9th European Conference on Thermoelectrics

September 28-30, 2011, Thessaloniki Greece

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Prof. David Michael Rowe
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Prof. Mas Subramanian Ph.D.
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Welcome to ECT2011,

It is our great pleasure to welcome you all in Thessaloniki to the 9th European Conference on Thermoelectrics (ECT2011). The ECT2011 is the 9th in the series of European Conferences on Thermoelectrics (ECT) which are promoted by the European Thermoelectric Society. Its aim is to provide a forum for exchange of information and achievements in the field of Thermoelectrics (TE), and to enhance the communication between research institutions and industries for promotion of TE applications.

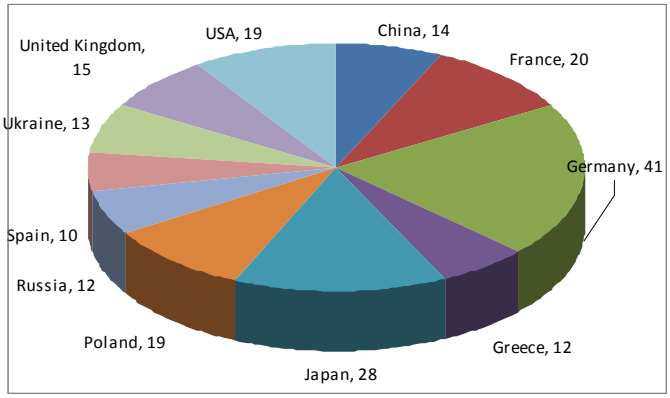
The ECT2011 invites experts, scientists and engineers from Research and Industry all around Europe and abroad to discuss the state-of-the-art of the technology, latest advances in material research, device design and market opportunities.

The scope of ECT2011 covers a wide range of research that bridges the gap between basic science and applications on thermoelectrics:

- *Theory:* theoretical studies of bulk materials, nanoscale and low-dimensional induced effects, novel concepts and related physical phenomena
- *Thermoelectric Materials:* Chalcogenides, skutterudites, antimonides, oxides, silicides & Heusler compounds, clathrates & zintl compounds, novel materials
- *Measurement & Characterization*: microstructure, properties
- *Thermoelectric Modules:* design and fabrication, thin film devices, device performance
- *System & Industrial Applications:* cooling applications, automotive applications, generator applications, other waste heat recovery, other industrial aspects

ECT2011 had a tremendous response by the scientific community: we have received a total of 243 abstracts for oral and poster presentations, a number that was beyond our expectations, and for this reason we want to thank every participant individually! The number of received abstracts ranks ECT2011 as one of the bigger events in Thrmoelectrics for 2011 and it underscores the rapidly rising interest in the field.

Out of the 243 abstracts, 12 were the presentations of invited speakers and only 10 were withdrawn by their authors. 34 countries have contributed to the abstracts, with 288 individual authors. Though ECT is a European Conference, we have received abstracts from many countries beyond Europe, like China, Japan, Korea, Taiwan, Israel, USA etc. Germany holds the lead with 41 contributions in abstracts, followed by Japan (28), France (20), USA (19) and Poland (19). The 10 most contributing countries are shown in figure bellow.



Descriptive chart of the 10 most contributing countries in ECT2011

TE materials lead in the distribution of abstracts, by 59%. In the figure bellow you may find the distribution of the abstracts in the various fields. This outlines the current dynamics on the field of thermoelectrics; still much of the effort is focused on the materials side as opposed to TE modules and industrial applications. The large number of received abstracts, and the limited time of the conference days, forced us to organize the conference in two parallel sessions; one on TE materials and another on the other fields.

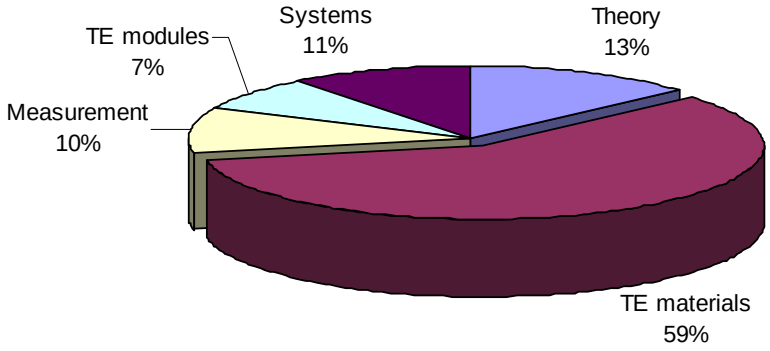


Chart of abstracts distribution in TE fields of application

Papers presented in ECT2011 are published:

- In the Conference Proceeding CD, which you may find in your bag.
- In a special volume of the American Institute of Physics (AIP) Conference Series. AIP Conference Proceedings is indexed in the major databases such as Web of Knowledge (ISI) and Scopus and one year free access will be given to all registered participants
- Also, selected papers will be published in a special issue of Journal of Solid State Chemistry (JSSC, impact factor 2009: 2.34). Authors of selected papers will be invited to extend their initial 4-page manuscript into a regular article, consistent with the standards of JSSC. These papers will be subjected to regular blind peer review.

We feel confident that you will enjoy ECT2011 both scientifically and socially and that it will also be a wonderful chance to meet old friends and make new ones, and that the conference will be a memorable event. We wish you a fruitful and stimulating scientific and touristic experience during your presence in Thessaloniki.

On behalf of the Organizing Committee,
Professor K.M. Paraskevopoulos, (AUTH, GRE) Chairman of ECT2011
Professor M.G. Kanatzidis (Northwestern, USA) Co-Chairman of ECT2011

INVITED
PRESENTATIONS

Some issues of history and prospects of thermoelectricity

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Keywords: *system & industrial applications*

Abstract:
This contribution analyzes approaches that led to discovery of thermoelectricity. They are compared to discoveries of new scientific and technical lines. A conclusion is made on the partial character of physical approaches in the discovery of thermoelectricity. Generalizations in the description of thermoelectric power conversion are considered that are based on the induction of thermoelectric currents. Consequences from this approach are analyzed and relevant lines in the development of thermoelectric power conversion are formulated.

History and progress in thermoelectric material science is analyzed. The data on the boundaries of thermoelectric figure of merit of materials – crystalline, powder, film, and nanostructured is given. The prospects of computer material science are estimated.

Thermoelectric restrictions imposed on the application areas of thermoelectric generators and, accordingly, the ensuing rational lines of their practical applications are considered. The possibilities of thermogenerator contribution to “green” technologies, in particular, to waste heat recovery from industry and heat engines are analyzed. Applications of photo- and thermoelectric methods in the renewable electric power sources are compared. The data on competitiveness of thermal generators with respect to chemical current sources is presented.

The data on the rational application areas of thermoelectric cooling is presented. Tellurium problem and the ways of tackling this issue are considered.

Attention is focused on the efficiency of computer methods for designing thermoelectric devices.

Particular attention is paid to prospects of thermoelectricity application in measuring technique and metrology. Conclusions are given that follow from the information-energy theory for thermoelectric measuring systems. Attention is drawn to the decisive role of using semiconductor materials in thermoelectric measuring instruments and the increasing role of measuring technique in future applications of thermoelectricity.

Information is presented on the organizations and specialists engaged in thermoelectricity and on the directions of their works. Attention is focused on the development of the scope of works on thermoelectricity, on the disproportions in the research and applications and the necessity of purposeful training of specialists in thermoelectricity for its more successful development.

High Performance Nanostructured Thermoelectric Materials

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Keywords: *Thermoelectric materials*

Abstract:
It is now amply clear that comprehensive and stable energy strategy would require commensurate attention to all three legs of the "energy stool"; supply (sources), demand (efficiency) and storage/transport (delivery). Further, within the "energy supply" side, a portfolio approach comprising appropriate supply sources is imperative to cater to diverse energy needs; ranging from widely deployable to niche' thematic applications. In this context, thermoelectric materials, that convert waste thermal energy into useful electrical energy, have an important thematic role to play.

The efficacy and efficiency of thermoelectrics is reflected in the figure of merit ZT, which is directly proportional to the power factor (comprising electrical conductivity and Sebeck coefficient) and inversely proportional to thermal conductivity (comprising carrier and lattice contributions). The recent emergence of nanostructured thermoelectrics has ushered in a new era for bulk thermoelectrics, which show considerable promise to enhance the "contra-indicating" parameters of high electrical conductivity and low thermal conductivity. This is achieved by introducing nanostructures in bulk thermoelectric host materials to significantly reduce lattice thermal conductivity via effective scattering of heat carrying phonon through hierarchical architecture of nanostructured thermoelectrics (nThEs)

The presentation will cover recent developments, current research in our EFRC and future prospects for high performance bulk nThEs. Systems based on lead chalcogenides (e.g., PbTe, PbSe) present key science challenges with promising properties and are given particular emphasis. We have achieved excellent control of synthesis and crystal growth of such materials resulting in record enhancements in the figure of merit. These enhancements derive from very large reductions in lattice thermal conductivity possible with nanostructuring. We have experimentally realized concurrent synergistic effect of phonon blocking and charge transmission via the endotaxial placement of nanocrystals in thermoelectric material host.

