelectric field is to identify new thermoelectric materials that have to be inexpensive, easy to synthesize, and comprised of Earth-abundant elements. On this basis, tetrahedrite mineral family (Cu12-xTrxSb4S13 where Tr= Cu, Mn, Fe, Co, Ni, Zn) seems to be an attractive p-type Pb-free thermoelectric material, showing a relatively high conversion efficiency. A figure of merit near unity was obtained at working temperature (about 450 °C [1,2]).

In this work, a solvothermal synthesis method was developed for undoped tetrahedrite $Cu_{12}Sb_4S_{13}$ and the introduction of Zn and Ni as substituents of copper was also tested. Preliminary sintering test were performed by Open Die Pressing [3].

The influence of dopant presence and consolidation process parameters on the tetrahedrite phase content, stoichiometry and density of the samples were investigated by X-ray diffraction and scanning electron microscope (equipped with energy dispersive X-ray spectroscopy). A complete thermoelectric characterization was carried out by Laser Flash Analysis, electrical conductivity, and Seebeck coefficient measurements.

Acknowledgments

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PA9.7

High-temperature thermoelectric properties of colusites $Cu_{24}Ni_2V_2Ge_6S_{32}$ and $Cu_{24}Co_2V_2Ge_6S_{32}$

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Abstract

Sulfur-containing minerals, such as tetrahedrites or bornite, have recently emerged as promising thermoelectric materials due to their extremely low lattice thermal conductivity. Colusites, composed of relatively earth-abundant and environmentally-friendly elements, belong to another class of interesting materials that enable achieving good thermoelectric performances around 700 K [1,2].
In this work, we present the successful synthesis of two colusites of chemical compositions $Cu_{24}Ni_2V_2Ge_6S_{32}$ and $Cu_{24}Co_2V_2Ge_6S_{32}$ that display promising thermoelectric performances around 700 K. These two compounds were prepared by a conventional powder metallurgy route and consolidated by spark plasma sintering. The thermoelectric properties were measured at high temperatures (300 – 690 K). Crystallographic structure and chemical homogeneity were verified by powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM), respectively. PXRD confirmed the successful substitution of Ni and Co for Cu. SEM analyses showed an overall good chemical homogeneity of the colusite matrix with some small amounts of secondary phases. Transport properties measurements revealed a favourable combination of electronic properties and very low lattice thermal conductivity giving rise to a maximum dimensionless thermoelectric figure of merit of 0.4 and 0.5 at 690 K in the Co and Ni sample, respectively.

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A10. Organics

PA10.1

ZT value determination of tetrathiotetracene based organic thin films

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Abstract

Organic materials attract increasing attention for thermoelectric (TE) applications due to the advantages of low thermal conductivity and low-cost synthesis. Theoretical calculations show that tetrathiotetracene (TTT) based materials are promising in TE application [1,2]. Growing a clean, perfect single crystal is very slow and complicated process, which would hinder the practical applications of this material. Therefore, the aim of this work is to study the TE properties of TTT based thin films, obtained by thermal evaporation in vacuum.

Often several samples and sample configurations are used for different measurements to determine ZT value, which could lead to errors of ZT value. We have shown that thin film morphology and thus electrical properties varies by changing thermal evaporation parameters [3].

In this work differential 3ω measurements [4] for thermal conductivity, 4 probe measurements for electrical conductivity and Seebeck coefficient measurements were realized on the same sample design, allowing us to determine ZT value of organic thin films using just one sample, thereby minimizing errors of ZT value.

Financial support provided by Scientific Research Project for Students and Young Researchers No. SJZ2015/13 realized at the Institute of Solid State Physics, University of Latvia is greatly acknowledged.

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PA10.2

Solution synthesis of telluride-based nano-barbell structures coated with PEDOT:PSS for spray-printed thermoelectric generators

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Abstract

Thermoelectric materials have attracted a great interest for their potential application in energy conversion. Especially, the low-dimensional nanostructured thermoelectric materials based on Te or Bi_2Te_3 have been widely investigated due to the advnatage of phonon scattering at the nanowire surface and compositional interfaces, which can provide a much higher power factor. Although the thermoelectric devices have been usually fabricated using the low-dimensional nanostructured materials, they have still limits to apply to the flexible thermoelectric devices due to their poor synthetic method and inapproproate frabrication process, such as chemical vapor deposition and hot press. In this study, telluride-based heterostructures coated with solution-processable poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (Te–Bi_2Te_3/PEDOT:PSS) were synthesized through a solution-phase reaction at low temperature. These hybrid solutions were deposited onto a flexible substrate by the spray-printing method to prepare thermoelectric generators. The synthesized Te–Bi_2Te_3/PEDOT:PSS hybrids showed an enhanced electrical conductivity, Seebeck coefficient, and power factor of 69.9 S cm^{-1}, 93.6 μV K^{-1}, and 60.5 μW m^{-1} K^{-2}, respectively.The flexible thermoelectric generator fabricated by spray-printing Te–Bi_2Te_3/PEDOT:PSS hybrid solutions exhibited a stable TE voltage of 1.54 mV with six legs at ΔT = 10 °C. This approach suggests the facile preparation of printing-processable hybrid thermoelectric materials is promising method for application in flexible thermoelectric generators [1].

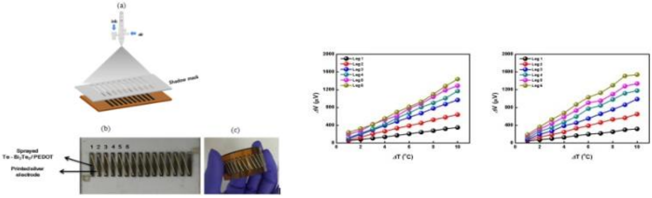

Figure 1. (a) Schematic drawing of the spray-printing process, (b) image of the planar thermoelectric generator consisting of 15 legs arranged on the glass substrate, (c) image of the flexible thermoelectric generator, and (d, e) open circuit thermoelectric voltage (V_{oc}) *vs.* temperature difference (ΔT) according to the number of TE legs of rigid and flexible TE generators.

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PA10.3

Structure and doping engineering in PEDOT films for printed and flexible thermoelectric generators

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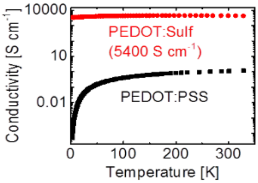
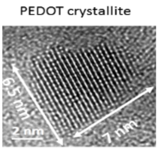
Abstract

Organic conductive materials such as poly(3,4-ethylenedioxythiophene) (PEDOT) are good candidates for inexpensive and large area thermoelectric generator (TEG) thanks to their low-cost and low-toxicity. They are highly compatible with printing techniques like spray-coating or screen-printing. Even though their thermal conductivity is generally low (<1 W/m.K), their power factors are still moderate mainly because of low electrical conductivity.

We demonstrate that using trifluoromethanesulfonate (OTf) anions as counterions allows to reach electrical conductivity up to 1200 S cm^{-1} [1]. The electrical conductivity of PEDOT: OTf can be further increased up to 1640 and 3600 S cm^{-1} by adding polymerisation rate controllers like pyridine or N-methyl pyrrolidone respectively [2]. The charge carrier concentration can be increased with a sulphuric acid treatment which allows to reach 5400 S cm^{-1}. Doping level, PEDOT films structure and transport mechanisms have been studied thanks to XPS, GIWAX analysis and conductivity measurements down to 3 K respectively. These experiments allows us to demonstrate that these cosolvents induce bigger crystallites and enhance the structure. We propose a heterogeneous conduction model that fit perfectly the experimental data from 3K to 300K which is a mixed of 1-D metallic conduction and disordered metal with Sheng-like conductions [2].





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PA10.4

Synthesis of processable n-type Polymers

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Abstract

We present a new method for the synthesis of a conductive n-type polymer, poly[Kx(Ni-ett)], which allow to obtain it as a printable paste.

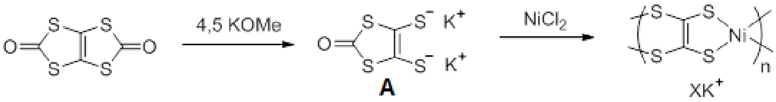

Figure 1: Synthesis of poly[Kx(Ni-ett)].

Among the currently known organic thermoelectric (TE) n-type materials, the highest power factor has poly[Kx(Ni-ett)] (poly(nickel-ethylenetetrathiolate) [1].
Although the synthesis of this polymer is fairly simple (Fig. 1), the structure of the intermediate **A** and the mechanism of polymer formation are the subject of discussions. Also, insolubility of the polymer significantly affects its processability and greatly limits its use. That’s why obtaining printable paste on the base of this material is an actual problem. Different composite materials on the base of these polymers resulting in greatly improve of its processability, but TE properties of such material decrease dramatically [2, 3]. In order to avoid degradation in the thermo-electrical performance we haven’t modified already prepared polymer, but have changed the procedure of its preparation. The advantage of this method is that the production of a paste-like material does not cause degradation in TE performance.
Additionally we have printed a flexible full-organic thermoelectric generator and successfully tested it in the ambient conditions.

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PA10.5

Influence of thermal environment on the thermoelectric performance and stability of PEDOT:PSS

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Abstract

In the field of organic thermoelectric material, PEDOT:PSS still holds an outstanding role as a p-type material. Much effort was put in the investigation of secondary doping with co-solvents like dimethylsulfoxide (DMSO) or ethyleneglycol (EG) [1] as well as primary doping with different methods [2] . In order to understand this modification and its influence on electrical conduction mechanism and Seebeck coefficient, mostly low temperature measurements were performed.

Unfortunately much less is known about its stability under thermal stress. In 2009 Vitoratos et al. [3] investigated the degradation of PEDOT:PSS thin films heated at 120 °C. Also Elschner et al. [4] [4] investigated the thermal induced decomposition of PEDOT:PSS films.

From an engineering standpoint, knowledge about the maximum operation temperature of PEDOT:PSS is crucial for its application in an thermoelectric generator. Therefore we investigated the electrical conductivity and Seebeck Coefficient of PEDOT:PSS films from room temperature up until degradation. Thermogravimetric analysis (TG, DTG) were performed in order to investigate the decomposition process.

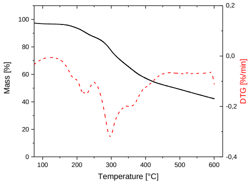

Figure 1: TG and DTG curve of PEDOT:PSS in air.

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A11. New materials

PA11.1

Crystal structure and high temperature thermoelectric properties of $La_{1/3}NbO_3$ perovskite

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Abstract

A combination of experimental and computational techniques has been employed to study the crystal structure and thermoelectric properties of A-site deficient perovskite $La_{1/3}NbO_3$ ceramics. The ceramics were prepared by the conventional mixed oxide route. Crystallographic data from X-ray and electron diffraction showed that the room temperature structure is orthorhombic with $a \sim 2a_p$, $b \sim 2a_p \sim$ and $c \sim 2a_p$ where a_p is the unit cell length of the ideal cubic perovskite, and *Cmmm* as space group. Atomically-resolved imaging and analysis showed that there are two distinct A-sites: one is occupied randomly with La and vacancies and the second site is fully unoccupied; the diffuse superstructure reflections observed through diffraction techniques are shown to originate from Nb vacancy ordering. $La_{1/3}NbO_3$ ceramics sintered in air showed a promising high temperature thermoelectric properties with a high Seebeck coefficient of S_1=-650 to -700 μVK^{-1} and a low and temperature stable thermal conductivity of k= 2.0 to 2.2 $Wm^{-1}K^{-1}$ in the temperature range of 300 to1000K. First-principles electronic structure calculations couple the temperature dependence of the measured Seebeck coefficient to the evolution of the density of states with temperature and show a way for its further optimization through the doping. Moreover, the lattice thermal conductivity calculations give an insight into dependence of the thermal conductivity with crystallographic directions of the material.

PA11.2

Novel nitride thin films in the Sc-M-N (M = Nb, Ta) system for thermoelectric applications

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Abstract

In the last few years, the early transition metal nitrides have attracted increasing interest for their potential for thermoelectric applications. For example, ScN has an anomalously high thermoelectric power factor [1,2]. A recent theoretical study predicted that the AMN_2 (A = Ca, Ti, Sr and M = Ti, Zr, Hf) layered nitride materials to exhibit a high Seebeck coefficient and good electrical conductivities [3]. First principles calculations of the phase stability of the Sc based nitride materials demonstrated a very low mixing enthalpy of the $ScMN_2$ phase (M = Nb, Ta) [4]. Furthermore, nitride alloy thin films is one of the strategy for reduction of the lattice thermal conductivity. The thermoelectric figure of merit (ZT) of ScN is about 0.2-0.3 at 800 K mainly due to the high total thermal conductivity. Insertion of heavy elements by alloying may introduce phonon scattering therefore reduce the thermal conductivity and increase the ZT.

This experimental study is focused on the deposition of the thin films in the Sc-M-N system by magnetron co-sputtering onto sapphire and MgO substrates. The different deposition parameters (power, pressure and temperature) played an important role in determining the phase formation. The system Sc-M-N can be found in different phases from the corresponding binary nitrides, the disordered cubic solid solution and more complex phases such as 2D layered hexagonal phase. The morphology and structural properties of the Sc-M-N thin films were investigated and their effects on the electrical and thermoelectric properties were evaluated.