In particular, we have shown that the enhanced performance is due nanostructuring of thermoelectric host matrix, with a compelling influence of hierarchy of length-scales associated with nThEs. Extensive characterization by scanning transmission, analytical, transmission and high resolution transmission electron microscopy (STEM, AEM, TEM and HRTEM, Atom Probe respectively) has elucidated in exquisite details the nature of nanostructure-matrix interfaces, associated plastic and coherency elastic strain and chemical partitioning or interdiffusion in nThEs.

The presentation will highlight the considerable potential and realistic prospects for enhanced performance for conversion of waste energy into useful electrical energy of bulk nThEs. The presentation will also outline possible future strategies for enhancing the thermoelectric figure of merit of bulk nThEs.

TiS_2-based Layer Sulfides for Thermoelectrics

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Keywords: *titanium disulfide, layer sulfide, thermoelectric, inorganic/organic superlattice*

Abstract:
Layered titanium disulfide has been reported to show a high thermoelectric power factor due to its two-dimensional electronic state. However, its high thermal conductivity makes its conversion efficiency too low for practical applications. We attempted to intercalate a layer of BiS, SnS or PbS into the van der Waals gap of the TiS_2 layers to form natural superlattices with general formula $(MS)_{1+x}(TiS_2)_n$ (M=Bi, Sn, Pb; n=1, 2) and the lattice thermal conductivity was significantly reduced by intercalation. Sound velocity measurement indicated that the chemical bond between the hetero-layers was greatly weakened by intercalation leading to the ultra-low lattice thermal conductivity.

HRTEM observations revealed the lattice disorder increased in the order of Pb, Sn, Bi for $(MS)_{1+x}(TiS_2)_2$, and the lattice thermal conductivity decreased significantly with increasing disorder. In contrast, the relaxation time of the electrons is almost insensitive to the lattice disorder, suggesting that the electron transport is unaffected by the lattice disorder though the phonons are strongly scattered.

A TiS_2 single crystal can be mechanically cleaved into nanosheets which can be termed as "titanium sulfene". Seebeck coefficient increases with decreasing thickness of a nanosheet. Band structure calculations indicated the DOS near the conduction band minimum is enhanced by decreasing thickness of a nanosheet, which is beneficial for large Seebeck coefficient. These findings inspired us to construct inorganic/organic superlattices to get high *ZT* based on the two possible phenomena occurring simultaneously; electron confinement and phonon confinement in a rigid inorganic layer. Accordingly, we have been attempting to intercalate organic compounds into the van der Waals gaps in TiS_2, and we will discuss the superlattice formation to achieve high TE performance.

Calculations of electronic structure and transport properties in thermoelectrics including defects

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Keywords: *electronic structure, thermopower, KKR-CPA method, disorder*

Abstract:

We present methodology and applications of the Green function Korringa-Kohn-Rostoker technique with the coherent potential approximation (KKR-CPA) to study electronic structure and electron transport properties in illustrative thermoelectric materials as doped Mg_2(Si-Ge), PbTe, Bi-Sb, skutterudites and half-Heusler phases. A special attention will be paid to disorder effects i.e. alloying, impurity, vacancy, anti-site defects or presence of interstital elements. Such defects commonly appear in real samples and strongly affect thermoelectric properties of ordered compounds.

In this work, we show that accounting for different kind of disorder in electronic structure calculations leads to more reliable determination of Fermi surface properties, which then help to interpret specific behaviors of charge conductivity and thermopower. Based on results of KKR-CPA calculations we discuss some unusual electron transport behaviours as e.g. metal-semiconductor-metal crossovers in half-Heusler alloys, a resonant-like state of dopants in PbTe or band degeneracy in Mg_2(Si-Sn).

Acknowledgments: This work was partially supported by the FP7-NMP-2010-SMALL-4 Collaborative Project ‘‘ThermoMag’’(No. 263207).

Rattler-Seeded Nanoinclusion Formation in $In_xCo_4Sb_{12}$ Thermoelectric Skutterudites

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Keywords: *skutterudites, indium-filled, nanoinclusions*

Abstract:
This study reports the synthesis and thermoelectric properties of bulk thermoelectric nanocomposites produced from indium-filled ($In_xCo_4Sb_{12}$) skutterudites. The bulk nanocomposites exhibit marked reduction in thermal conductivity compared to nanoinclusion-free $In_xCo_4Sb_{12}$. This is the first study to provide unequivocal evidence demonstrating that the InSb nanoinclusions are seeded by some of the indium atoms diffusing *from* the icosahedral void-site. This discovery clarifies the source of the InSb nanoinclusions in high figure of merit (ZT) double and triple-filled indium-based antimonide skutterudites, and is expected to produce exceptional ZT's when applied to optimally doped indium-filled skutterudites.

Stability and Efficiency Considerations upon Development of IV-VI based Thermoelectric Alloys

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Keywords: *Thermoelectric materials*

Abstract:
Lead telluride, tin telluride and germanium telluride based alloys, are known as superior candidates for *p*-type legs in thermoelectric application for the temperatures range of 50-500^{o}C. The state of the art lead telluride and tin telluride alloys obtain slightly lower thermoelectric figure of merit values compared to GeTe accompanied with improved structural and chemical stability at the operating temperatures. The improved chemical stability is mainly due to a lower vapor pressure and thereby lower sublimation rates in PbTe and SnTe. The improved structural stability is mainly due the uni-phase cubic NaCl structure of PbTe and SnTe for the whole operating temperatures range, compared to the rhombohedral to cubic NaCl phase transition at 427^{o}C in GeTe.

Improvement of the thermoelectric performance of PbTe based alloys was recently obtained by several leading research groups all around the globe using several approaches based on optimal doping; nano-structuring for reduction of the lattice thermal conductivity; development of functionally graded materials with a desired dopant concentration profile; Fermi-level pinning effect, etc. Using these approaches both *n*- and *p*-type PbTe based alloys were prepared with maximal *ZT* values of about 1.7.

However, although *ZT* values were dramatically increased over the last years, no correspondent increase in the efficiency of practical devices was observed. Possible reasons for that are deteriorating of nano-structures at the operating temperatures, poor mechanical properties and chemical instability. Therefore, a global goal should be focused on achieving both high *ZT* and stability (mechanical, chemical and structural) characteristics.

The present communication puts forward the overall factors affect the performance of alloys based on IV-VI compounds for thermoelectric power generation applications. Several practical alloys will be examined in terms of these factors as guidelines for development of both stable and efficient thermoelectric materials.

Thermoelectrics for High Temperatures – The material Contest

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Keywords: *High temperature materials, thermoelectric modules, economic aspects*

Abstract:
The quest for methods of recycling the high amount of lost thermal energy at least partly leads to a technology that has been known for well over a hundred years: thermoelectric.

Currently, thermoelectric energy harvesting, is enjoying high popularity. It has triggered a worldwide research race in particular for materials with better conversion capabilities for high temperatures.

Thermoelectric gained large publicity due to our common goal/objective of using waste heat to feed e.g. board electronics in automobiles. Converting heat into electrical energy resorting to car's waste heat will no longer remain a vision: it was demonstrated frequently with preliminary systems. But in order to enable thermoelectric for exploiting waste heat and thus contribute to a more efficient utilization of natural resources, thermoelectric materials and high-temperature modules for high temperature differences – 500 °C or even more – are necessary.

When thermoelectrics will enter mass markets as automotive industry, additional aspects like availability, commodity prices, processability, long-term stability, large scale production (e.g. some 100 kg per batch) and environmental aspects will play a more important role. The most prominent example for economic aspects is the highly sensitive fever chart of the Tellurium price, which was under speculation due to the increasing thermoelectric market and the boom for CdTe solar panels. The environmental aspects reflect the RoHS exceptional rule until 31.12.2018 for PbTe used in thermoelectric generators for cars.

Future tasks in thermoelectrics inclusive basic research will encompass the entire value-added chain, from physical effect via technological implementation of components to the function within the system – only in this way will marketable products result. As a first order assessment of the recent and current material development it is reasonable to expect “high-temperature material” in technical ripeness within a mid-term time scale. Parallel to the progress in thermoelectric material development, increasing efforts have been started to process the new materials to modules in standard vertical design.

Thus, a survey of state-of-the-art high-temperature thermoelectric materials is presented based on thermoelectric properties, technical level, and their potential for standard device technology and system implementation.

Thermoelectrically self - powered sensor systems

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Keywords: *system & industrial applications*

Abstract:
Sensors are the eyes and ears in the service of people - especially in inaccessible areas where regular maintenance or battery replacement is extremely difficult. A solution can be the implementation of self-powered sensor networks that autonomously collect their required energy from their surroundings. After installation of the sensors they collect and transmit their data without any need for further maintenance like battery replacement.