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PA11.3

Synthesis and modification of the structure of the ionic liquids to optimize their thermoelectric properties

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Ionic Liquids (IL) are organic salts with melting temperature typically below 100 °C. The unique properties of ionic liquids such as their excellent chemical and thermal stabilities, their low vapor pressure, their important ionic conductivity makes them interesting compounds in material science and especially in thermoelectric generators (TEGs) for medical, pharma or electronic applications [1].

A big advantage of ILs is the endless number of cation/anion combinations, which allows synthesizing task-specific ionic liquids for TEG applications (Fig.1). The term "iLiquid" is also used to describe the vast potential of ionic liquids [2].

$R{-}\overset{\oplus}{N}H_3 \quad X^{\ominus}$

R^+ = Me, Et, Pr, Bu
X^- = NO_3^-,BF_4^-, CF_3COO^-

Figure 1. Ammonium-base IL synthetised in this work.

In our work, we describe the synthesis, physical and electrochemical characterization of novel IL for application in thermoelectric generators (TEGs). We discuss the optimization of the chemical structure of IL regarding their thermoelectric properties via a structure-activity relationship approach [3].

References:

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PA11.4

Structural and physical properties of Y and Yb boron-rich compounds

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Abstract

Boron-rich solids constitute an important class of materials with useful physical properties such as chemical inertness, high temperature stability and high hardness. Among them, [B_{12}] icosahedral compounds attract considerable interest as promising candidates for high temperature thermoelectric conversion due to their high melting temperatures and low values of thermal conductivity [1,2]. Our work on synthesis and structural studies of boron rich phases in the {Y, Yb}-Pt-B systems revealed a new platinum doped yttrium boride featuring a complex boron atom framework of YB_{50}: $YB_{45-x}Pt_y$, x=2.42, y=0.21, space group *Pbam*, a=16.6246(4) Å, b=17.6453(4) Å, c=9.4167(2) Å; single crystal XRD.

Formation of compounds in boron-rich sections of RE-B binary boundary systems has been studied from ytterbium containing samples: $YbB_{\sim 61}$, YbB_{66} type structure, space group *Fm*-3*c*, a=23.3587(6) Å; single crystal and powder XRD; and $YbB_{\sim 50}$, space group *Pbam*, a=16.53(1) Å, b=17.54(1) Å, c=9.46(1) Å; single crystal and powder XRD.

Crystal structures of these three compounds exhibit complicated networks of boron icosahedra. The rare earth atoms are located in voids within icosahedral frameworks. Insertion of Pt into the boron atom framework of YB_{50} leads to a partial transformation of the -[B_{12}]-[B_{12}]- icosahedral chain into a -[B_{11}]-Pt-[B_{11}]- chain and induces disorder in the [B_{15}] polyhedron and neighboring interstitial B site. Structural details and physical properties of compounds will be presented.

Acknowledgements:

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PA11.5

On the structural and TE properties of Zr doped *β*-rhombohedral boron

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Abstract

Boron and borides are considered to be promising thermoelectric materials for use at high temperatures of more than 1300 K, however, the performance of elemental boron by itself is insufficient [1,2]. Metal doping into *β*- rhombohedral B can control the bonding nature in and between the clusters, delivering the variation of physical properties such as electrical and thermal conductivities and Seebeck coefficient [3]. The doping effect of zirconium on the structure, Seebeck coefficient and electrical resistivity of *β*-rhombohedral B was studied for the metal rich concentration range Zr_xB_{100-x}, $1.88 \leq x \leq 2.75$ within 370 K- 870 K from HTS and SPS samples. The refinement of X-ray single crystal and powder diffraction data established the Zr atoms mainly in the *E* and *D* voids for metal rich compositions and elucidated the minor Zr occupancies of the *N*, *F* and A_1 holes. It was found that the Seebeck coefficient can be effectively modified by varying the Zr content. Electrical resistivities generally followed the Mott's relation for the variable-range hopping. Excellent compositional agreement has been observed between structural and TE properties dependencies.

Acknowledgements:

The research work of O.S. and L.S. was partially supported by Austrian FWF project V279-N19.

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PA11.6

Characterization of electrodeposited $Bi_2(Te_xSe_{1-x})_3$ and $(Bi_xSb_{1-x})_2Te_3$ thick films for integrated thermal management applications

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Abstract

The increased need for energy efficiency, and fundamental phenomena related to topological states of matter has brought fundamental and applied research on thermoelectric materials to a new blooming [1]. The ability to implement thermoelectric elements either as generators or coolers make them interesting for energy harvesting or thermal management applications. In particular, the increased density of lasers in optical telecommunications devices requires of integrated thermal management micro components [2]. In contrast to physical thin film deposition techniques, electrochemical deposition allows to grow material layers with thickness in the range of microns to some ten microns in relatively short periods of time over relatively large areas, and is compatible with current CMOS processing technology. This makes this method ideal for the realization of integrated micro-coolers. We report on the electrodeposition and characterization of optimized thermoelectric n and p doped Bi_2Te_3-based ternary compounds. Variations in the electrolyte composition and deposition parameters enabled an enhancement of Seebeck coefficient and electrical conductivity in the as-deposited samples. Further improvement would make annealing steps, undesired in an integrated device, unnecessary. Porosity and surface roughness of the obtained deposits were improved for device fabrication.

The funding from the European Union’s Horizon 2020 research and innovation programme through the TIPS project, under grant agreement No 644453 is acknowledged.

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PA11.7

Ball milling effect on the thermoelectric properties of glass-ceramic Cu-As-Te materials

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Within the new material families explored to spread the use of thermoelectricity near room temperature in our societies, we have followed an approach quite different from the conventional one, which leads to reduce the thermal conductivity from existing crystalline materials. We begin with glassy materials with high Seebeck coefficient, S (>1 $mV.K^{-1}$), very low thermal conductivity, κ (down to 0.3 $W.m^{-1}.K^{-1}$ at 300 K) and we increase their electrical conductivity, σ, in order to enhance their dimensioneless figure of merit ZT. To do this, we have previously explored a glass-ceramisation process in the Cu-As-Te family using Spark Plasma Sintering (SPS) [1]. In this paper, we will discuss the influence of high energy planetary ball-milling on the glass-ceramisation process. We will describe the microstructure, composition and thermal stability of the ball-milled samples before and after SPS and correlate them with the electrical and thermal transport properties. Finally, the fine control of the microstructure and composition provided by this modified process leads to ZT = 0.25 at 400K, a value improved by 67% over non ball milled samples.

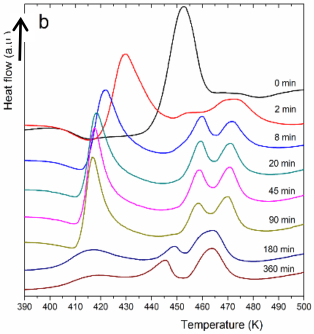

Figure 1: DSC curves of the $Cu_{15}As_{30}Te_{55}$ for different ball timing time.

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A12. Nanomaterials

PA12.1

Thermoelectric enhancement in the two-dimensional electron gas of AlGaN/GaN heterostructures

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Abstract

This paper reports Seebeck coefficient (S) enhancement in the two-dimensional electron gas (2DEG) of AlGaN/GaN heterostructures, and the semi-quantitative analysis of the phenomena. AlGaN/GaN heterostructures for the experiments were fabricated as already described elsewhere [1]. The data plots except for the solid triangles in Figure 1, namely $|S|_{\text{measured}}$ and $|S|_{\text{2D}}$, are originally reported in Ref. [1]. $|S|_{\text{measured}}$ denote the measured S, and $|S|_{\text{2D}}$ the S values modified by removing the contribution of underlying GaN layers to the $|S|_{\text{measured}}$ [1]. As clearly seen in Fig.1, $|S|_{\text{2D}}$ positively correlates to the sheet carrier concentrations (n) of the specimen, contrary to the conventional case. The authors took the Hicks-Dresselhaus theoretical model [2] to analyze this anomalous relationship. The theoretical calculated results ($|S|_{\text{cal}}$) are plotted in Fig.1. The model succeeds in reproducing the slope of $|S|_{\text{2D}}$–n correlation, while there still remains a certain offset. More detailed discussions will be provided in the presentation.

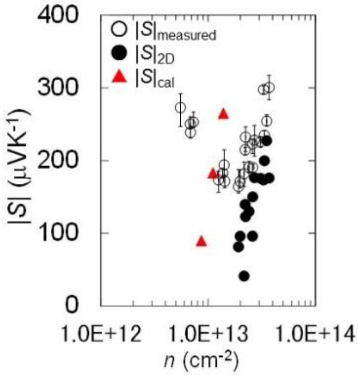

Figure 1: $|S|$ values are plotted as a function of n. The open circles denote the measured $|S|$ ($|S|_{\text{measured}}$), the solid circles $|S|$ originated from 2DEG ($|S|_{\text{2D}}$), and the solid triangles theoretical $|S|$ ($|S|_{\text{cal}}$).

References:

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PA12.2

Nanoarchitecting to induce flexibility in $Ca_3Co_4O_9$ thin films for flexible thermoelectric applications

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Abstract

Although bulk $Ca_3Co_4O_9$ is inherently rigid and brittle, structural architecting at nanoscale is found to induce flexibility in $Ca_3Co_4O_9$ thin films. Samples have been grown by thermally induced phase transformation from CaO-CoO thin films to final phase of $Ca_3Co_4O_9$ on semiwettable substrate. CaO-CoO thin films is deposited by rf-magnetron reactive co-sputtering from metallic targets of Ca and Co [1]. The pattern of nanostructural evolution during solid state phase transformation is determined by the combined influence of interaction between the oxide phases and the substrate and their surface energy. If the interaction is weak, i.e., semiwettable substrates, the different architectural pattern can be induced by tuning the relative arrangement of CaO and CoO phases in as-deposited films. Different deposition schemes, e.g. co-deposition and sequential deposition of CaO and CoO phases, are employed to tailor the relative arrangements of CaO and CoO phases in as-deposited films. Figure 1 shows a SEM image of a typical $Ca_3Co_4O_9$ thin film with nanolaminated grains perpendicular to the substrate plane, which is obtained by heat treatment of co-deposited film in oxygen atmosphere. Such arrangement of the grains induce flexibility in the film without significant deterioration of electronic properties. Electrical conductivity of the film is obtained around 10 mΩ-cm at room temperature, which is several times lower than bulk polycrystalline samples.

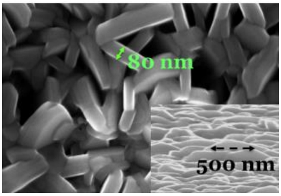

Figure 1: A typical SEM image of flexible $Ca_3Co_4O_9$ film showing nearly vertical orientation of grains obtained by annealing co-sputtered film. Inset shows the tilted view of the film.

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PA12.3

Synthesis of nanostructured, cadmium doped ZnSb and investigation of the thermoelectric properties

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Abstract

ZnSb is an interesting *p*-type thermoelectric compound for the intermediate temperature range (450 K-650 K). Besides its relatively high electric conductivity and Seebeck coefficient, ZnSb possesses a low thermal conductivity. Furthermore, both constituent elements are cost-efficient and non-toxic.[1 - 2] Aim of this work was the synthesis of nanostructured ZnSb by mechanical alloying and doping with different amounts of cadmium to replace the zinc atoms in the lattice and so improve its thermoelectric properties. The synthesized samples were analyzed regarding their structural and thermoelectric properties. After synthesis, X-ray diffractograms and transmission electron microscopy images were taken from the samples. TEM images (Fig.1) are showing agglomerates, which consisting of smaller particles of 20 – 50 nm in diameter. Cadmium-doping resulted in little change of the electrical conductivity compared to the undoped material but in an increase of the Seebeck coefficient. The thermal conductivity decreased by cadmium-doping and a figure of merit between 0.6 and 0.75 at 623 – 650 K was obtained.

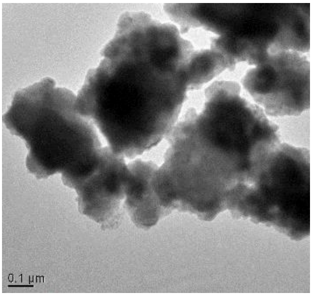

Figure 1. TEM image of the synthesized ZnSb.

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PA12.4

Thermal diffusivity of flexible material with ZnO nanostructures

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Abstract

For high-efficiency wearable power generator, we have investigated the ZnO nanostructures grown on cotton fabric (CF) as a novel flexible thermoelectric material. We have fabricated ZnO nanostructures on CF by two-step growth method consisting of a seed creation process and a nanostructure growth process [1]. It has been confirmed from ultraviolet transmittance spectra that the ZnO nanostructures are strongly fixed on the CF even after laundering them ten times. In the present study, ZnO nanopillar-nanosheet composites were formed on CF by the two-step growth method, as shown in Fig. 1(a). By means of an ac calorimetric method, the thermal diffusivity of the ZnO nanostructure/CF sample was 1.4×10^{-4} m^2/s, evaluated from relationship between time delay (δt) and distance shift (δL). This value was larger than the thermal diffusivity of pure CF, 3.9×10^{-5} m^2/s. These facts suggest that most of the cotton surface is covered with ZnO nanocomposites or ZnO nanocomposites make a continuous layer on the cotton since another path of heat flow is considered to be formed.

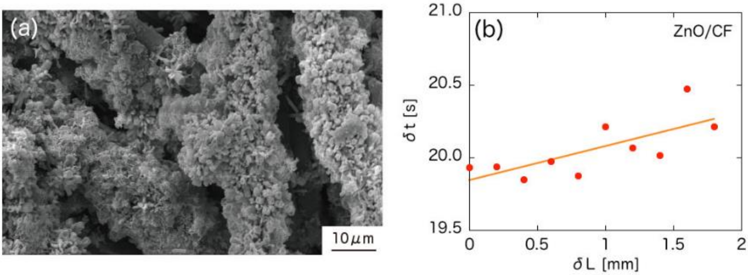

Figure 1: (a) SEM image of a ZnO/CF sample and (b) its δt-δL relation.

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PA12.5

Synthesis and characterisation of boron rich boron carbide containing nano-TiB_2 inclusions for thermoelectric applications

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Abstract

Thermoelectric materials could serve as source of reliable, maintenance free, sustainable alternative source of energy. Several strategies have been tried so far to suit the material requirements for thermoelectric applications. Boron carbide appears to be a potential candidate material for very high temperature range, due to its unique crystal structure and also due to better Carnot efficiency. Boron rich carbides have shown promising properties for thermoelectric applications with improved ZT [1]. Based on several studies, nanostructuring has been proven to significantly improve the figure of merit of boron carbide [2]. Further extension of this work involving nano-inclusions of TiB_2 in boron rich boron carbides could lead to much improvement in ZT. Boron rich boron carbide is initially prepared by reaction of boron carbide and elemental boron. Different sintering methods are tried out for better densification and nano TiO_2 powder is included to form nanocomposites of boron rich boron carbide and TiB_2. The material is characterised using XRD, FESEM and the dependence of thermoelectric properties on the TiO_2 content is studied.

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PA12.6

Realizing band structure modification and energy filtering in β-Zn_4Sb_3 based nanocomposites

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Abstract

β-Zn_4Sb_3 is one of the most promising thermoelectric materials on account of its low glasslike thermal conductivity and good electrical properties at moderate temperature. We found that La-substitution in β-$(Zn_{1-x}La_x)_4Sb_3$ enhances electrical conductivity and power factor (PF) over a wide temperature range while it substantially reduces the lattice thermal conductivity. These synergistic effects of La-substitution are discussed in terms of the substitution-induced variation in carrier concentration and effective mass as well as stronger phonon scattering by point defects. Further in β-Zn_4Sb_3 based composites incorporated with nanophase Cu_3SbSe_4, we concurrently realize ~30% increase in PF through an energy filtering effect (EFE) caused by carrier scattering at interface barriers, and around twofold reduction in lattice thermal conductivity. Finally, we achieve ~40% increase of PF by simultaneous resonant distortion in electronic density of states via Pb-substituting and EFE via introduction of interface potentials and an approximately twofold reduction of the lattice thermal conductivity due to interface scattering in Cu_3SbSe_4/β-$(Zn_{1-x}Pb_x)_4Sb_3$ nanocomposites.

PA12.7

Skutterudite ($CoSb_3$) thermoelectric nanomaterials fabricated by pulse plasma in liquid

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Abstract

In this work we present a new way of fabrication of thermoelectric nanomaterials using Pulsed Plasma in Liquid (PPL) with a low-energy spark discharge. Thermoelectric (TE) materials can be used for direct energy conversion from heat into electricity. TE materials are of particular interest because of their enabling both clean energy transformation and waste heat energy harvesting. The efficiency of the conversion process depends on a Carnot cycle and the material properties described by the thermoelectric figure-of-merit (*ZT*). This parameter is based on both electrical conductivity and a square of the Seebeck coefficient divided by the thermal conductivity. We can increase the *ZT* value by reducing the thermal conductivity through the nano-structuring of TE materials, at the same time anticipating its low impact on the electrical properties. For our study we chose $CoSb_3$, a state-of-the-art TE material from the skutterudite family which is a narrow-band gap semiconductor with a parabolic bottom of the conduction band.

Binary skutterudite $CoSb_3$ polycrystalline ingots were synthesized by a direct fusion technique from pure elements. The densified materials with a cylindrical shape were used as substrates in the fabrication process of $CoSb_3$ nanoparticles via the modified Pulse Plasma in Liquid method. The nanopowders were consolidated using rapid Spark Plasma Sintering (SPS) with the processing time in minutes. The X-ray diffractometer (XRD), scanning electron microscope (SEM/EDS) and scanning transmission electron microscope (STEM) were used to characterize the synthesized powders and sinters. Thermal conductivity was determined by the laser flash technique (LFA). Electrical properties: resistivity and Seebeck coefficient were measured by the four probe technique, both as a function of temperature.

Acknowledgements:

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PA12.8

The synthesis & property of artificial meta-stated telluride and silicide compound

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Abstract

A coexistence of various intrinsic meta-state domains as like 3rd phase, meta crystalline, nano-grain, twinning, dislocation in matrix have been reported in a several typical thermoelectric compounds, recently. It might be natural state considering solid reaction process accompanying non-equilibrium state to bulk synthesis. But its existence made it difficult to understanding of thermoelectric property by existing theory. We have studied about the role of various intrinsic meta-states in Bi-Te, Pb-Te and Mg_2Si compounds [1][2][3][4]. Especially, the previous work about new complex crystalline rearranged by stacking fault induced Ag interstitial layer in BST show the various extrinsic meta-states can coexist with matrix thermoelectric materials, stably [1][5]. In this presentation, we report that the meta-state design method based on lattice & band gap matching and the effect of meta-state microstructure on thermoelectric property in artificial meta-stated Bi-Te, Pb-Te and Mg_2Si thermoelectric compounds.

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PA12.9

Diffusive and ballistic phonon transport in GaP nanowires

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One of the strategies to decrease the thermal conductivity of a material is to reduce its dimensions because it leads to a reduction of the mean free path due to boundary scattering. It has been demonstrated that the thermal conductivity of nanowires can be reduced by about one order of magnitude compared to their bulk value [1]. This strategy is applicable when diffusive boundary scattering takes place. However for thin wires with a smooth surface, some phonon modes may scatter specularly with a long mean free path, resulting in a transition from diffusive to ballistic transport [2]. Here we show experimentally that this effect is observable for Gallium Phosphide nanowires with a length up to 12 µm. Thermal conductivity of nanowires increases when the diameter is reduced below 50 nm showing a transition from diffusive to ballistic transport. The experimental data is understood using the Landauer model for conduction. These results demonstrate the existence of ballistic phonons in long structures which could be used to increase heat extraction in nanostructures and as means of controlling phonon transport for thermoelectric applications.

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PA12.10

Demonstrated amorphous bulk Al-Mn-Si for nano-structured thermoelectric materials

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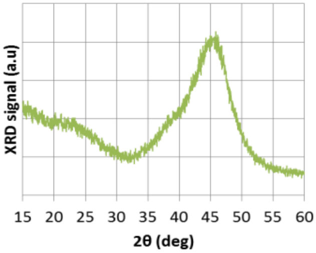
Abstract

Thermoelectric generators (TEG), with which one can directly convert waste heat to useful electric power, have attracted considerable attention as one of the most efficient techniques leading to a low carbon, sustainable society. The figure of merit ZT of constituent thermoelectric materials is generally used as a measure for the efficiency of energy conversion in TE generators, and it has not reached a large values exceeding 2 for the last half century, despite that ZT > 5 is required for automobile exhaust heat utilization system. This large gap between the required values and obtained values strongly let us believe that TEG is not usable in practical applications. We need to employ new, innovative techniques leading to a breakthrough for developing high-performance thermoelectric materials.

In this study, we tried to develop bulk materials consisting solely of the nano-structured grains for obtaining a large ZT value. The concept is to control the nano structured particles from amorphous materials through annealing. As the frist step, we developed amorphous materials.

An amorphous bulk containing nano particles was reported for magnetic materials such as NANOMET© [1] prepared by a melt-spinning method, however, this method has not been used for thermoelectric material. To develop amorphous thermoelectric materials, we searched the compositions possesising a low-melting-point in the Al-Mn-Si alloy system. As a result, we succeeded in obtaining the amorphous ribbons of ~2mm in width, showing halo pattern in X-ray diffraction (XRD). In order to develop bulk size, we plan to utilize a highly pressure technique. In the presentation, we will show the results of sintering and the TE characteristics of prepared samples.



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PA12.11

The role of oxidation in tellurium/PEDOT:PSS hybrid composite thermoelectric materials

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Abstract

Thermoelectric devices are those capable of directly converting temperature differences into electricity by means of the thermal diffusion of charge carriers generating an electric potential gradient. Their performance is typically discussed in terms of a dimensionless figure of merit, $ZT=S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the thermal conductivity. Several approaches are currently being investigated to improve ZT through interface engineering and nanostructuring. One example has arisen through the development of hybrid organic-inorganic nanocrystal composites, which are designed to take advantage of the intrinsic low thermal conductivity of the organic material, while maintaining efficient thermopower. Hybrid composite devices based on poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) and nanostructured tellurium have emerged as model composite systems that are also easy to synthesize and process by solution routes. The addition of chemical additives before or after synthesis, including ethylene glycol and DMSO, have been shown to dramatically improve the electrical conductivity and thermopower of these systems relative to their untreated analogs.[1] This has been attributed to a structural refinement in the organic material at the nanocrystal interface.[1] While performance differences have been observed depending on whether these chemical additives were added during or post-synthesis, it has been argued that any changes are due to residual additives in the composite in the post-synthesis case.[1] We propose, however, that surface oxidation of the nanocrystals is also an important and neglected element in these hybrid systems that impacts the overall thermoelectric performance. We perform extensive structural characterization via TEM, XRD, XPS, and Raman in order to elucidate how different synthetic schemes affect the ultimate structure of these composites. We find that we can significantly influence the level of oxidation at the tellurium nanowire surface depending on whether additives are included during or post-synthesis. We aim to show how these changes in the interface structure relate to the thermopower and electrical conductivity in these hybrid composites in an effort to develop a more complete understanding of these material systems.

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B1. Measuring techniques

PB1.1

Improving Thermoelectric Properties by Nanoparticle Inclusion in Bi_2Te_3 Thin Film

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Nanostructural inclusions have been introduced into thermoelectric (TE) films of Bi_2Te_3 in order to improve their performance by attempting to enhance phonon scattering [1]. We have utilized Bio-Nano-Process (BNP) to fabricate nanoparticles with uniform size and controlled their distribution [2]. The thickness of Bi_2Te_3 films with and without nanoparticles was kept at 200 nm. The microstructure of films was examined by scan transmission electron microscopy (STEM). Preliminary temperature dependent (80 - 300 K) transport measurements indicate that, upon the inclusion of 9 layers of nanoparticles in Bi_2Te_3 films, the room temperature (RT) Seebeck coefficient (S) increased from 168 to 172 μV/K, while the RT electrical resistivity (ρ) increased from 10.8 to 14.5 μΩm. Measurements of the thermal conductivity (κ) using the 3ω method are currently underway.

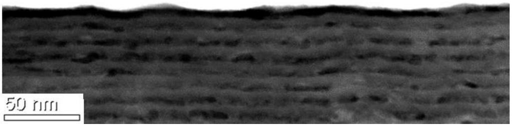

Figure 1: STEM image of sample with 9 layers NPs.

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PB1.2

Development of impedance spectroscopy for the characterization of thermoelectric materials

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Abstract

Impedance spectroscopy has been reported as a promising charaterization method for thermoelectric materials [1]. Under suspended conditions all the thermal properties of the materials can be calculated if the Seebeck coefficient is known or a complete characterization can be achieved when attached to a material with known thermal conductivity, such as the ceramic plates of the modules.

In this work we present new developments to this method, which include a new setup for characterization at high temperatures, new strategies to facilitate the complete characterization, and the evaluation of the method with different thermoelectric materials.

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PB1.3

Thermal conductivity measurements by scanning thermal microscopy of TiO_2 nanotubes

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Abstract

The efficiency of thermoelectric (TE) materials through the figure of merit zT is linked to the thermal conductivity of the material. Although, evaluate the thermal conductivity of TE materials can be very challenging due to the micro/nanoscale interaction between the probe and the sample. Some of the current thermal methods have spatial resolution issues, which make the evaluation more difficult in the case of nanostructures materials [1]. However, the 3*w*-SThM (Scanning Thermal Microscopy) is a powerful technique for thermal measurements and using a commercial silicon nitride probe with palladium film is possible to achieve more than 100 nm of spatial resolution. In this work, the thermal conductivity measurements with this spatial resolution is very important to analyses anodic TiO_2 nanotubes layers (TNTL), since the Magnéli phase titanium oxides exhibits interesting properties for TE applications [2]. The thermal behaviour of TNTL is determined with the SThM technique that can measure simultaneously, topographic and thermal images of the samples; electrical and morphological characterization of TiO_2 nanotubes is also discussed.

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PB1.4

Thermoelectric properties determination of multilayered semiconductor materials at harmonic single-frequency excitation of temperature field

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Abstract

In this work, the measurement method of multilayered semiconductor thermoelectric materials including segmented branches of the thermoelements is described. Developed method allows in a common measurement cycle obtaining of the main parameters researched structure, which are required for thermoelectric Q-factor determination both multilayered structure and individual material layers.

In this method, the phenomenon of phase shift between heater's power of the measurement bench and its temperature at harmonic thermal excitation is used.