The large progress in the development of low-power sensors, power management and radio communication combined with the availability of high efficiency thermoelectric generators opens the possibility to run an energy-autarkic sensor node with temperature gradients as low as 2K.

In this paper, three different examples of energy-autarkic sensor system driven by thermoelectric generators developed at the Fraunhofer IPM are discussed: a communicating coffee pot, a wireless environmental measurement unit as well as a structural health monitoring system for aircrafts. With the help of these examples, some theoretical aspects on the importance of the thermal impedance matching for maximization of the power output of thermoelectric generators for energy-autarkic sensor nodes are given and a simulation tool for the adaptation of the thermoelectric generators to the surroundings is introduced.

Antimony based thermoelectric materials

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Keywords: *Zn_4Sb_3, $FeSb_2$*

Abstract:
Some of the most promising thermoelectric materials contain antimony, which is an extremely flexible element with respect to chemistry and properties. $FeSb_2$ exhibits the highest power factor ever seen and the material has great potential for low temperature (< 77 K) cooling applications [1,2,3,4]. The challenge is to lower the thermal conductivity, and this can e. g. be done by synthesizing thin films. Zn_4Sb_3 is one of the cheapest thermoelectric materials known [5,6,7], and for this material recent results on new synthesis methods, nanocomposites, thin films and electronic structure calculations will be discussed.

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Thermoelectric Harvesting of Low Temperature Natural/waste Heat

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Keywords: Zn_4Sb_3, $FeSb_2$

Abstract not presented

A Bottom-Up Approach for Nanostructured Thermoelectrics

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Keywords: *Thermoelectric materials*

Abstract:
Nanostructured thermoelectric (TE) materials are currently of intense interest as they offer the potential for controlling both thermal and electronic properties due to the presence of nano-scale domains or inclusions. Ball milling, melt spinning or other "top-down" approaches are typically employed for the synthesis of these material. I will describe synthetic strategies for the preparation of bulk nanocomposite TE materials employing a two-step "bottom-up" approach whereby composition and size controlled syntheses of TE materials as nanocrystals is accomplished by facile solution based processes, followed by densification of the nanocrystals into bulk polycrystalline pellets using Spark Plasma Sintering (SPS). "Dimensional nanocomposites", with nano-scale grains, show enhanced TE properties as compared to that of the bulk. Doping of the nanocrystals prior to SPS consolidation allowed for modification of the carrier concentration of the polycrystalline nanocomposites thereby revealing an approach towards TE properties optimization. Electrical and thermal transport properties of the nanocomposites were evaluated experimentally, and modeled theoretically, in order to compare their TE properties to that of bulk materials. Device-related results will also be presented. This "bottom-up" strategy was investigated, in part, in the context of research into cost-effective, scalable, and reproducible materials processing for the preparation of nano-scale TE materials.

Automotive Thermoelectric Generators and Air Conditioner/Heaters

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Abstract:
The US Department of Energy initiated the application of thermoelectric generators (TEG's) to vehicles in 1994. This TEG was built by Hi-Z Technologies evaluated on a dynomoeter test stand then tested successfully installed on a fully loaded Heavy Duty Diesel truck on the PACCAR test track for the equivalence of 550,000 miles. Today every major automobile manufacturer is investigating thermoelectric applications. The US Department of Energy is supporting the development of production prototype TEG's with teams headed by BSST and GM to integrate TEG's to directly convert engine waste heat directly to electricity in the BMW X6, the Ford Fusion and the Chevy Suburban. These first generations TEG's will provide a nominal 5 percent improvement in on-highway fuel economy by allowing the alternator to be downsized by at least 1/3. The 2nd generation TEG is planned to replace the alternator and provide a nominal 10 percent improvement in fuel economy.

DOE/NETL conducted a completive procurement for automotive thermoelectric air conditioners/heaters (TE HVAC) development and selected teams headed by Ford and GM to develop this technology. Current air conditioners use the R134a refrigerant gas, which has 1300 times the "Greenhouse Gas Effect" as Carbon Dioxide (CO2)., the primary "Greenhouse Gas". Approximately 41 Million Metric tons of CO2 equivalent (CO2e) are released to the atmosphere in the US annually from compressor seal leakage and frontal collisions wherein the the R134a refrigerant gas containment was ruptured. The TE HVAC's are candidates to eliminate refrigerant gases from vehicles. A problem with maintaining occupant comfort in an electrically assisted vehicle was illustrated by Bob Lutz, Vice Chairman, and General Motors, who drove a Chevy Volt in January in Detroit and had to turn on the 5 kW resistive heaters which reduced the battery propulsion mileage from 40 to 28. Preliminary analysis indicates that with TE HVAC a single occupant can be made comfortable using about 640 Watts. Whereas current compressed refrigerant gas air conditioners typically use 3500 to 4,500 Watts. The TE HVAC uses design advantages afforded by Thermoelectrics as a dispersed or zonal system wherein only the occupants are cooled/heated not the whole cabin. As TE HVAC is a DC electrical system it only requires a switch to go from a cooling mode to heating. The Zonal System will consist of a thermoelectric seat, thermoelectric units in the overhead and dash focused on each occupant. There will be a cooling loop with a dedicated radiator. TE HVAC is designed for specific vehicles. In this program they are the Cadillac SRX, the Chevy Volt and the Ford Fusion. The latter 2 will also have TEG's.

The Department of Energy has initiated a jointly funded program with the National Science Foundation (NSF) to fund university and industrial teams to develop advanced commercially viable Thermoelectrics for vehicular applications for 2nd generation automotive thermoelectric applications. Awards were made to 9 of the 48 universities who, with their industrial partners, responded to the DOE/NSF announcement. In early 2011 the Department of Energy conducted a competitive procurement to accelerate scale up and manufacture of advanced thermolelectric materials. The Teams selected and their approaches will be presented.

ORAL
PRESENTATIONS

Thermoelectric Power Factor of Low Dimensional Silicon Nanostructures

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Keywords: *thermoelectrics, nanostructures, atomistic, Boltzmann*

Abstract:
Low dimensional silicon channels, such as nanowires (NWs) and 2D ultra-thin-body (UTB) layers, have attracted significant attention as efficient thermoelectric materials since the work of Hicks and Dresselhaus [1], who pointed out that low dimensionality can be beneficial to the Seebeck coefficient. Recently, Boukai *et* al. [2], and Hochbaum *et* al. [3] showed that it is indeed possible to achieve *ZT*~0.5 at room temperature in Si NWs of diameters less than 50nm (compared to bulk Si *ZTbulk*~0.01). This, however, is mostly a result of significant reduction in the thermal conductivity. To fully understand the properties of low dimensional channels and exploit the potential benefits for the power factor as well, proper modeling tools that account for all important features of the low dimensional electronic structure are necessary.

We employ atomistic electronic structure calculations and Boltzmann transport theory to calculate the electrical conductivity and Seebeck coefficient of 1D silicon NWs and 2D UTB layers. For a comprehensive study, we examine: i) n-type and p-type channels, ii) confinement length scales, i.e. NW diameters and UTB layer thicknesses from 3nm up to 12nm (~5500 atoms), iii) various confinement and transport orientations, and iv) different carrier concentration levels. We show that improvements to the Seebeck coefficient due to lower dimensionality appear at length scales below ~7nm and can reach up to ~70% as the confined sides are scaled to 3nm. We show, however, that most of this improvement does not originate from the sharp features in the DOS(E) function as it is commonly believed. Furthermore, the influence of feature size reduction appears to affect the conductivity more, which finally determines the power factor. In most cases, enhanced scattering strongly degrades the conductivity with feature scaling, resulting in power factor reduction. We identify subband engineering techniques, however, that largely improve the conductivity resulting in improved power factors. Our results provide understanding of the changes that the power factor undergoes when channels are confined from 3D to 2D and finally to 1D, and provide guidance for efficient nanostructure thermoelectric device designs.

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Thermopower in different regimes of a single-electron transistor with superconducting island

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Keywords: *single electron transistor; parity effect, two-electron tunneling*

Abstract:
Single electron devices show interesting properties not only in the conductance, but also in the thermopower. The latter is especially interesting because it gives information about the average energy at which transport processes take place, thus giving insight in the tunneling mechanisms which are involved.

One of the simplest systems with interesting properties beyond the well-known saw-tooth characteristics [1] is the single electron transistor with a superconducting island and normal-conducting leads (NSN SET). To date, its properties have only be calculated in the regime where the temperature is larger than the parity crossover temperature and the charging energy larger than the gap of the superconductor [2].

We study the properties of NSN SETs outside this regime. When leaving that regime, additional effects and processes have to be considered, like the parity effect and coherent pair tunneling. We investigate how those affect the thermopower of the NSN SET.