When measurements, the sample is fixed between two heat-exchange units insulated from flat resistive heaters by insulated layers (Fig. 1). At the same time, the temperature of the structure edges T_0 is constantly maintained. Heaters' power 3 and 9 are changed harmonically with the equal frequency in antiphase.

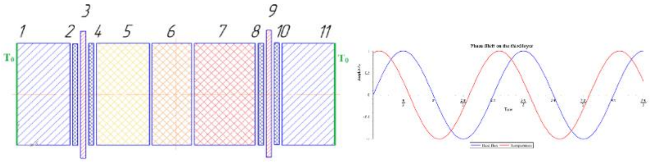

Figure 1: Layers 1, 11 – copper heat-exchange units; 2, 4, 8, 10 – insulated layers; 3, 9 – heaters; 5, 6, 7 – segments of the sample.

To obtain the thermal conductivity coefficient at this temperature, the thermal mode of the heaters is set. At the same time, the temperature of each heater is changed with the same frequency, as the power, but delayed from it on a certain phase shift angle depending on physical properties of each layer of the structure. After this phase angle measurement, thermal conductivity coefficient is calculated at specified average temperature by means of developed mathematical model.

Electrical resistivity and Seebeck coefficient are determined from the equations of current transport through the sample [1].

Acknowledgements:

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PB1.5

Recent developments in analysis of thin films and thermoelectrics

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Abstract

The analysis of thin film materials is getting more and more interesting to many fields of research. Especially the field of thermoelectric applications reaches more and more nano scales. The behavior of thin layers differs completely from bulk samples due to several surface effects. This makes it complicated to use common known techniques of analysis to get proper results and a lot of groups developed their own solutions for these problems. With the new Linseis Thin Film Laser Flash analyzer and the Linseis Thin Film Analyzer, that uses a chip design to get all interesting information like thermal conductivity, specific heat capacity, electric resistivity, hall constant or seebeck coefficient, there are a few novel methods to investigate all these effects. This talk will introduce this new generation of thin film analyzing devices and their functionality, how they were developed and also the advantages of their use.

B3. Theory and Modelling

PB3.1

First-principles calculation of the thermoelectric figure of merit of polymeric systems

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Thermoelectric (TE) materials are currently studied for the promising perspectives foreseen in the enhancement of their efficiency in converting thermal gradients into electrical currents [1]. Even though, traditionally, only inorganic semiconductors were considered for TE applications, recent advances in research opened the way to a new generation of organic TE materials. Organic materials have the advantages of low cost, lightweight, mechanical flexibility, and low-temperature solution processability over large areas [2]. The prerequisites for good TE performances are high electronic and low thermal transport. So, from a theoretical point of view, it is fundamental to achieve a deep understanding of the transport phenomena at the molecular scale.

In this work [3], we carried out a fully quantum mechanical study on a set of organic polymers, namely polyfluorene (PFO), poly-3,4-ethylenedioxythiophene (PEDOT) and polyaniline in its leucoemeraldine base form (PANI). PEDOT and polyaniline are two of the most widely used molecules in organic thermoelectric applications [2], polyfluorene has not yet been proposed for thermoelectrics but it is a well-known system used in optoelectronics [4] and is considered for comparison. The aim of the study is gaining an atomistic understanding of the physical and chemical mechanisms that affect the electronic and thermal transport and the thermoelectric power in low-dimensional systems. We will adopt an original method [5] to compute ballistic electron and phonon transport using an integrated Landauer approach. We combine this technique with a fully first principles approach based on DFT for both the electronic and the thermal properties of the systems.

As a crosscheck test on the structure and composition of polymeric systems, we simulated a few electronic (DOS) and vibrational spectroscopies (e.g. IR) and we compared our results with the experimental data reported in literature [6,7,8], finding very good agreement. On the other hand, the analysis of the ZT figure of merit at different temperature underlines an overestimation of one order of magnitude of the thermoelectric response of our samples, with respect to experiments. This is ascribable to the maximization of the electronic contribution and the quenching of the thermal one in pure 1D polymeric chains. Inclusion of solid-state effects and disorder are expected to provide ZT values closer to the experimental findings.

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PB3.2

Thermoelectric efficiency and fluctuations in nanosystems

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Abstract

We study the relation between the efficiency and electric and heat current fluctuations in nanoscale thermoelectric devices using non-equilibrium Green's function formalism. In the linear response regime in temperature and voltage, we know that the efficiency is directly related to the figure of merit. This is no longer the case outside the linear response. For a quantum dot, we show that at low transmission the efficiency is related to the correlator between the electrical current and the heat current provided that these currents are considered in distinct reservoirs [1]. This mixed cross-correlator can thus provide information on the thermoelectric conversion. Our calculations show that the expression for the heat current takes a form similar to the Landauer expression for the electrical current and that the expression for the mixed correlator takes a form similar to the Büttiker expression for the electrical current fluctuations. We also discuss the possibility to have fluctuations of efficiency around its macroscopic value in quantum systems [2].

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PB3.3

Theoretical studies of electronic structure and transport properties of locally ordered ternary chalcogenides

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Abstract

Cation sublattice ordering in $AgXY_2$ chalcogenides is an important factor influencing their electronic structure and thus thermoelectric properties [1]. Several selected ordering configurations (Fig. 1) were specified for $AgXY_2$ chalcogenides (X = Sb, Pb, Sn; Y = Te, Se) and full-potential linearized augmented-plane wave (FP-LAPW) calculations carried out using WIEN2k package [2]. Relationship between local ordering and cohesive energy is discussed and most preferable systems are indicated. *Ab initio* calculated electronic structure properties of chosen model configurations are analyzed and densities of states are used to determine respective transport properties derived from semiclassical Boltzmann theory.

Detailed analysis of electron density topology carried out within Bader's QTAiM formalism [3] is presented, including bonding properties and atomic net charges, in order to determine the influence of local ordering on properties essential from a point of view of thermoelectricity.

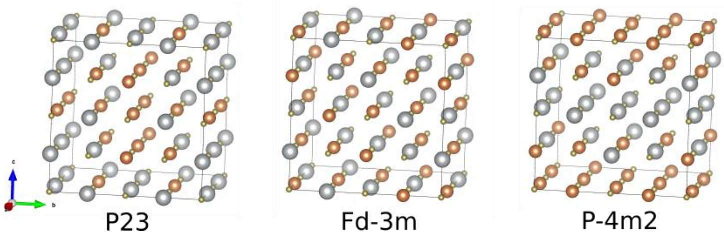

Figure 1: Various ordering of cation sublattice (large and medium balls) in analyzed $AgXY_2$ systems (applied crystal symmetries are denoted).

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PB3.4

Ab-initio study of transport properties of p-doped PbTe

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Abstract

Using density functional theory electronic structure calculations and semi-classical transport theory in relaxation time approximation we compute transport properties of p-doped PbTe. To avoid possible errors due to rigid band approximation (RBA) we use supercell model of doped crystal and tune carrier concentration explicitly by portion of impurity atoms. In such a way we verify the validity of RBA. Na and Tl dopants were considered. The usage of supercell model instead of RBA brings the results closer to the experiment. The possible influence of resonant states on transport properties is discussed.

PB3.5

In-plane and cross-plane lattice thermal conductivity of single-layer to bulk MoS_2 by using molecular dynamics study

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Abstract

As an atomically thin 2-D material, Molybdenum Disulfide (MoS_2) has drawn considerable interest due to its unique electronic structures and easy to exfoliation. Despite experimental [1-2] and theoretical [3-4] groups have examined the in-plane and cross-plane lattice thermal conductivity intensively, but the fundamental value of lattice thermal conductivity for MoS_2 is still controversial.

Here, we calculate the lattice thermal conductivity of MoS_2 by using non-equilibrium molecular dynamics simulation to find the diffusive lattice thermal conductivity of in-plane and cross-plane MoS_2. It is strong anisotropic behavior is observed and length dependence of the lattice thermal conductivities is found to present up to about 3 μm. We also found that only small amount of sulfur vacancies would bring about great reductions of thermal conductivity in single layer MoS_2.

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PB3.6

First principles study of heavily doped full Heusler Fe_2 YZ for high thermoelectric power factor

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Abstract

Using a combination of first-principles calculations based on density functional theory and Boltzmann semi-classical transport theory, we investigate the properties of heavily *n*-type doped full Heusler $Fe_2YZ_{1-x}A_x$ compounds. Using a supercell approach and including explicitly the dopant impurities, we recover in some cases giant thermoelectric power factors as previously predicted under doping within the rigid band approximations [1]. In other cases, however, we highlight that the system evolves toward a ferromagnetic half-metallic ground state so that the power factor is strongly modified. We rationalize the appearance of this magnetic instability, showing that it is consistent with the Stoner model. The uncovered properties of the heavily doped phases of the studied $Fe_2YZ_{1-x}A_x$ compounds appear promising for Seebeck and spin-Seebeck applications.

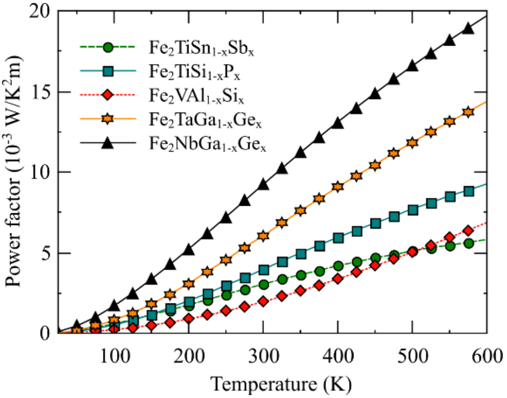

Figure 1: Calculated power factor of $Fe_2YZ_{1-x}A_x$ compounds (x = 0.0625) from Boltzmann transport theory.

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PB3.7

Spin-configurations in thermoelectric MnCoGe materials

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Abstract

In the last decades, research for improved thermoelectric materials focused on the introduction of nanostructures. However, only modest enhancement of the thermoelectric efficiency could be achieved. For improved thermoelectric performance another approach is required. In this respect, temperature driven spin transport in magnetic materials offers great potential. The ternary Mn-Co-Ge, for example, shows interesting magnetocaloric and thermoelectric properties in this respect. Magnetic properties of ferromagnetic $Co_xMn_yGe_{1-x-y}$ thin films, for example, have been shown experimentally to vary with composition x and y [1], suggesting a possible tuning of the $Co_xMn_yGe_{1-x-y}$ properties to meet application's requirements.
In this study, structural and magnetic transitions in MnGe-based materials with varying composition have been investigated using ab initio calculations. In particular, the effect of chemical composition on the stability of the hexagonal Ni_2In-type and the orthorhombic TiNiSi-type structure has been examined focusing on their magnetic configurations. It has been found that compressive strain promotes the formation of the Ni_2In-type structure which can be advantageous for the magnetostructural transition in thermomagnetic devices. The so-called spin-Seebeck coefficient [1,2] has been estimated for several magnetic configurations of such materials based on the Boltzmann transport.

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C1. Modules and thermoelectric generators

PC1.1

Ag-Ni multi-layer metallization characteristics on polycrystalline SnSe

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Abstract

SnSe is getting particular attention with their world record high figure of merit (ZT) results reported in 2014 [1]. From this first report, many research groups are chasing novel high performance SnSe thermoelectric device development however no research result on SnSe thermoelectric module has been reported yet. In this work the microstructural and electrical characteristics of the Ni-Ag multi-layer metallization on thermoelectric SnSe will be investigated for the first time. The electrical contact resistance characteristics will is reported and their promising applicability to highly efficient SnSe thermoelectric module will be discussed in detail.

Figure 1: Photograph of Ag-Ni mulit-layer metallization on SnSe thermoelectric leg

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PC1.2

Development of Mn/Mn and Mn/Mg High Temperature TE Devices

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Abstract

Skelton-type 20-pair $MnSi_{1.74}/Al_3Mn_3Si_4$ and $MnSi_{1.74}/Mg_2Si$ devices, usable below 600℃, are fablicated successfully. Ni top-electrodes are brazed to the p- and n-thermoelectric(TE) blocks. 50×40×2mm^3 aluminum bases are used. The TE-blocks, 10×3×7 mm^3 in size, are cut-out from the 30ϕ × 7mm pelletes synthesized by the spark plusma synthesis(SPS) technique. The thermoelectric performance of the Mn/Mn and Mn/Mg devices are 1.44W and 2.79W between 600 ℃(hot side)-100 °(cold side), respectively. While the internal resistance is 0.43 and 0.55 Ω. Two devices are shown in the photograph.

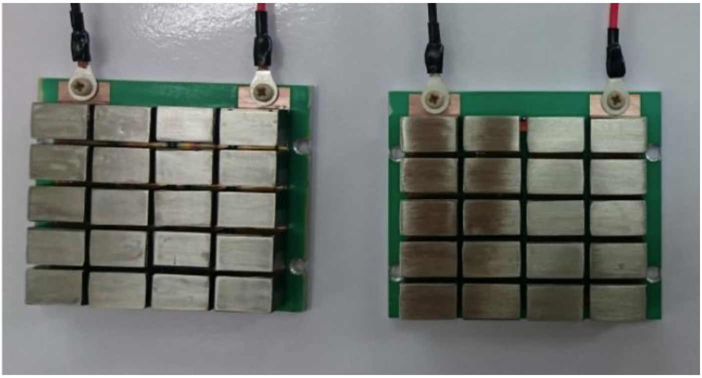

Figure 1: 20-pair $MnSi_{1.74}/Mg_2Si$(left) and $MnSi_{1.74}/Al_3Mn_3Si_4$ (right) devices.

PC1.3

Design and characterization of thermoelectric generators for wearable electronics via optimizing structural parameters

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Abstract

With growing attention to wearable electronics, thermoelectric (TE) generator has been focused for solving limited battery-time, via harvesting limitless human body heat. Although the TE materials have been considered a key factor, structural parameters for TE generator such as fill factor, shape of TE elements, density of TE couples, substrate, and filler materials are also crucial for the TE generator performance. Recently, there have been studies for the effect of structural parameters on TE generators [1-2]. However, to our knowledge, most of the studies have relied on theoretical approaches, not on experimental data. Here we study the effects of structural parameters on TE generators under the fixed temperature and the convective thermal boundary conditions. To verify our prediction, TE modules using Bi-Te based alloy with different structures have been fabricated and tested. Specifically, we varied the fill factors from 0.05 to 0.4, temperature difference from 0K to 80K, and types of filler materials to study the effect of heat transfer on the generating performance of the TE modules.

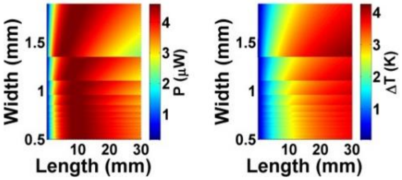

Figure 1: Calculated output power and temperature gradient of a TEM with different structural parameters.

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PC1.4

Flexible thermoelectric generator fabricated using bulk materials

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Abstract

A prototype flexible thermoelectric generator, which couples entropy current and electrical current to convert thermal power into electrical power [1], has been fabricated using bulk materials [2]. Mineral-fiber band and copper tape were used as flexible substrate and electric connectors. The applied active thermoelectric materials were $Ca_3Co_4O_9$ ceramic [3] and Cu-Ni alloy for hole (p) and electron (n) conduction, respectively. Thermal parallel and electric series connections of the mentioned materials were realized in the prototype flexible thermoelectric generator. When the hot-side was at 420 K and a temperature difference of 31 K was applied, the 3 cm long device, made of four basic units of n-p pairs and electrical connector, delivered an open-circuit voltage of ca. 17 mV and a short-circuit current of ca. 19 µA. The device can be made longer easily and coiled up to be adapted to the needs of the practical application.

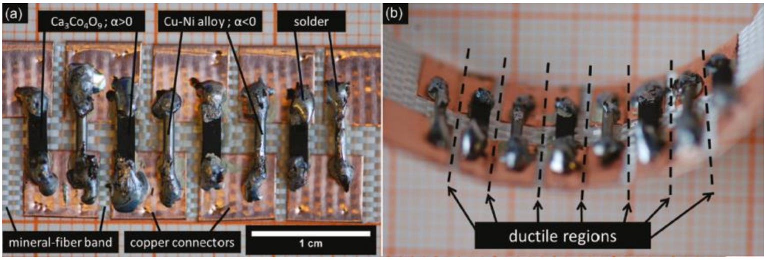

Figure 1: Microphotography of the prototype flexible TEG: (a) side view on plan side, (b) perspective view on bend device.

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PC1.5

Portable thermoelectric power generation base on catalytic combustor for low power electronic equipment

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Abstract

In the past years, much work has been reported on thermoelectric generators (TEGs) as power supplies and as alternative technology [1, 2]. In this work, a TEG based on catalytic combustion has been built up and developed having as output target the powering of portable electronic equipment. TEGs based on catalytic combustors have been already realized in several works reported in literature [3]. The relatively small size of the TEG system proposed opens interesting opportunities for thermoelectric solution due to the increased portability and its applicability to any type of low power requiring devices. Small size, reliability in continuous operating conditions and fast source recharging are all strategic features of the system described offering the chance to be considered a breakout for the power supply technology.

From the preliminary results the system can provide about 1.5 V and 2.2 A by a fuel consumption of about 1 g/hr, an output close to common portable batteries used for electronic devices.

In order to calibrate the operating conditions, the analysis of the temperature values and distribution across the combustor surfaces have been carried out. The overall TEG efficiency is evaluated by parallel characterization of thermoelectric modules and exhaust gases composition and the best performing conditions have been investigated in the target voltage and current range. Finally, a dimensioning estimation of overall TEG size is performed in case of passive cooling system for future developments.

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PC1.6

Performance of planar µTEG as a function of polySi properties and device membrane-based topology

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Abstract

Silicon based planar micro thermoelectric generators (µTEGs) were realized by CMOS compatible technology then were evaluated to harvest low to high level of heat. The µTEGs are build up with a thermopile periodically suspended onto dielectric membranes. The thermopile is based on a poly-Silicon (pSi) TE layer; it is a series of pSi/Au or Al thermocouples (TC) patterned into a zig-zag strip that covers a surface about a third of cm². This planar topology with membranes and long TC result in modules with a high thermal resistance [1] and a performance slightly impacted by the TE thermal conductivity but rather efficiently improved by any increase of the TE power factor ($PF=\alpha^2.\sigma$, α is the Seebeck coefficient, σ the electrical conductivity).
The presented modules integrate different kinds of pSi layers, with a PF varying from 3 µW/K²/cm, for standard P doped pSi, to 24 µW/K²/cm for "optimum" pSi obtained by very high dose implantation doping with B or As and annealing. The evaluation of their performance is carried out using a heat concentrator placed above the µTEG and periodically in thermal contact with the thermopile at half of the junctions. The characterisation is done by injecting power to a resistance printed on the upper surface of the concentrator. The power is varied from 0 to 10 W/cm². A periodic gradient of temperature ΔT is created at each TC. This results in a Seebeck open-circuit voltage Vs that is seen to vary linearly with the input power. Typically, for an input heat flux density of 4W/cm², ΔT experienced by each TC varies up to 30, 100 and 150K for respectively 10-, 5- and 2-membranes based modules, which is consistent with the whole structure modelling. The optimum behaviour is experimentally obtained for 5-membranes based µTEGs. In these cases, Vs is in the range 6-15V depending on the pSi properties and corresponds to a maximum output power P_{max} in the range 49 – 306 µW/cm² on adapted loads. The best performance is obtained for µTEGs integrating highly B doped pSi layer (large PF). Surprisingly, the As+P codoped-based µTEGs are only moderately better than those based on standard pSi (P_{max} is 4 times better though the PF is a decade higher). This can be partly explained by an increase of the thermal conductivity associated to a microstructure modification via codoping. On the other hand, microstructure changes in highly B doped pSi has already been reported to improve the PF [2]. In this work we show that it is also effective to make performant planar modules.

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PC1.7

Experimental investigation of the behaviour of a high performance MPPT algorithm for TEG systems operated under constant heat conditions

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Abstract

Maximum Power Point Tracking (MPPT) algorithms are commonly used in order to extract the maximum amount of energy from a Thermoelectric Generator (TEG). There are some well-known methods that, while usually applied to Photovoltaics, can also be used with TEGs. Whilst these techniques can be easily and effectively implemented for a TEG operating under constant temperature conditions [1], they can be inefficient when applied to TEGs operated under constant heat conditions. Under such conditions, TEGs and PV cells behave very differently due to the variation in thermal conductivity of the TEG as a consequence of the changing load current. Hence the Incremental Conductance (IC) and Perturb and Observe (P&O) methods can take significant time to respond to changes in the operating conditions of the TEG, are slow to converge to the MPPT, are computationally expensive and do not readily accommodate the induced variation in thermal gradient across the TEG module. Fractional Open circuit techniques to establish the MPP are fast and computationally light but in general do not accurately track the maximum power point.

The work presented will show the experimental results obtained from an innovative MPPT algorithm implemented in firmware on a power converter that combines the accuracy of the P&O and IC techniques and the rapid response of the fractional open-circuit method. The converter used is based on a Boost (step-up) topology switched mode power supply and its real-time control is implemented using a microcontroller. The converter is connected to an array of TEGs operated on a hot gas test system representative of a typical constant-heat environment found in e.g. exhaust gas systems or industrial waste heat streams.

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PC1.8

Determination of silicide-based thermoelectric modules efficiency

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Abstract

In this work, thermoelectric module (TEM) prototypes based on magnesium silicide and higher manganese silicide were developed (Fig. 1). Different designs of modules and different brazing materials were tested, with a focus on device feasibility and reliability. Contact resistivity measurement of the silicide/metal brazed electrode and finite element analysis of thermal induced stress were also performed, to guide the design of TE modules. The electrical power and the efficiency were evaluated with a specially developed testing system. [1] Furthermore, infrared thermography was used as a diagnostic tool to investigate internal thermal and electrical interfaces.

The testing apparatus (Fig. 1) is based on the heat flow meter method at the cold side of the module and it is conceived to test TE modules (single or in cascade) with a footprint up to 60x60 mm^2. The system works from room temperature up to about 900 K, under vacuum or inert atmosphere. Electrical characterizations were performed both in a steady state condition, and with fast pulsed current-voltage (I-V) measurements, thus without disturbing the measurement, providing high reliability on the efficiency determination. Measurements of commercial modules and of silicide-based module prototypes are presented.

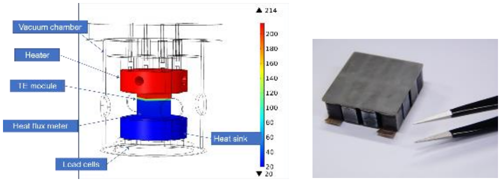

Figure 1: Scheme of the testing apparatus and photo of a silicide-based TE module prototype.

References:

[1] H. Wang, R. McCarty, J.R. Salvador, A. Yamamoto and J. Koenig, Determination of Thermoelectric Module Efficiency: A Survey, *Journal of Electronic Materials* 43 (2014) 2274-2286.

PC1.9

Joining of thermoelectric material with a metallic electrode using Spark Plasma Sintering (SPS) technique

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Abstract

One of the most important problems while producing thermoelectric module elements is the development of an appropriate joining technology affecting on the performance of the whole thermoelectric generator. The produced joints must be characterised not only by high mechanical strength and good adhesion, but also high electrical conductivity, high heat conductivity and, due to the working conditions, good chemical and temperature stability.

This paper presents lead-free junctions between a skutterudite material ($CoSb_3$) and a metallic electrode for middle-range application. Production process and the properties of obtained junctions are described. The materials were joined by the resistance brazing technique using the Spark Plasma Sintering (SPS) apparatus. The properties of the samples, including their thermal diffusivity (Netzsch Laser Flash Analyser LFA 457), electrical conductivity and Seebeck coefficient (PESS SeebTest) were determined and presented. The scanning electron microscopy (SEM, Zeiss AURIGA CrossBeam Workstation) was used to investigate the microstructure, whereas electron dispersive spectroscopy (EDS) was employed to analyse the distribution of the elements. All this was aimed at examining the progress of diffusion between the bound surfaces. This work summarizes properties of obtained junctions and their effect on the performance of thermoelectric module.

Acknowledgements

Research presented in this paper was supported by the National Centre for Research and Development (NCBR, Poland) within a framework of the project entitled "Innovative thermoelectric modules for energy harvesting" (project no. PBS3/A5/49/2015). This scientific work was partially financed as a research postdoctoral project no. DEC-2014/12/S/ST8/00582 from the resources assigned for science by National Science Centre (NCN, Poland).

PC1.10

A silicon nanowire thermoelectric device fabricated by top-down process

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Abstract

Thermoelectric device (TED) is a promising candidate of what supplies electrical power to a trillion sensor network which realizes internet of things (IoT). In recent years, silicon nanowire (Si-NW) is expected as a promising thermoelectric (TE) material thanks to the decreased thermal conductivity specific to nanostructured materials [1]. In this paper, we will report a device characteristic of Si-NW TED fabricated by top-down process (Fig.1). The width and length of NW are 140 nm and 10 µm, respectively. 50 Si-NW were patterned by the electron-beam lithography and a reactive ion etching process. Originally developed AlN ceramic heat probe was employed to evaluate the TE characteristics. The temperature of the heat probe is maintained at T_{HOT}=338K, and it is applied on an Al thermode film deposited on the TED. The bottom surface of the silicon substrate is kept at T_{COLD}=273K on a prober chuck. Fig. 2 shows the measured P_{TE} curves, which is normalized by the total width of the NWs. Open circuit voltage V_{OC} and max P_{TE} are 242 µV and 0.83 fW/nm, respectively. Thus the fabrication and characterization of nanoscale TED has been realized by the process technology compatible with Si LSIs. The TED performance will be lots more improved by decreasing series electric and thermal resistances.

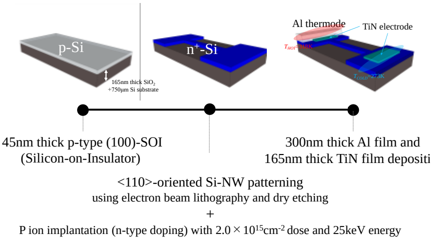

Figure 1: Fabrication procedure of Si-NW TED.