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Phonon-drag thermopower of extrinsic semiconducting single-wall carbon nanotubes

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Keywords: *thermopower; electron-phonon coupling, carbon nanotubes*

Abstract:
The phonon-drag thermopower, S^g, is the contribution to thermopower that arises from the momentum interchange between carriers and acoustic phonons via the carrier-phonon coupling [1]. In this work we present a unified theoretical model for the calculation of S^g in degenerately doped semiconducting single-wall carbon nanotubes (SWCNTs) in both the diffusive [2] and the ballistic [3] transport regimes. In both cases we calculate the heat current produced when isothermally accelerated carriers transfer a part of their momentum to phonons in the presence of a weak electric field or a small voltage difference across the nanotube. In the diffusive regime the electron transport is described within the Boltzmann equation approach while in the ballistic regime we use the Landauer-Buttiker formalism. Phonons are treated semiclassically. The carrier-phonon coupling is described via a deformation potential and we consider intrasubband carrier scattering by stretching phonons [4].

Detailed calculations of S^g are performed in the temperature range 1-300 K for various values of the nanotube radius and the Fermi level. At low temperatures we derive a simple analytical expression for S^g that can be used as a probe for the estimation of the free carrier density. An interesting outcome of our work is that phonon drag shows a strikingly similar behavior in both the ballistic and the diffusive transport regimes. Finally, our theoretical estimates are in remarkably good agreement with experimental data in p-type bulk SWCNT samples [5,6].

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A 3D TCAD simulation of a thermoelectric module connected for thermoelectric power generation, heating and cooling

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Keywords: *Power generation, cooling, heating, TCAD simulation*

Abstract:
This paper documents the novel design, modelling and 3D simulation of a thermoelectric module using the Technology Computer Aided Design (TCAD) semiconductor simulation software package by Synopsys. Simulation results are presented for thermoelectric power generation, heating and cooling, and successfully demonstrate the fundamental thermoelectric effects.

The paper begins with an overview of a typical thermoelectric module's construction, highlighting the main elements and material structure. A brief overview of the TCAD simulation suite is given, followed by a description of the simulation methodology and test procedure. The 3D modelling of a thermoelectric module is presented, along with the simulation results obtained for the thermal and electrical characteristics of the device when it is connected for thermoelectric power generation, heating and cooling. Different material structures, thermoelectric couple and module designs have been investigated, and the simulation results are discussed with reference to fundamental thermoelectric theory. The paper draws conclusions on the validity and effectiveness of the 3D TCAD simulation model.

The Synopsys TCAD semiconductor simulation package has been chosen for this work as it is widely used in the semiconductor industry to simulate semiconductor device behaviour, and has the additional capability to simulate the semiconductor manufacturing process along with the device simulation. Modelling a thermoelectric module in TCAD enables a more detailed analysis of the thermoelectric electrical and thermal effects to be undertaken than has been published in previous simulation studies, and extends and builds upon our earlier work into modelling and simulation of a single thermoelectric couple in TCAD.

The 3D thermal and electrical simulation of a thermoelectric module in TCAD has been successfully achieved, and can be used for further analysis into thermoelectric effects, optimisation of material structure, module design and technology.

Strong reduction of the lattice thermal conductivity in superlattices and quantum dot superlattices

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Keywords: *thermal conductivity, phonons, quantum dots, superlattices*

Abstract:
We have investigated theoretically the phonon and thermal properties of Si/Ge superlattices (SL) and Si/Ge quantum dot superlattices (QDSL) in the framework of Face-centered cubic cell model of lattice dynamics. We have demonstrated that in Si/Ge SL and Si/Ge QDSL structures a strong reduction of the lattice thermal conductivity down to 0.5 W m^{-1} K^{-1} can be achieved depending on layer and quantum dot sizes and Si/Ge interface quality. These findings are in line with the recently measured values of the thermal conductivity in multilayered quantum dot arrays [1]. The effect is explained by the removal of the high-energy and high-velocity phonon modes from the heat flux due to their localization in superlattice segments and the phonon scattering on the interfaces. Fig. 1, left panel shows the dependence of the room-temperature thermal conductivity κ on thickness of Si layers d_{Si} for Si/Ge SLs with different Ge layers of thickness d_{Ge} under the assumption that the phonon mean free path for scattering on defects is fixed ($<L>$ = 18 nm). In the SLs with $d_{Si}>>d_{Ge}$ the thermal conductivity weakly changes with d_{Si} . The dependence on d_{Ge} is more pronounced: a rise of d_{Ge} from 2 to 4 monoatomic layers (ML) decreases the thermal conductivity by a factor of 1.5. A further rise of d_{Ge} attenuates the reduction effect due to the behaviour of the spectral density of the phonon thermal conductivity (Fig. 1, right panel).

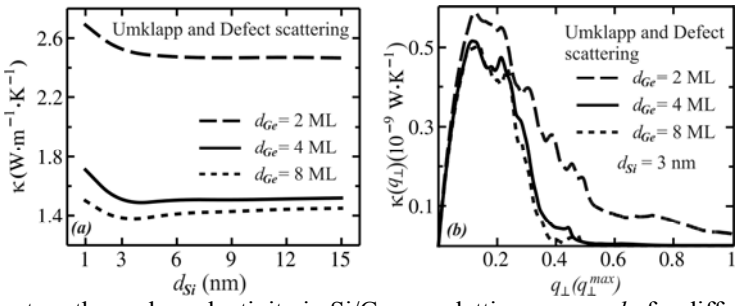

Fig. 1. Room temperature thermal conductivity in Si/Ge superlattices versus d_{Si} for different d_{Ge} (left panel); spectral density of the phonon thermal conductivity as a function of the reduced in-plane wave vector [$\kappa = \int_0^{q_\perp^{max}} \kappa(q_\perp) dq_\perp$] (right panel).

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Electron and phonon transmission in diameter-modulated nanowires

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Keywords : *nanowires, thermal conductance; transmission*

Abstract:
Manipulation of heat transfer through nanostructures is crucial for efficient thermal to electrical energy conversion. Maximum efficiency requires minimum thermal conduction. In nanostructures, electron conduction and phonon conduction are affected by low dimensionality and inhomogeneities. Recently [1,2], we proposed that increase of the thermoelectric energy conversion efficiency could be achieved by modulating the diameter of nanowires. We showed that the electron thermoelectric properties depend strongly on the geometry of the diameter modulation. This has been interpreted by the modification of the electron transmission coefficient compared to that in uniform straight wires. In diameter-modulated nanowires, the phonon transmission coefficient is also modified and phonon conductance decreases. Here, we discuss our findings on the total thermal conductance of diameter-modulated nanowires in the ballistic transport regime. The electron and phonon transmission coefficients have been calculated using the scattering matrix method. The electron thermal conductance has been found to decrease significantly at transmission resonances and transmission thresholds. Phonons give the dominant contribution to the thermal conductance. The phonon conductance, κ_{ph}, in non-uniform wires is lower than in uniform straight wires due to the modification of the transmission coefficient. It decreases with increasing number of dots in arrays. The decrease is found maximum for the superlattice structure. Even more significant decrease of κ_{ph} has been obtained for non-perfect arrays of dots. Disorder favours the decrease of the thermal conductance but it also induces unwanted decrease of the conductance. Discussion is devoted to the issue of designing the nanowire geometry so that to optimize the effects of diameter-modulation and disorder on the electron and phonon transport properties.

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Fast solution of thermoelectric equation for inhomogeneous devices

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Keywords: *Thermoelectric device modeling; Segmentation and FGM, fast algorithms*

Abstract:

Simulation of 3D-thermoelectric (TE) devices with finite element tools meanwhile is an established technique (e.g. [1], [2]). For fast optimization calculations still 1D-simulations of the TE-legs are needed by solving the nonlinear 1D-TE differential equation for the temperature profile T(x) along the TE-leg with el. current density j and heat flux Q(x) as sum of Fourier and Peltier heat [3]:

$$\frac{d}{dx}Q(x) = \rho(x,T)j^2 + j\alpha(x,T)\frac{dT(x)}{dx},\quad Q(x) = -\lambda(x,T)\frac{dT(x)}{dx} + jT(x)S(x,T)$$

The material parameters S(x,T(x)) (Seebeck), r(x,T(x)) (el. resistivity), and l(x,T(x)) (thermal conductivity) are generally simultaneous functions of location x and local temperature T(x), e.g. for segmented TE-generators. The TE-equation has been solved numerically with standard software packages for differential equations, e.g. in [4, 5, 6]. Especially in the context of "functionally graded materials" (FGM) potential increase of device performance by inhomogeneous design of coolers and generators is of interest [7, 8, 5, 6]. Segmented TE-devices exhibit material discontinuities within the TE-legs, which sometimes can pose numerical problems for the differential equation solvers. In these cases it is advantageous to make use of other solution techniques, which start from few chosen sampling points xi along the leg. In [7] piecewise constant and temperature independent material parameters are assumed between the sampling points. From the general TE-equation it can be concluded that heat current Q(x) and T(x) are continuous everywhere, even at the boundaries of material discontinuities. From this an equation system is derived which can be solved swiftly for T(x) and Q(x). Then TEperfomance parameters like efficiency and power output/input can be calculated.

Our work will demonstrate that by making use of the continuity conditions, the general nonlinear problem with position- and temperature-dependent material properties can be solved quickly and precisely. Use is made of a standard algorithm for nonlinear equations to solve for the temperatures Ti at the sampling points xi. Different algorithms are presented with calculation times of typically 0.1 s to 0.2 s on a 3GHz PC. Especially robust is a recursive algorithm which only solves for the single variables Ti one after the other. So optimization of e.g. TE-leg length and optimum el. current can be done within seconds. It is important to include thermal contact resistors to the heat reservoirs in the calculation, which can be done easily by setting the Seebeck S equal to zero in the ceramic contact segments. The methods are equally suitable for performance calculations of TE-generators and coolers.

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Charge Kondo theory of PbTe doped with Tl impurities

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Keywords: *charge Kondo effect, Lead Telluride, Thermopower enhancement*

Abstract:
Semiconducting PbTe is one of the most interesting materials for thermoelectric applications. When doped with a small concentration of Tl impurities, acting as acceptors, a number of anomalous low temperature properties are found: e.g., beyond a critical concentration of about 0.3 at. % Tl, the system exhibits superconductivity with remarkably high critical temperatures for such a low carrier system [1]. This and other anomalous phenomena prompted the idea that Tl impurities act as negative U centres leading for large enough doping to a charge Kondo effect and to superconductivity [1,2]. The charge Kondo effect is also known to provide a mechanism for enhanced thermopower [3]. In this work, we combine ab-initio calculations for PbTe [4] with a numerical renormalization group treatment [5] of the charge Kondo effect to explore the consequences of this model for the normal state properties of PbTe doped with Tl impurities, showing that it can explain a number of anomalous features in the temperature and doping dependence of the resistivity, carrier density and thermopower [6].

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Tailoring Thermoelectric Properties of Bismuth: Theoretical Investigations

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Keywords: *bismuth, magnetic field, nanostructuring, composites*

Abstract:
Thermoelectric materials have potential applications such as power generation from waste heat and environmentally friendly refrigeration. Much effort has been devoted over the past decade in developing techniques and materials to enhance their figure of merit, which is directly related to the efficiency of thermoelectric devices. Bi and $Bi_{1-x}Sb_x$ alloys are of particular importance, since they have the highest figure of merit at low temperatures. Although Bi has been studied since the 1950s, this material is still a great source of new scientific discoveries. We find some surprising results for the thermoelectric transport in Bi when external factors, such as magnetic field and nanostructures, are present. Our findings are directly related to the anisotropic energy band-structure and semi-metallic nature of Bi. We provide fundamental understanding of the intricate relationship between the characteristics of the charge and heat carriers and the effects from an external magnetic field, its direction and magnitude and nanostructures, imbedded in the bulk. Guidelines for practical advantages and limitations of thermoelectric enhancement are also outlined.

Electronic and Thermoelectric properties of $RuIn_{3-x}A_x$ (A=Sn, Zn) from first principles

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Keywords: density functional theory, Boltzmann transport

Abstract:
Recently, substitution derivatives of the intermetallic compound $RuIn_{3-x}A_x$ (A = Sn, Zn) have been shown to exhibit relatively high Seebeck coefficients. Substitution by Sn results in n-type behavior while p-type is the norm for substitution of In by Zn. We discuss in detail the electronic structure of the parent compound and the substitution derivatives obtained from density functional theory (DFT) based calculations using the Full Potential Local Orbital (FPLO[1]) code. The substitution effects have been studied using three different approximations: the simple virtual crystal approximation (VCA), the ordered supercell approach and the disordered coherent potential approximation (CPA). Both Sn and Zn prefer different site symmetry positions in the unit cell. While the parent compound $RuIn_3$ is a semiconductor, the substitution derivatives are not. For small doping concentrations, we observe a rather rigid-band-like behavior due to the parabolic nature of the bands forming the valence band maximum and the conduction band minimum. Transport properties calculated using the semi-classical Boltzmann transport equations (BoltzTraP[2]) based on the constant scattering approximation are consistent with the experiments.

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Defect and phase stability of solid solutions of Mg2X with antifluorite structure. An ab-initio study

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Keywords : *silicides; ab-initio; defect, phase stability*

Abstract:
Silicides are attractive thermoelectric materials because they are based on cheap, abundant, and non toxic elements. Among them, the cubic compounds with antifluorite structure, Mg2X, have attracted the attention in the last years, notably after the report by Zaitsev and coworkers [1] that Mg2Si0.4Sn0.6 has a figure of merit higher than 1 at about 700 K with an adequate doping. However, only n-type highly effective thermoelectric compounds can be obtained in this class of materials and Mg2Si can only be of n-type when it is not intentionally doped while it is possible to have also p-type compounds when X = Ge and even more so when X = Sn. This suggests that it is important to understand what the most stable defects in these different compounds are, in order to find the best way to optimize their thermoelectric properties by doping. The first aim of our study is thus to report the stability of the different types of defects. We find that multivacancies are among the most stable defects. When X = Ge or Sn, the magnesium vacancy and the stoechiometric trivacancy become more stable than in the case of Si which explains why it is easier to have p-type doping in these cases. We have also studied the quasi-binary phase diagram of Mg2Si-Mg2X (X = Ge, Sn) and confirmed that there is a miscibility gap only for X = Sn with a much smaller solubility of Mg2Si in Mg2Sn than of Mg2Sn in Mg2Si as found recently by Kozlov et al [2]. Therefore, the material of composition Mg2Si0.4Sn0.6 is probably a mixture of Sn and Si rich compounds. As a consequence a thorough study of the thermodynamic properties of the Mg2X solid solutions is mandatory in order to evaluate if these materials can be used for long time high temperature thermoelectric applications.

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Ab-initio study of zinc antimonide: electronic structure, mechanical properties, lattice dynamics and defect formation energies

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Keywords: *antimonides; ab-initio*

Abstract:
In the intermediate temperature range, zinc antimonide alloys are among the most promising compounds for thermoelectric applications. Since the renewal of thermoelectric research, most of the attention was attracted by Zn_4Sb_3 because of its large figure of merit (ZT = 1.4 at about 600 K) [1]. However, although lots of works have been dedicated to overcome this problem, the lack of stability of Zn_4Sb_3 at high temperature due to its metastability is still a fundamental problem for future thermoelectric applications [2]. ZnSb has a ZT two times smaller than the one of Zn_4Sb_3 [3] but it has nevertheless the potential of being useful for thermoelectric applications and should therefore be studied more intensively.

In the present work, using ab-initio studies, we report the electronic structure of ZnSb (which has an indirect narrow bandgap) and other physical properties of primary interest for thermoelectric applications. In order to evaluate its potential for high temperature applications, we report its mechanical properties and lattice dynamics. We find that he has a bulk modulus of about 50 GPa very similar to the one of Zn_4Sb_3. Although ZnSb has a thermal conductivity two times smaller than Zn_4Sb_3, the lattice dynamics calculations indicate a strong similarity between the two compounds, notably the presence of a large phonon density of states at about 5 meV related to low energy optical modes. Finally, we find that the most stable point defect is the zinc vacancy and this explains the intrinsic p-doping of ZnSb.

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Coupled theoretical interpretation and experimental investigation of the lattice thermal conductivity of Bi_2Te_3 single crystal

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Keywords : *Kinetic theory, anisotropy, lattice thermal conductivity, cutoff-frequency, Debye model, sound velocity, Christoffel's equation, relaxation time, bismuth telluride.*

Abstract:
An essential challenge in thermoelectric material research is the selection of materials having potentially a high figure-of-merit and their improvement by the reduction of their lattice thermal conductivity. In the present article the Debye model is modified and used to gain insight into the anisotropy of the thermal conductivity of bismuth telluride (Bi_2Te_3) single crystals. The minimum wavelength of phonons that moved, which is closely related to the concept of cutoff frequency, is not taken to be twice the atoms separation. The Debye temperature cannot be used and is not used to estimate the cutoff frequencies of the phonons that carry heat indeed. The cutoff frequencies are defined in this work by setting an upper limit to the energy of acoustic phonons using the complete dispersion relations. The study of previous publications summarized in the present article seems to indicate that the cutoff frequencies of acoustic phonons are anisotropic in Bi_2Te_3. The anisotropy of the thermal conductivity is surprisingly found to be unrelated to the anisotropy of the sound velocities that are calculated as a function of the tensor of the elastic constants. The thermal conductivity is almost isotropic when the longitudinal and transversal waves are taken into account and when other sources of anisotropy are not considered. In addition it is suggested that the relaxation time is also a function of the cutoff frequencies and may counterbalance the anisotropy arising from the variation of the number of acoustic phonons traveling in various directions. Finally, the anisotropy of the thermal conductivity of Bi_2Te_3 single crystal is found to be mostly related to the Grüneisen's constant if the main scattering mechanism is a phonon-phonon interaction.