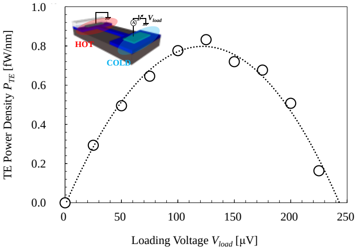

Figure 2: TE power curve of the TED

References:

[1] A. I. Boukai, Y. Bunimovich, J. Tafir-Kheli, J. Yu, J.-K. Yu, W. A. Goddard III, J. R. Heath, Silicon nanowire as efficient thermoelectric materials, *Nature* 451 (7175) (2008) 168.

PC1.11

Designing of a short leg thermoelectric generator on silicon

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Abstract

Miniaturized thermoelectric generators (TEGs) is anticipated as a key technology for realizing a trillion sensor network. In order to apply a sufficient temperature gradient in thermoelectric legs, the resistance of the thermal contact should be smaller than that of the leg [1]. Therefore, short leg structures have been considered to be unfavourable for the TEG. Figure 1 shows an estimated power generation as a function of the length of leg. In case that the thermal resistance of parasitic elements is larger than that of leg, a long leg structure is favourable. However, if the parasitic thermal resistance is sufficiently small, the shorter leg structure is rather advantageous and has a potential to generate a much larger electric power. In this research, we are designing a short leg TEG which can be fabricated by the standard Si-CMOS process. Figure 2 shows a temperature distribution in a planer TEG. Between the comb-shaped thermal electrodes, horizontally oriented Si-NW legs are located. We found that a steep thermal gradient is established in Si-NW legs, even without hollowing out the Si substrate underneath the thermoelectric legs. Thus a substantial improvement of the TEG can be realized by employing the shot thermoelectric legs together with the optimized structure of parasitic elements.

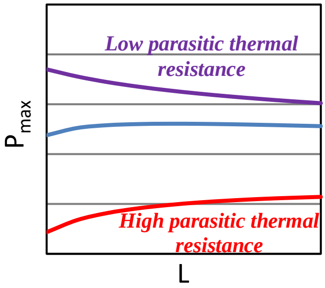

Figure 1: Dependence of maximum power, legs' length and parasitic thermal resistance.

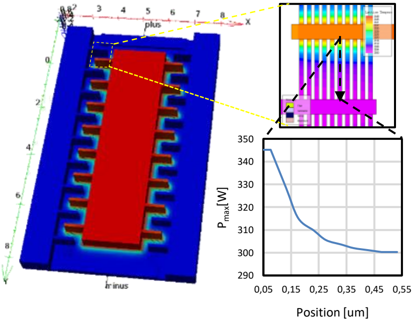

Figure 2: 3-D TCAD simulation model.

References:

[1] G. Min, Thermoelectric Module Design Theories. In: *Thermoelectrics Handbook* D.M. Rowe (Eds.), Boca Raton, Florida: CRC Press, (p. 11-7).

PC1.12

Reliability evaluation of mid-temperature thermoelectric joints - A comparative study of different techniques

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While the thermoelectric market is growing constantly, the fabrication of a mid-temperature working range thermoelectric device continue to present an important challenge. There are many limitations faced by thermoelectric modules for scalable manufacture and development including materials production, device design and system integration. A particular emphasis should be placed on the joining of the thermoelectric material to the metallic interconnects. These joints must have a low electrical and thermal resistance, be thermally stable and withstand stresses generated by the mismatch of thermal expansion coefficient (CTE) among thermoelectric material, interconnect and electrode.

We present results of different joining approaches used for fabrication of chemically and thermally stable mid-temperature interconnections. The suitability has been evaluated through characterisation of the joints electrical properties while the durability has been examined by observation of the interfacial diffusion of the thermoelectric/joint/electrode interconnection. Identification of appropriate brazes, possible contact materials as well as different joining techniques has been conducted, and is reported here.

PC1.13

Implementation of a three-dimensional model of thermoelectric generators in OpenFOAM to improve the efficiency of a heat recovery system using an impinging jet heat sink

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Abstract

The electric power produced by a thermoelectric generator (TEG) is strongly influenced by the applied heat sink. While a TEG is aimed at harvesting waste heat, the optimization of the efficiency of the heat sink is a key task for the design of waste heat recovery systems implementing TEG. A three-dimensional thermoelectric generator model is proposed and implemented in a computational fluid dynamics (CFD) simulation environment (OpenFOAM) to perform optimizations of the heat sink using a commercially available TEG as basis. This model includes the nonlinear multi-physics thermoelectric coupled effects. Conservation principles of energy and current are considered simultaneously. This includes thermal conduction, Peltier effect, Joule heating, electrical conduction and the Seebeck effect. Particular attention is given to the modelling of the boundary conditions e.g. electrical load. The thermoelectric model is implemented in such a way that it can readily be combined with other physical models in OpenFOAM. The model is validated by analytical results, measurements and simulation data from other models of a TEG.

Single-phase liquid microchannel and confined-submerged impinging jet heat sinks achieve both very high heat removal rates with minimal energy costs. The optimization of the geometric properties of a microchannel heat sink was investigated by Rezania and Rosendahl [1].

The developed model, implemented in OpenFOAM, can be used to optimize the geometric quantities of an impinging jet cooling a TEG. The objective function is the overall efficiency of the heat removal system. The geometric input quantities are the number of jets, jet-to-jet-spacing, jet diameter, jet-to-plate distance and volumetric flow rate.

References:

[1] A. Rezania, L. A. Rosendahl, New Configurations of Micro Plate-Fin Heat Sink to Reduce Coolant Pumping Power, *Journal of Electronic Materials* 41 (2012) 1298–1304

PC1.14

Joining of ceramic based TEG-modules

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Ceramic materials such as TiO_x ($x < 2$) or B_nC ($4 < n < 9$) are promising materials for thermoelectric modules. The thermoelectric efficiency of ceramic materials is minor compared to established thermoelectric materials. However TiO_x and B_nC are very attractive for economic reasons: ceramics are non toxic and can be produced cheaply. Furthermore there are still expectations for efficiency rise by modification of the material structure. A manufacturing process for unileg modules was established including sintering of ceramics by hot pressing, economic machining of ceramic legs, coating with oxidation protection layer, assembly and joining of modules with reliable electrical connections and supporting substrates. Modules with Cu-metallized AlN, Al_2O_3 and Si_3N_4 substrates were built to evaluate the influence of ceramic substrate material on module performance. A testing device was build up for experimental analysis of the module behaviour during operation at 600 °C at the hot side and 100 °C at the cold side. The test revealed similar power output and internal resistance of all fabricated modules. Furthermore thermal cycles with increasing and decreasing temperatures at the hot side were investigated to characterize the reliability and stability of the modules. The characterization of the module resistance and microstructural investigations of cross sections after 1000 cycles showed differences in the behaviour of the modules which are correlated to the substrate ceramics used.

PC1.15

Lab-scale pilot line for thermoelectric modules based on half-Heusler compounds

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Abstract

During the last few years, the production of new high-temperature materials in kg-scale with identical properties as described in the literature was demonstrated. This was an important step towards the industrialization of the thermoelectric waste heat recovery. The next steps are the proof of cost reduction by scaling up leg production and automatization of module assembling as well as verifying the module long-term stability in field tests.

At Fraunhofer IPM a half-automated pilot line (fig. 1) for thermoelectric module fabrication was installed in the beginning of 2016. Fraunhofer IPM fabricated successfully more than 200 identically constructed thermoelectric modules using half-Heusler compounds produced in kg-batches. In this presentation experimental data on the modules' performances are shown and compared with handmade thermoelectric modules. Further data regarding reproducibility in modules' properties like internal resistance, power outputs as well as size accuracy are discussed. In addition, results of long term stability tests are presented.

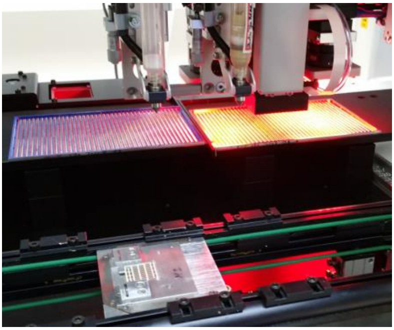

Figure 1: Half-automated thermoelectric module fabrication.

PC1.16

Flexible thermoelectric generators: from modelling, a roadmap towards applications

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Abstract

The integration of the Internet of Things into smart grids has been recognized of primary importance for today society to pursue a sustainable supply of energy in the next future, addressing the needs of a sustainable exploitation of delocalized and renewable energy sources to power the sensors and the actuators the networks are made of. Among the variety of energy conversion technologies, thermoelectric is expected to play a decisive role due to its capability of harvesting energy at the microscale, in the dark. In this framework, flexible devices based on conducting polymers are studied with the aim to extend the potential applications of thermoelectrics to all those ones not viable by the present technology based on rigid architectures. In this contribution, a dedicated study, conducted by means of an appositely derived model, is carried on in order to identify strengths and limitations of the technology based on flexible materials. Depending on the operative conditions, such as external temperature difference and thermal coupling with the environment, the study identifies a minimum in the thermocouples thermoelectric properties needed to address a series of applications, thus paving the way towards practical implementation of flexible devices in everyday life. Some insights about an effective large area fabrication method will be also given.

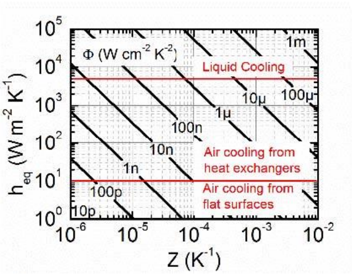

Figure 1: Thermoelectric efficiency factor Φ as a function of the thermocouple figure of merit Z and of the equivalent heat transfer coefficient heq. The graph distinguishes among three different types of thermal coupling with the environment at the cold side.

PC1.17

Thermoelectric heat pump for space applications

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Abstract

Reduction of energy consumption on manned space stations is an important and vital task. A major electric energy consumer on such objects is water regeneration system for cosmonauts based on distillation, owing to which it consumes 0.5 – 1 kW of electric energy. This consumption can be reduced by thermoelectric heat pumps in heating mode. In this context, it is clear that they must possess possibly greater heating coefficient. In Ref. [1] it reaches the value of 2.2, and in [2] – 2.4.

The purpose of this paper is further increase of this parameter. Such increase is achieved by using in the heat pump design of various thermoelectric modules with optimal characteristics based on the thermal conditions of their operation in the design. A search for parameters of each module is a complicated multi-parameter problem that was solved by computer methods of object-oriented simulation. It was established that with the number of various modules greater than 6-10, heating coefficient is saturated and reaches ultimate value 3.2 for the presently attained level of thermoelectric materials. However, due to the use of a large number of various modules, the heat pump design on the whole is complicated. It was established that with the use of two different groups of thermoelectric modules heating coefficient increases from 2.4 to 2.85, with the use of four groups - to 3. Further increase in the number of groups results in minor heating coefficient increase.

The results obtained were experimentally proved on a heat pump comprising 2 groups of 40 modules. The achieved value of heating coefficient was 2.85 at thermal power 1 kW and electric power consumption 350 W, which yields 19 % of additional electric energy saving on board the space stations as compared to counterpart [2].

References:

[1] L.R. Erickson, E.K. Ungar, Vapor Compression and Thermoelectric Heat Pumps for a Cascade Distillation Subsystem: Design and Experiment, *AIAA Space 2013 Conference and Exposition, San Diego, CA, United States,* 10-12 Sep. 2013.

[2] V.G. Rifert, L.I. Anatychuk *et al.*, Development and Test of Water Regeneration System from Liquid Biowaste on Board Piloted Space Vehicles with the Use of Thermoelectric Heat Pump, *J.Thermoelectricity* 2 (2011) 63 – 74.

C2. Applications (general, automotive, industrial)

PC2.1

Thermoelectric applications for home use: thermostat and green barbecue 2.0

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Abstract

This contribution presents two thermoelectric applications for home use. One is an energy harvesting system (EHS) at a heating to supply an electronic thermostat valve, see Fig. 1 left. The other is the revised green barbecue from [1], see Fig. 1 right. In the case of the former one, the temperature difference between radiator surface and ambient temperature is used to produce electrical energy and supply the electronic thermostat valve. The green barbecue 2.0 is a thermoelectric EHS, which converts the thermal energy from a fire to electrical energy. Hereby, it is possible to load a mobile phone, hear music or use a 12 V vehicle plug, beside the operation of the cooling fans. Due to the different temperature levels in either cases, Peltier elements or thermoelectric generators are used for power production.

The development of both systems will be described in this contribution. Measurement data are recorded, during the winter period of 2015/2016 for the thermostat and during different barbecues for the green barbecue, and will be presented. Moreover, simulation models for both applications are done in Modelica®/Dymola® and will be compared with the real data. Thus, potential for improvement can be identified and possible improvement opportunities will be addressed.

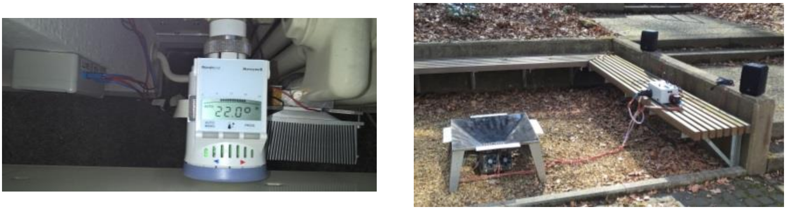

Figure 1: Thermoelectric applications; left: electronic thermostat valve, right: green barbecue

References:

[1] M. Nesarajah, G. Frey, *Energy Harvesting from Open Fireplaces*, 2nd International Congress on Energy Efficiency and Energy Related Materials, Oludeniz, Turkey, Oct. 2014; in: A.Y. Oral et al. (Eds.): 2nd International Congress on Energy Efficiency and Energy Related Materials (ENEFM2014), Springer Proceedings in Energy, pp. 525-531, 2015.