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Electronic structure of Ba and In filled skutterudites: a combination study of XPS and XAS

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Keywords: *filled skutterudite; electronic structure, charge transfer, orbital hybridization*

Abstract:
Valence band and conduction band electronic structure of Ba and In filled skutterudites were characterized by X-ray photoelectron spectrum (XPS) and X-ray absorption spectrum (XAS). The effects of Ba and In fillers on the electronic structure of $CoSb_3$ framework were investigated based on the combination of the theoretical ground state electronic structure and multiple scattering calculation. The valence band XPS revealed that Ba and In fillers gave rise to strong local resonance state in the range of -6~-4 eV due to the interaction with Sb-Sb bonding state, suggesting that Ba and In fillers could alter the shapes of Sb_4 ring and Sb-icosahedron. The XAS of L_{III} edge for Ba and K edges for In, Sb, and Co demonstrated that Ba filler was pure ionic and In filler was covalent in the filled skutterudites, implying the charge transfer from Ba to Sb and the orbital hybridization between In and Sb.

Acknowledgments: We are grateful to the staff on the XAFS beamline for the XAS experiment at SSRF. This work was supported by the National Basic Research Program of China (2007CB607506) and the National Natural Science Foundation of China (50930004, 50972114).

Molecular Dynamics Simulation of mechanical properties of Nanoporous Single-Crystal bulk Bi_2Te_3

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Keywords: *Bi_2Te_3; nanoporous; molecular dynamics; mechanical properties*

Abstract not presented

Modification of sodium cobaltate for improved thermoelectric properties

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Keywords: *Oxides; modelling;*

Abstract:
The layered oxide Na_xCoO_2 (sodium cobaltate) has demonstrated promising thermoelectric properties with an optimal sodium content around x = 0.7. We have investigated the effect of changing the composition of this compound on its thermoelectric properties. Particular emphasis has been put on the oxygen stoichiometry, but substitution of Co has also been investigated. The main tool of this study is density functional theory calculations, but some of the results have also been checked experimentally.

Acknowledgments: Funding from the Research Council of Norway and a grant of computational resources from the NOTUR consortium are gratefully acknowledged.

Thermoelectric properties of strained silicon: an ab initio study

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Keywords: *Si, strain, (001), (111), ab initio, Boltzmann theory*

Abstract:
Starting from bulk silicon, we study the change in thermoelectric properties due to symmetry breaking in rolled-up and layered Si [1] which might lead to nanostructured thermoelectrics. Valley splitting in strained Si caused by tetragonal distortion was studied recently with respect to the enhancement of electron mobility [2]. Our results along (001) and (111) directions show that the unidirectional distortion has a strong influence on the electronic transport properties. The electronic structure is calculated self consistently within the framework of density functional theory. The transport properties are studied in the diffusive limit applying the Boltzmann theory in relaxation time approximation [3]. In detail, the anisotropy of the electrical conductivity, the thermopower and the resulting powerfactor in the in-plane and off-plane directions are studied in dependence on strain, doping level and temperature. It is shown, that applying strain along (001) direction the powerfactor at a given temperature can be enhanced slightly for p-doping, in contrast a decrease of the powerfactor of up to 20% is obtained for n-doping [4]. While for strain along the (001)-direction the change of the thermoelectric properties can be assigned to the band shift related redistribution of electrons, the changes in these properties for strain along (111) direction have a different source. Here a drastic change of the anisotropic transport effective mass tensor under applied change at maintained degenerated bands leads to a noticeable enhancement of the powerfactor at certain temperatures and doping conditions.

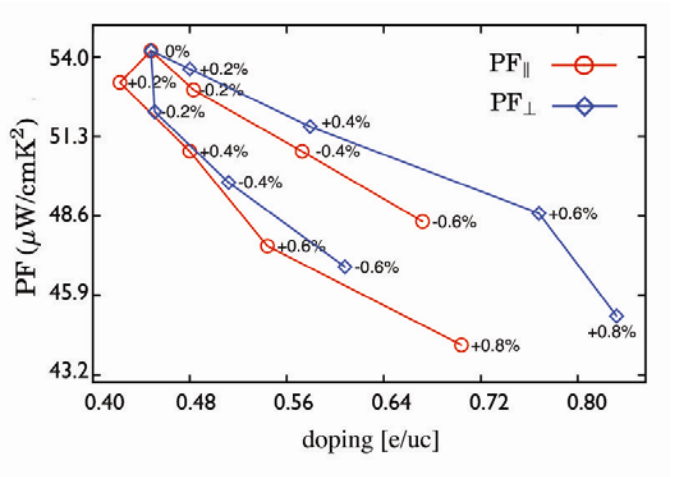

Fig. 1: Anisotropic power factor optimized by the carrier concentration at given (001)-strain state for electron-doped silicon. The in-plane (cross-plane) powerfactors are drawn as red circles (blue diamonds). Lines are shown to guide the eyes. The temperature is fixed at 900 K.

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The influence of Zn vacancy on thermal conductivity in β-Zn_4Sb_3: A molecular dynamics study

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Keywords : □-*Zn_4Sb_3, vacancy, molecular dynamics, thermal conductivity*

Abstract:

The vacancy of Zn atom is the critical defect in the crystal structure of β-Zn_4Sb_3, which leads to its excellent thermoelectric properties. Thus, in our present work, the effect of Zn-vacancy concentration on the lattice thermal conductivity of β-Zn_4Sb_3 at room temperature has been studied by using nonequilibrium molecular dynamics approach. The results show that with increasing Zn atom vacancy proportion, the lattice constants nearly linearly increase, resulting from weaker bond forces due to increased vacancy proportion. Both along the [1 0 0] and [0 0 1] direction, the lattice thermal conductivity of single crystal bulk β-Zn_4Sb_3 rapidly decrease when there exists Zn atom vacancy, then the lattice thermal conductivity slowly decrease with increasing Zn atom vacancy proportion, which suggests that Zn atom vacancy (n_v) to lattice thermal conductivity (k_v) leads to a scaling law of $k_v \sim n_v^{-\alpha}$ [1]. This phenomenon is attributed to vacancy scattering and increased phonon scattering due to increasing Zn atom vacancy. When the vacancy proportion of Zn atom reaches 10%, that is the vacancy model of β-Zn_4Sb_3, the lattice thermal conductivity of β-Zn_4Sb_3 are 1.32 W/mk and 1.62 W/mk along the [1 0 0] and [0 0 1] direction, respectively, which reduce by 90% than that of its full occupancy model. So, from our present work, it is shown that the 10% Zn atom vacancy in β-Zn_4Sb_3 crystal structure is the main reason to its exceptional low thermal conductivity.

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Acknowledgments: This work is supported by the National Basic Research Program of China (973 Program, Grant No. 2007CB607506) and National Natural Science Foundation of China (NSFC, Grant No. 10672127, 10832008) and A3 Foresight Program (50821140308).

Phase Stability, Structures and Thermoelectric Properties of the $(Bi_2)_m \cdot (Bi_2Te_3)_n$ Infinitely Adaptive Series

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Keywords: *Bi_2Te_3, powder X-ray diffraction, thermoelectric properties.*

Abstract:
Materials suitable for thermoelectric refrigeration and power generation are currently attracting much interest [1]. One of the important goals is to find materials that are suitable for thermoelectric refrigeration below room temperature.

We have studied a large number of binary Bi-Te thermoelectric materials that are part of the $(Bi_2)_m \cdot (Bi_2Te_3)_n$ infinitely adaptive series. This series is characterized by the layered stacking of Bi-Bi and Te-Bi-Te-Bi-Te blocks and is obtained through low temperature solid state reactions.

Initially we prepared and characterized nine members of the series [2], and proposed a new structural description based on a modulated structure approach. This allowed for a detailed correlation of the structure and thermoelectric properties. The most promising power factors for the intermediate compositions are 9 $\mu W\ K^{-2}\ cm^{-1}$ at 240 K for Bi_2Te (m:n = 5:2) and 11 $\mu W\ K^{-2}\ cm^{-1}$ at 270 K for Bi_7Te_3 (m:n = 15:6), yielding an estimated thermoelectric figure of merit, $zT \approx 0.2$ for these materials.

More recently we have investigated the phase stability of the title series through the synthesis of a number of new binary $Bi_{1-x}Te_x$ compositions [3]. In this contribution we will report on the results of this recent work, and the correlation between the structures and thermoelectric properties of the $(Bi_2)_m \cdot (Bi_2Te_3)_n$ infinitely adaptive series.

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Biomolecule-assisted hydrothermal synthesis and in situ synchrotron x-ray diffraction study of Bi_2Te_3 nanoparticles

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Keywords: *Thermoelectric, Nanostructure, Synchrotron radiation, Bi_2Te_3*

Abstract:
Nanostructuring of materials is an effective way to improve the thermoelectric properties. A simple biomolecule-assisted hydrothermal approach is developed for the fabrication of Bi_2Te_3 thermoelectric nanomaterials. The method not only allows synthesis of well defined nanostructures, but it also has the significant merit of being a green process using environmentally benign biomolecules as the reductant. A nanostring-cluster hierarchical structure which composed of ordered and aligned platelet-like crystals is synthesized. The possible growth mechanism of the hierarchical structure is suggested based on crystallographic and electron microscopy experimental results. The particle size and morphology can be controlled by adjusting the concentration of NaOH, which plays a crucial role on the formation mechanism of Bi_2Te_3. The synthesis of Bi_2Te_3 under high-temperature and high-pressure hydrothermal condition was further studied by in situ synchrotron radiation powder X-ray diffraction, which gives direct evidence of the phase formation and grain growth of Bi_2Te_3.

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Thermoelectric properties of Bi_2Te_3, Sb_2Te_3 and Bi_2Se_3 single crystals with magnetic impurities

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Keywords: *bismuth-antimony-telluride, thermoelectrics, magnetic impurity, diluted magnetic semiconductors*

Abstract:
Semiconductors containing transition or rareearth ions in an amount excluding direct exchange interaction between their magnetic moments are referred to as diluted magnetic semiconductors (DMS) [1]. Ferromagnetism was observed at low temperatures in AIIIBV and later in Bi_2Te_3, Sb_2Te_3 DMS [2]. In $Bi_{2-x}Fe_xTe_3$ the Curie temperature, T_c, increases as a function of x up to T_c = 12 K for x = 0.08. In n-$Bi_{2-x}Fe_xSe_3$ samples ferromagnetism was not detected. In $Sb_{2-x}Cr_xTe_3$ the value of T_c is about 5.8 K at x=0.43at%. It is not only of a scientific interest but is also practically important because it offers strong possibilities of using a magnetic field for the control of properties of various devices. From this point of view, of special interest are thermoelectric compounds, especially those based on Bi_2Te_3, Sb_2Te_3, and related mixed crystals, because they are the most efficient currently available thermoelectric materials. In the present study temperature dependence of Seebeck coefficient S, electrical conductivity, heat conductivity and figure of merit of single crystals of p-Bi_2Te_3, n-Bi_2Se_3 doped by Fe and Sb_2Te_3 doped with Cr were carried out in the temperature interval 7<T<300 K. At T=4.2 K Shubnikov-de Haas and Hall effect measurements have been measured in high-magnetic field up to 40 T. By increasing the Fe content, the hole concentration decreases in p-$Bi_{2-x}Fe_xTe_3$, while the electron concentration increases in n-$Bi_{2-x}Fe_xSe_3$. The hole concentartion in $Sb_{2-x}Cr_xTe_3$ decreases with Cr-doping. This demonstrates that Fe or Cr act as donors. The Seebeck coefficient increases in p-$Bi_{2\_x}Fe_xTe_3$ and $Sb_{2-x}Cr_xTe_3$ with increasing Fe or Cr content, while it decreases in n-$Bi_{2-x}Fe_xSe_3$. We found that magnetic impurity significantly increases Seebeck coefficient in p-Bi_2Te_3 and Sb_2Te_3 and decreases thermal conductivity. For $Bi_{2-x}Fe_xTe_3$ and $Bi_{2-x}Fe_xSe$ the value of ZT increase at T<100 K. In the case of $Sb_{2-x}Cr_xTe_3$ dimensionless figure of merit ZT increase at T>150 K.

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Correlation between Microstructure and thermoelectric Properties in $AgPb_{18}SbTe_{20}$ (LAST-18)

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Keywords: *LAST; microstructure analysis; HRTEM*

Abstract:
One feasible way to enhance the ZT value of a thermoelectric (TE) material is to decrease the thermal conductivity κ by introducing nanoprecipitates acting as phonon scatterers. Therefore, precipitation of nanosized secondary phases in $AgPb_{18}SbTe_{20}$ (Lead-Antimony-Silver-Tellurium, LAST-18) is highly promising for TE applications in the mid-temperature range.
The high thermoelectric performance of LAST – ZT values of ~2.2 at 800 K have been reported – is assumed to be caused by nanoscale precipitates formed by nucleation and growth and/or spinodal decomposition.
Based on properties monitored by a Seebeck scanning microprobe, structure-property relationships are studied by SEM and TEM analysis. Site-specific liftout of TEM lamellae from thermoelectrically characterised samples is made by focused ion beam (FIB) machining. Compositional analyses by energy-dispersive X-ray spectrometry are combined with phase analyses via electron diffraction to give a detailed picture of the microstructure. In addition high-resolution TEM and energy-filtered TEM are used to reveal orientation relationship and size distribution of the nanoprecipitates, respectively.
Moreover, various secondary phases are formed on the microscale during melt synthesis. The aim is to reduce number and size of the latter in order to get a high-performance thermoelectric material. The studies are showing different types of phase formations like domain structure in monoclinic Ag_2Te and possible spinodal decomposition in the $AgSbTe_2$/LAST-6 composition which could further contribute to the electronic properties of the material.
In the framework of a gradient-annealing experiment, a ZT value of ~ 1.05 at 425 °C was obtained in a sample that was annealed at 505 °C for one week. In agreement with the quasi-binary phase diagram of Ag_2Te-PbTe, monoclinic Ag_2Te nanoprecipitates are observed and exhibit a relationship between annealing temperature and particle size. Based on gradient annealing, a favourable temperature range (T_{ann}=500-550 °C) for good TE performance could be defined. Further investigations will deal with a new set of temperature-gradient samples referring to a finer gradient and optimization of Ag/Sb ratio to study the impact on the electrical conductivity σ.

Thermoelectric properties of metastable Ge/Sb/Te and Ge/Bi/Te compounds

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Keywords: *phase-change materials, real structure, chalcogenides, in-situ investigations*

Abstract:
A broad range of high-performance thermoelectrics are based on tellurides, and nanostructuring is one important way to increase their figures of merit.[1] Such structures are, of course, metastable and thus comparable to the tellurides used as phase-change materials (PCMs) for optical or electrical rewritable data storage (DVD-RW, BD-RE, PC-RAM). In addition to the metastability which is crucial for the fast phase change between amorphous and metastable states, the required materials properties such as low thermal and intermediate electrical conductivity are similar for both fields of application. Metastable crystalline phases of PCMs exhibit simple but highly disordered structures, e.g. the B1 (rocksalt) or the A7 (gray arsenic) type. Whereas in PCMs, the relevant transition occurs between the metastable and the amorphous phase, the partial transition from the metastable to the stable state may yield interesting thermoelectrics, because the intermediate-range diffusion of vacancies and atoms leads to a broad range of nanostructures and real-structure effects. The thermal treatment strongly influences the structure and thus the properties.

Quenched B1-type high-temperature bulk phases similar to those in thin-film PCMs of $(GeTe)_n(Sb_2Te_3)$ (n = 12, 19) reach *ZT* values of ~1.3.[2] Nanostructuring involves vacancy diffusion and twinning due to the onset of the transition to stable layered phases. Temperature-dependent diffraction experiments with synchrotron radiation elucidate the diffusion mechanism which leads to pronounced hysteresis effects in measurements of the thermoelectric properties.

Quenching disordered high-pressure phases ($GeBi_2Te_4$, various Ag/In/Sb/Te phases) yields a broad range of real-structure effects, e.g. domain structures where the domain size and orientation distribution can be influenced by the temperature program. This strongly affects the electrical resistivity. For HP-$GeBi_2Te_4$, the temperature characteristics can be changed from metallic-like to semiconducting behavior, depending on the domain or grain size, respectively. *ZT* values of $GeBi_2Te_4$ change by more than one order of magnitude, depending on grain-boundary effects induced by different sample treatment.

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Thermoelectric properties of Sn-doped In_4Se_3

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Keywords: *Thermoelectric, In_4Se_3, Spark plasma sintering*

Abstract:
Recently, In_4Se_3 has received considerable attention due to its high thermoelectric performance. The performance of the thermoelectric material is quantified by dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$, where S, σ, T and κ are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively. In_4Se_3 consists of quasi 2-dimensional covalent bond layers and 1-dimensional In chains, and this unique low dimensional structure leads to very low thermal conductivity (κ) and moderate power factor ($S^2\sigma$).

In literature, Te-alloyed In_4Se_3 and the mixture of In_4Se_3-In_4Te_3 have been suggested to control the thermoelectric properties due to their similar characteristics between Se and Te. However, there has been no report on Sn-doped In_4Se_3. Because the covalent bond radius of Sn is similar to that of In, and because the electronegativity of Sn is not quite different from that of In, Sn can be proposed as a promising dopant for the In_4Se_3.

In this work, we report the doping effect of Sn on the thermoelectric properties of In_4Se_3. The $(In_{1-x}Sn_x)_4Se_3$ ternary alloys were successfully synthesized by simultaneous melting of In, Se, and Sn in evacuated quartz tube and following two-step annealing processes. After the synthesis, the sintered bodies of the alloy were prepared by spark-plasma sintering. Thermoelectric properties of the sintered body were characterized by using 4-point probe method and laser flash method up to 750 K and details on the properties will be discussed.