PC2.2

Thermoelectric cooling of electronic systems

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Abstract

Modern electronic industries are facing serious technical challenges to deal with the thermal management of their high performance devices. Traditional cooling approaches are not capable of sufficiently cooling those devices, whereas like most of the emerging techniques [1-2], thermoelectric coolers [3] show promises in cooling them. An electrical cooler which creates heat flux between the junctions of two different types of semiconductors through the Peltier effect, is called thermoelectric cooler (TEC). Fig.1 shows the cooling concept of TEC, which transfers heat from one side of the device to the other with consumption of electrical energy. Due to simple working principle, TECs are popular in many applications.

TECs are also compact, highly reliable, environmental friendly with no moving parts and offer great potential to enhance the cooling rate of electronic module packages and other devices [4]. TECs can also be integrated into electronic packages for their hotspots cooling [5]. Some components in electrical systems and computer such as microprocessors and power amplifiers are cooled by this cooling technique. In this paper, an overview of this cooling technique in cooling electronic devices and systems will be presented.

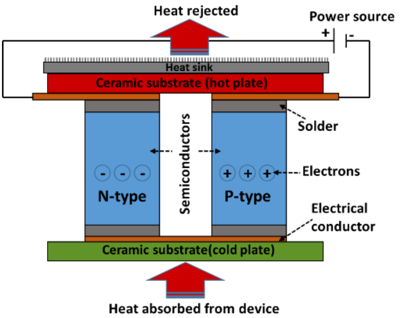

Figure 1: Thermoelectric cooling concept.

References:

[1] Y.F. Maydanik, S.V. Vershinin, M.A. Korukov, J.M. Ochterbeck, Miniature loop heat pipes-a promising means for electronics cooling, *IEEE Trans. Compon. Pack. Technol*. 28 (2005) 290-296.
[2] Y. Wei, Y.K. Joshi, Stacked microchannel heat sinks for liquid cooling of microelectronic components, *J. Elect. Pack.* 126 (2004) 60-66.
[3] R.E. Simons, Application of thermoelectric coolers for module cooling enhancement, *Elect. Cooling* 2000.
[4] R.E. Simons, R.C. Chu, Application of thermoelectric cooling to electronic equipment: A review and analysis, *Proc. 16th Ann. IEE Semiconductor Thermal Measurement and Management Symp.*, USA. 2000. pp.1-9.
[5] W. Seifert, V. Pluschke, N.F. Hinsche, Thermoelectric cooler concepts and the limit for maximum cooling, J. Phys. Condens. Matt. 26 (2014) 255803.

PC2.3

Theoretical investigation of a novel thermoelectric laundry dryer concept

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Abstract

The environmental impact of conventional heat pump dryers lies, apart from its energy consumption, in the use of a noxious refrigerant. By utilizing a thermoelectric heat pump laundry dryer, a refrigerant-free heat pump process is conducted making especially the disposal of a laundry dryer more convenient. Moreover, the drying process is more efficient compared to a conventional condensation dryer as both the hot and cold side of the thermoelectric heat exchanger are used in the process.

A novel cycle is introduced that combines thermoelectric heat pumping and air cooling by means of ambient air (Fig. 1). This cycle is at first theoretically compared with the two conventional cycles of a heat pump dryer and a condensation dryer. Furthermore, a comprehensive system model is developed to evaluate the performance of such a dryer. Within the fully transient model temperature dependent material properties, contact resistances as well as thermal and electrical resistances are taken into account. The performance of the thermoelectric heat exchanger is analysed and significant influencing variables are identified. Simulation results are compared with validated simulation results of a condensation and heat pump dryer. It is shown that the energy consumption of a thermoelectric heat-pump based tumble dryer lies between the two conventional dryers and thus can be seen as a promising technology.

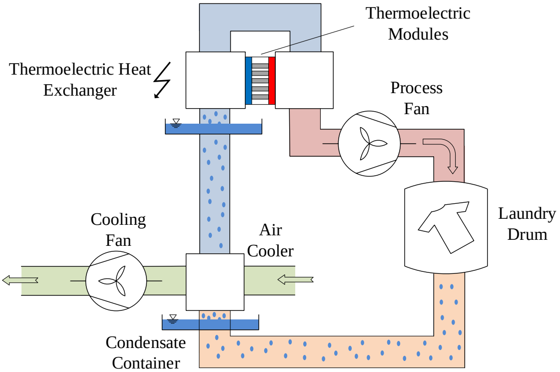

Figure 1: The thermoelectric laundry dryer combines the characteristics of a heat pump dryer and a condensation dryer.

PC2.4

Effective use of thermal energy at both hot and cold side of thermoelectric module for developing efficient water distillation system

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Abstract

An efficient water distillation system has been designed and constructed to produce drinkable water employing a thermoelectric module. The unique design of this system is to use the heat from hot side of the thermoelectric module for water evaporation and the cold side for vapour condensation. This novel design significantly reduces energy consumption and improves the system performance. The results of experiments show that the average water production is 28.49 mL/h with the energy consumption of 0.0324 kWh. The results also show that a maximum temperature difference between the hot and cold side of the thermoelectric module is 42.25 ^{o}C and the increase in water and water-vapour temperatures were 26.35 ^{o}C and 8.43 ^{o}C respectively.

PC2.5

Fabrication and characterization of single pair thermoelectric generator of Bi_2Te_3 using silver sintering technology

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[2]*Laboratory for Emerging Nanometrology (LENA), Braunschweig, Germany*
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Abstract

Silver powder sintering-based joining technology was proposed to assemble thermoelectric generators (TEGs) designed to work under elevated temperatures [1]. Commercial Bi_2Te_3 pellets were employed, on which nickel was deposited electroless for 30, 60, and 90 minutes, respectively, to serve as an anti-diffusion barrier between Ag and Bi_2Te_3. The impact of different fabrication conditions (i.e. sintering temperatures from 210 to 265°C and pressures from 5 to 7 MPa, respectively) on the properties of single-pair TEGs was investigated. We found lowest internal resistances between 0.1 and 0.2 Ω (Fig.1(a)) at a temperature of 265°C and pressures of 5 to 6 MPa. A specific contact resistance of $(0.71\text{-}6.17) \times 10^{-4}$ Ωcm^2 was calculated to, which is better by about one order of magnitude with respect to our previous work [1]. The TEGs were operated at temperatures of cold and hot sides risen from room temperature to 60°C and 250°C, respectively. Thermal power was measured ranging from 0.25 to 0.32 mV/K. With TEGs sintered at 6 MPa and 265°C long-term operation tests were performed at temperature gradients across the TEG around 190°C for 216 hours. The Seebeck power remained constant between 0.25 and 0.28 mV/K (Fig.1(b)) with the TEGs comprising the thickest nickel layer (90 min) showing distinctly the lower values. Simultaneously, the internal resistance rised by about 0.4 Ω for the TEGs with the thinnest nickel layer (30 min), while the other two TEGs did not yet show any increase.

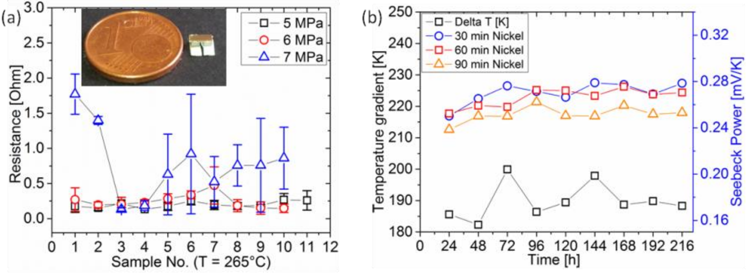

Figure 1: (a) Internal resistance of TEGs fabricated at different processing pressures and 265°C and (b) Seebeck power of TEGs (6 MPa, 265°C) with different nickel diffusion-barrier layers at a temperature gradient about 190°C operated over more than 200 h.

References:

[1] A. Stranz, A. Waag, E. Peiner, Investigation of Thermoelectric Parameters of Bi_2Te_3: TEGs Assembled using Pressure-Assisted Silver Powder Sintering-Based Joining Technology, *Journal of Electronic Materials* 44 (2015) 2055-2060.

PC2.6

Thermoelectric material library via laser melting

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Abstract

Discovering new materials with desired properties has been a fundamental subject, and yet it has been a challenging issue. One might approach through material informatics—surveying a suitable combination of elements for a certain crystal structure based on the density functional theory—and most of the others have been searching the material through the time-consuming experiment, which is partly because of the difficulty in predicting the scattering parameter by the theory. Here we demonstrate a rapid synthesis of thermoelectric compounds via laser melting to meet with a demand from experimentalists [1]. It has been proved that the laser melting is a versatile synthetic route enabling to form various compounds including Bi-Sb and Mn-Si binary systems, Mn-Al-Si ternary system, rare-earth doped $SrTiO_3$ and so on. Those compounds were synthesized using a continuous laser diode with a 940 nm light source. Owing to the high power density of the laser (60 W/mm^2 at the maximum), the precursor powders immediately melted and reacted when irradiated by the laser. Subsequent quenching led to the stabilization of high temperature phases in the resultant compounds. Any compositional differences between the laser treated compounds and the starting materials were negligible. The thermoelectric properties varied according to the composition, as expected, demonstrating the feasibility of laser melting as a rapid synthesis tool for thermoelectric compounds. Several advantages and limitations of the synthesis conditions are also discussed.

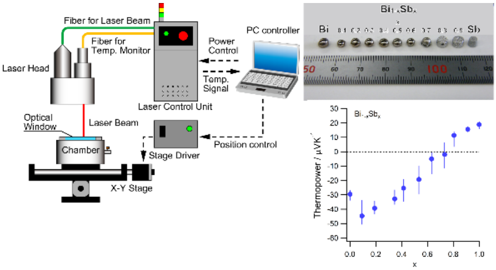

Figure 1: The system of laser melting and an example of thermoelectric material library.

References:

[1] Y. Kinemuchi, M. Mikami, I. Terasaki and W. Shin, Rapid synthesis of thermoelectric compounds by laser melting, *Mater. Des.*, (2016) DOI:10.1016/j.matdes.2016.05.093.

Acknowledgment: This work is based on results obtained from the Future Pioneering Program "Thermal management materials and technology" commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

PC2.7

Development of a Thermoelectric heat booster for thermal energy storage in a concentrated PV CHP system

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Abstract

This work presents the experimental results obtained from the development of a novel thermoelectric heat amplifier to boost the thermal energy supplied to a Phase Change Material (PCM) energy storage system. Thermal energy is captured from a CCPC (crossed compound parabolic concentrator) reflector system for photovoltaic solar cells with an integrated heat exchanger. This thermal energy can be used to recharge a PCM based heat battery using a SAT (salt-hydrate) solution.

The PCM heat battery stores thermal energy in the liquid phase and when triggered this energy is released as the material changes to a solid state. The heat battery can be recharged by circulating water above the PCM‘s melting temperature. This enables thermal energy captured during daylight hours to be stored in such a heat battery for release at any desired time.

In order to maintain high performance of the PV system the fluid flowing through the cell heat exchanger is kept close to ambient temperature. To ensure the fluid temperature is at the required temperature to recharge the heat battery, a heat amplifier is required. The heat amplifier considered for this experimental system consists of several solid-state Thermoelectric heat pumps operated at very high CoP, heat exchangers and controlling electronics. The aim of such a heat amplifier is to boost the temperature and thermal energy of the water to a PCM based heat battery to ensure the fluid is above the PCM melt temperature whilst concurrently returning the coolant to the PV system at a low temperature.

PC2.8

Design of flexible thermoelectric generator as human body sensor

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Abstract

Flexible thermoelctric generator (TEG) became an attractive technology for its widely used especially for curved surfaces applications. This study aims an optimal design of a flexible TEG for human body application. The flexible TEG is part of a sensor and supplies required electrical power for data transmission by the sensor.

The TEG module includes ink based thermoelements made of nano-carbon bismuth telluride materials. One flexible fin conducts the body heat to the TEG module and there are two fins that exchange the heat from the cold side of the TEG to the ambient. The proposed design is supposed to produce 10 μV to feed the used sensor in the thermoelectric system. In this design, the effect of ambient conditions, such as temperature and heat transfer coefficient due to natural convection, and also dimension of the TEG thermoelements on the power generation are studied.

PC2.9

Flexible thermoelectric nanogenerators: from numerical simulations to device fabrication

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Abstract

U.S. Energy Information Agency recently released that the world energy consumption will grow by 56% between 2010 and 2040, from 524 to 820 quadrillion British thermal units [1]. This growth will come from non-Organization for Economic Cooperation and Developing Countries, where demand is driven by strong economic growth [1]. Thus EU Heads of State and Government set a series of demanding climate and energy targets to be reached by 2020 to increase the use of renewable energy sources, thus reducing the consumption of primary energy sources, leading to a reduction on CO_2 emissions [2]. Up to now, the way the world's overall energy resources have been consumed and transformed in other more practical energy forms is mostly via thermal mechanism. However, the majority of the thermal energy produced is rejected to the atmosphere and oceans as waste heat (~60%). Thermoelectric generators (TEGs) appear as an attractive alternative to transform part of this wasted energy into electricity, namely in the temperature range RT–600°C [3].

In this work, a prototype of a flexible TEG based on n-type Bi_2Te_3 is presented, where the fabrication procedures and output power of the device under different conditions are analysed and discussed [4]. Moreover, through the use of the COMSOL Multiphysics software, the thermoelectric device is numerically simulated and the obtained results are compared with the achieved experimental outputs. Finally, new routes for the devices optimization will be discussed, namely concerning geometrical parameters [5].

References:

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[4] P. Resende, A.M. Pereira, Flexible N-type Bi_2Te_3 based Thermoelectric Generator for Small Scale Energy Harvesting, to be submitted to ACS Energy Letters.

[5] S. Ferreira-Teixeira, A.M. Pereira, Geometrical optimization of a thermoelectric device: numerical simulations, to be submitted to Applied Energy.

PC2.10

Design of a hybrid household thermoelectric refrigerator and its efficiency optimization

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Abstract

This research presents the development of a high efficiency Hybrid Household Thermoelectric Refrigerator (HHTR), which combines the high efficiency of vapour compression systems and the optimum temperature control of Thermoelectric coolers (TECs). The HHTR has three compartments: the classical cooler and freezer and the novel compartment provided with the thermoelectric technology. The latter is designed to reduce to a minimum the oscillation of the inner temperature due to the compressor cycles, obtaining a constant temperature (with a maximum oscillation of ±0.2ºC) and thus, a better conservation of the food.

A computational model has been developed to design and optimize this application, allowing to simulate the complete hybrid refrigerator (vapor compression - thermoelectricity). Three configurations have been studied: the first is the classical one with the thermoelectric modules expelling the heat to the ambient, and the two others are cascades configurations expelling the heat to the cooler compartment (config. II) and to the freezer compartment (config. III) as Figure 1 shows.

Several prototypes were built showing the third configuration as the optimal HHTR. The electric power consumption of the TEC is only 1.1 W while the total consumption of the refrigerator is 45.2 W (1.11 kWh/day), which is low enough to be included into energy efficiency class A, according to European rules and regulations. Thus, the combination of vapour compression and thermoelectrics is an attractive alternative to current domestic refrigerators. This application has been protected under patent by Bosch-Siemens.

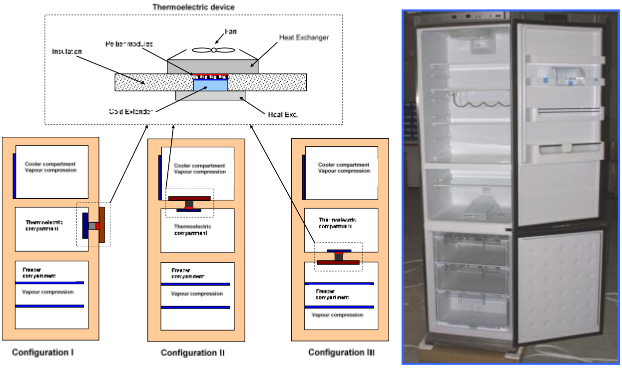

Figure 1: Configurations of the thermoelectric device in the hybrid refrigerator.

PC2.11

Tests of a combined heat and power thermoelectric generator for autonomous performing cooking stoves

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Abstract

According to the International Energy Agency, deployment of advanced biomass cook stoves and additional off-grid biomass electricity supply in developing countries are key measures to improve the current situation and achieve universal access to clean energy facilities by 2030. In order to reduce wood consumption, emissions of carbon dioxide and black fumes, companies develop efficient biomass cooking stoves combining space heating, production of domestic hot water and cooking. Due to the high efficiency of these stoves and as almost all the produced heat is used, the temperature of the smoke is quite low, often less than 100°C. In this case, chimneys are not able to provide a good ventilation to the outside atmosphere and an electrical extractor must be added. An electrical generator is necessary to operate this extractor. This paper presents a combined heat and power thermoelectric generator (TEG) which was built to power a performing cooking stove. The design of the TEG is firstly presented. The TEG include a maximum power point tracking DC-DC convertor which allows to store electricity in a small battery and to directly power the extractor. Secondly the results of a TE module ageing test representing approximately 15 years of stove using are presented. Afterwards, several different trials (quality of wood, duration of cooking) of the TEG incorporated into the cooking stove are presented. All these results show that this thermoelectric solution allows to use these efficient stoves in locations without electricity and even some extra power can be used for mobile phone charging or for lighting.

PC2.12

Advantages of water-cooled Peltier current leads for HTS devices

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Abstract

Efficiency of high-temperature superconducting (HTS) devices can be increased by reducing the heat leak into the cold zone through the current leads. There are many models of cryogenic current leads; however, the Wiedemann-Franz law severely restricts the possibility of their optimization. According to our experience, the qualitative improvement of the characteristics of the current lead can be achieved using Peltier elements as a heat pump, which prevents the penetration of heat inside the HTS device [1]. Test samples of Peltier current leads (PCLs) were mounted on the experimental HTS DC power transmission lines [2, 3]. Currently we are studying the possibility of increasing the PCL efficiency using additional water cooling of the hot side of the elements (Fig. 1). The results of the experiments will be reported.

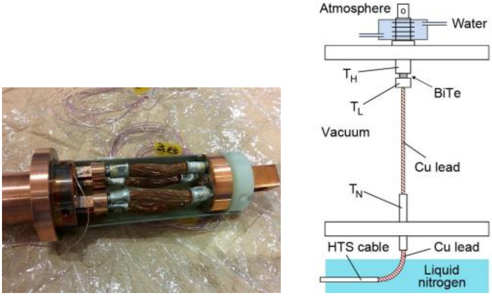

Figure 1: Photo of the inner part of 4-element type PCL (left). Sketch of PCL (right).

References:

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[2] M. Hamabe, T. Fujii, I. Yamamoto, A. Sasaki et al., Recent progress of experiment on DC superconducting power transmission line in Chubu University, *IEEE Trans. Appl. Supercond.* 19 (2009) 1778-1781.

[3] S. Yamaguchi, H. Koshizuka, K. Hayashi, T. Sawamura, Concept and design of 500 meter and 1000 meter DC superconducting power cables in Ishikari, Japan, *IEEE Trans. Appl. Supercond.* 25 (2015) 5402504.

PC2.13

Reliability prediction of thermoelectric modules for power generation applications

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Abstract

Thermoelectric module (TEM) emits heat and absorb at each side simultaneously. It occurs temperature gradient which causes expansion and contraction of the substrate. And finally it stresses the internal parts of the thermoelectric device and soldering. It means that structure of TEM is vulnerable in an aspect of reliability but research on reliability of TEM was not performed a lot. Recently, the more the utilization of thermoelectric power generators grows, the more the needs for reliability prediction of TEM are increasing [1].

In this study, reliability testing system was developed to evaluate fatigue life of TEM under thermal cycling loads. It consists of power supplier, cooling block, chiller, load cell, screw and thermocouples. The thermal cycling loads were applied to the upper side of TEM controlling the lower side temperature of TEM by 30 ℃.

During the reliability testing, the changes of the electrical resistance and ZT (figure of merit) of TEM were measured. As a result, temperature difference – fatigue life relationship for TEM was obtained. Thermal stress – fatigue life relationship can be acquired through thermoelectric analysis and stress analysis by using finite element method. These procedures of reliability prediction on TEM is expected to be useful in the commercialization of thermoelectric power generators.

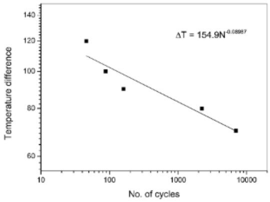

Figure 1: Temperature difference – fatigue life relationship.

References:

[1] H.-S. Choi, W.-S. Seo, D.-K. Choi, Prediction of Reliability on Thermoelectric Module through Accelerated Life Test and Physics-of-Failure, *Electronic Materials Letters* 7 (2011) 271-275.

PC2.14

Highly integrated Thermoelectric Generators for application in hybrid cars considering the WLTC

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Abstract

The limits imposed on CO_2 emissions decrease every year while the challenge to reduce emissions in the automotive sector continues to increase with the introduction of more dynamic test cycles as the Worldwide harmonized Light duty driving Test Cycle (WLTC) [1]. Therefore an increase of the motor vehicles efficiency is needed. A promising technology is the use of thermoelectric generators (TEG) to convert the waste heat into electrical power. To maximize the reduction of CO_2 emissions the influence of the TEG on the overall system has to be considered. The DLR Institute of Vehicle Concepts (DLR-FK) created a holistic method for thermodynamic dimensioning of the TEG. According to the results obtained using this method weight had the biggest negative influence on the system. Thus the aim is to significantly raise the power density. Studies have shown higher potential in hybrid cars than in conventional ones due to the narrow range of temperatures and mass flows [2]. The optimisation is done under WLTC conditions for use in hybrid cars in order to be attractive for manufacturers. The resulting highly integrated TEG-design will be presented. With >50W/kg and >130W/dm^3 it has the actual world highest TEG power density for automotive application. To validate the results of the CFD-simulation measurements were done with a functional prototype (Fig. 1).

Figure 1: Functional prototype of the highly integrated TEG for use in hybrid cars.

References:

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PC2.15

Low energy passenger comfort systems based on the Joule and Peltier effects (JOSPEL project)

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Abstract

The aim of JOSPEL project is the development of a novel energy efficient air conditioning system for the optimization of interior temperature control management in electrical vehicles.

This is made through an integrated approach that combines the application of the thermoelectric Joule and Peltier effects, the development of an efficient insulation of the vehicle interior, the energy recovery from heat zones, battery life increase duration enhancement as a side effect of thermal management, battery consumption reduction by Peltier cooling integration, innovative automated and eco-driving strategies and the electronic control of power flows.

The main objective is the reduction of at least 50% of energy used for passenger comfort (<1,250W) and at least 30% for component cooling in extreme conditions with reference to electric vehicles currently on the market.

PC2.16

Thermoelectric devices for the diagnostics of diseases, oncologic included

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Abstract

As a result of research pursued by Institute of Thermoelectricity (Ukraine) and a number of medical institutions it has been established that information on temperature and heat flux distribution on the surface of human body can be an efficient means for creation of novel diagnostic approaches to various diseases, namely ascite, pancreonecrosis, nephritis, rheumatoid arthritis, etc. Of particular interest is the possibility of using such measurements for early diagnostics of oncologic diseases.

The paper presents the results of research on the requirements to temperature and heat flux sensors with such measurements. It was established that the use of conventional heat metering sensors can lead to essential errors due to the impact of phase transition processes on the skin surface, change in ambient temperature and sensor attitude in space. To minimize these effects, special heat flux meters have been developed [1] allowing to separate the drift of heat from skin surface due to convective heat exchange and phase transition. The paper describes the results of research on computer design and optimization of such sensors whose operating principle is based on transfer of heat of phase transition processes from skin surface to the surface of heat metering sensor contacting to ambient air. It was established that in this case the error of heat flux measurement can be reduced by a factor of 2-10.

Based on this research, heat flux sensors have been developed that simultaneously determine the temperature on skin surface through use of the temperature dependence of the internal resistance of sensors. These sensors were used to create automated measuring instruments with computer control, read-out and processing of information. The instruments were created both with one temperature and heat flux sensor [2], for instance, for detection of postsurgical inflammatory processes, and multi-element [3] – to detect the anomalies of temperature and heat flux distribution for the diagnostics of various internal organs.

References:

[1] L.I. Anatychuk, R.R. Kobylianskyi, *Patent of Ukraine 72032*, InCl H01L 35/00, Thermoelectric Sensor for Temperature and Heat Flux Measurement, 2012.

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PC2.17

Computer simulation and real possibilities of using thermoelectric generators for cars

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Abstract

The paper presents a thermodynamic description of thermoelectric generator (TEG) using the exhaust heat of internal combustion engine. For these investigations a physical model of TEG as part of a car was considered and computer simulation on its basis was made. The purpose of the model is to describe energy distribution in a car with TEG and the effect of different factors on this distribution.

The effect of the following factors on TEG efficiency was analyzed: the necessity of heat removal from TEG, the effect of exhaust system, the necessity of TEG voltage stabilization, the expenditures on additional car weight due to TEG, the effect of motion modes (steady-state and dynamic car motion modes). It was established that of the above factors the effect of intensity of heat removal from TEG should be optimized. With the aid of computer simulation the heat removal system was optimized.

The following results were obtained:

1. TEG-inlet maximum hot temperature of modules is approximately half the temperature of hot gases entering the generator. It means that for TEG one should use thermoelectric material with operating temperatures: ~300-400$^{\text{O}}$C for petrol engines and 200-300$^{\text{O}}$C for diesel engines. TEG power for the best known thermoelectric materials is ~1 – 1.5% of engine power. The use of multi-stage TEG with different operating temperature of stages can improve this parameter to 2.25%.
2. The expenditures on heat removal from TEG are 15-25% of TEG power and depend on the engine type and ambient temperature. In the operation of TEG for a car preference should be given to climatic conditions with reduced ambient temperature.
3. The expenditures due to TEG weight are minor.
4. For the NEDC the average power of TEG will make ~25% of maximum TEG power. For the extra urban cycle it will make ~60%.

The obtained results are governing in the calculation of economic and technical parameters of TEG for a car.

Author Index

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