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Near-room temperature power factor of metal sulfide films

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Keywords: *Metal Sulfide; thin film; Seebeck; XRD; SEM*

Abstract:
The thermoelectric effect permits the direct conversion of heat into electric energy, that it is very attractive to improve the efficiency of applications that waste residual heat (combustion engines and others). At present, among the different compounds investigated, the metal sulfides are very promising to be used like thermoelectric materials, due to its variety, its relatively high figures of merit and, mainly, low cost [1]. Furthermore, the simple synthesis as thin film provides an excellent framework to investigate the influence of microstructural parameters (crystallite size, strains, etc) and the effects of dimensionality on electron transport properties.

In this work the influence of the temperature (RT – 473 K) on the thermoelectric properties and stability of thin films of several metal sulfides (CoS_2, FeS_2, PdS, NiS_2,) were investigated. For this purpose, the power factor ($\alpha = S^2/\rho$) of these metal sulfide films was obtained and their thermal stability under vacuum was confirmed.

The films were deposited by thermal evaporation of different transition metals (Co, Fe, Pd, Ni). The sulfuration process was carried out through a solid-gas reaction at T=673 K. The morphology, structure an composition were investigated by profilometry, XRD and EDX-SEM. Measurements of resistivity and thermoelectric coefficient were performed using the differential method in a home-made experimental system.

Different behaviour of transport properties are observed depending on the metallic cation. For instance, CoS_2 and FeS_2 exhibit semi-metallic and semiconductor behavior, respectively. These results will be discussed and, moreover further improvements will be suggested.

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Thermoelectric Property Characterisations and Structural Analysis of Nanoalloyed Sb_xTe_{1-x} Multilayer Thin Films

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Keywords: *Sb_xTe_{1-x}, thermoelectric properties, structural disorder*

Abstract:

Thin film samples in the antimony rich region of binary systems Sb_xTe_{1-x} were prepared in an alternating layered fabrication (Fig.1) using a molecular beam epitaxy (MBE) system. Each layer of the elements was varied for different samples within the range 10 to 33 Å in thickness to yield different stoichiometry. Energy dispersive X-ray (EDX) spectroscopy was employed to determine the composition of the samples, of which the content of Te ranged from 39% to 51%. For all samples studied, the electrical conductivity, charge carrier mobility and concentration and Seebeck coefficient were measured at room temperature. A high power factor (PF) of 20 μW $cm^{-1}K^2$ was observed at room temperature for the annealed film with Te content of 41.76%. The thermoelectric properties were also measured at elevated temperatures (up to 250 ºC) for selected samples after annealing. Crystalline phase formation and transitions were observed in the in-situ X-ray diffraction (in-situ XRD) data collected on the as-deposited samples. Rietveld analysis of the XRD data combined with high resolution transmission electron microscopy (HRTEM) images on the annealed samples exhibit an intrinsically disordered polycrystalline structure due to the deviation in compositions from the classical Sb_2Te_3 stoichiometry. In the current studies, the physical properties in correlation with their micro-structures are also discussed.

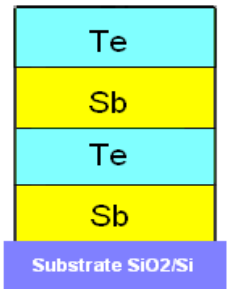

Fig. 1 Scheme of the fabrication pattern of film samples from the cross-section direction.

Thermoelectric properties of compacted $Bi_{2-x}Sb_xTe_{3-\delta}$ nanoplatelets with nominal composition of x = 1.5

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Keywords: *thermoelectric materials; bismuth tellurides; Hydrothermal synthesis*

Abstract:
Nanoplatelets of $Bi_{2-x}Sb_xTe_{3-\delta}$ with nominal composition of x = 1.5 are synthesized using hydrothermal methods [1,2]. The resulting powders are cold pressed and sintered in an evacuated ampoule at various temperatures between 300 and 360°C. The effects of sintering temperature on the thermoelectric properties of compacted $Bi_{2-x}Sb_xTe_{3-\square}$ are investigated. We find that the compacted $Bi_{2-x}Sb_xTe_{3-\delta}$ sample sintered at 340°C has the highest power factor of 11.6 μW/cm-K^2 and its thermal conductivity is 0.37 W/m K at 295 K. The resulting dimensionless figure of merit ZT is 0.93 at 295 K. Hall effect measurements are also carried out to study the scattering mechanism for samples sintered at different temperatures.

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Influence of Processing Parameters on the Thermoelectric Properties of $(Bi_{0.2}Sb_{0.8})_2Te_3$ Sintered by ECAE

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Keywords: *$(Bi_{0.2}Sb_{0.8})_2Te_3$, ECAE sintering, nanopowders, grain orientation*

Abstract:
Equal Channel Angular Extrusion (ECAE) has been recognized as one of the most successful process for nanopowder consolidation. By operating at lower temperatures than needed for Hot Pressing, it allows a better control of the competition between powder consolidation and coarsening. In this work, we report preliminary results on the influence of ECAE parameters on the thermoelectric properties of *p*-type $(Bi_{0.2}Sb_{0.8})_2Te_3$ nanopowders. The latter, prepared by ball milling elemental chunks, were compacted at room temperature under Ar atmosphere, and encapsulated into a Cu can for ECAE processing. The so called route C was used, with a punch speed of 5 mm min^{-1}. Two ECAE passes at 300 °C were sufficient to consolidate the material; however, the electrical conductivity was depressed, because of the introduction of *n*-type defects at this temperature. A satisfactory compromise among α, λ, and σ, was achieved by operating at 385 °C, both with two and four ECAE passes. A value of ZT close to 1, from room temperature to 95 °C, was reached. Enhancement of the factor of merit is expected by further increasing the number of ECAE passes at this temperature (material texturing improvement), provided the total processing time is substantially shortened, in order to preserve the nanograined structure.

CuAsTe a New Family of Thermoelectric Glasses

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Keywords: *Chalcogenide glasses, Thermoelectric materials*

Abstract:
Glasses and chalcogenide glasses especially, have a potential yet to be explored as thermoelectric materials. They already possess a low thermal conductivity and can have an high Seebeck coefficient (S). The challenge lies on making them more electrically conducting without affecting too much the previously mentioned transport properties. We have recently shown [1] that the power factor, S^2/ρ (ρ: resistivity) of the $Cu_{x+y}Ge_{20-x}Te_{80-y}$ family of glasses, is strongly improved by increasing the Cu concentration.

Here we report the studies on a new family of glasses obtained in the Cu-Te-As system and prepared by melt spinning. Our results show that the melt spinning technique allows us to extend the Cu-Te-As glassy domain and leads to T_g values, that permit the use of these glasses in applications up to 100°C. A maximum S^2/ρ value of ~100$\mu WK^{-2}m^{-1}$ [2] was obtained for the $Cu_{30}As_{15}Te_{55}$ composition, a power factor twice that of the best value obtained for the Cu-Ge-Te system, confirming these chalcogenide glasses as potential candidates in the quest for new high-performance thermoelectric materials

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Mid-temperature thermoelectric performances in PbS and PbTe

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Keywords: *IV-VI materials, Thermoelectric, Seebeck, thermal conductivity*

Abstract:
Dependence of Seebeck coefficient, thermal conductivity, and electrical conductivity for PbS and PbTe films was measured in the temperature range of 300-700K. The Seebeck coefficient of PbTe at high temperature was relatively low, owing to an indirect gap which decreases with temperature increase, and electronic part of thermal conductivity for the PbTe increased significantly, owing to a minority carrier effect[1]. The Seebeck coefficient and thermal conductivity for the PbS and PbTe were compared with theoretical values, and good agreements between experimental and theoretical values were obtained. Dependence of thermoelectric figure of merits on carrier concentration and temperature was calculated, and a high thermoelectric figure of merits was expected for the materials with carrier concentration exceed $1\times10^{19}cm^{-3.}$

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Thermoelectric properties of c-axis aligned Bi-Te materials

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Keywords: *thermoelectric, Bi-Te, crystal alignment, magnetic field*

Abstract:
Single crystalline Bi-Te thermoelectric materials have a rhombohedral structure with van der Waals bonding along c-axis direction. This structure gives intrinsic anisotropy in thermoelectric properties like electrical resistivity, thermal conductivity, Seebeck coefficient, as well as electron/hall mobility. Recent research works report that nano structures in polycrystalline thermoelectric materials improve thermoelectric performance by reducing thermal conductivity or by enhancing Seebeck coefficient. We investigated the effect of adjusting crystal orientation in the microstructures containing sub micro-sized grains on the thermoelectric properties for polycrystalline Bi-Te materials. Bi-Te powder, prepared through the conventional pulverization process, was sufficiently dispersed in an appropriate solvent, and then was formed into c-axis aligned green body under a designated high magnetic field. The green bodies were sintered with spark-plasma-sintering machine. The degree of crystal alignment of sintered bodies was examined with the electron-back-scatter-diffraction SEM and the X-ray diffraction patterns. It was observed that for both p and n type thermoelectric Bi-Te materials, aligning crystal orientation properly made electrical resistivity decreased with keeping Seebeck coefficient and thermal conductivity remained unchanged.

Thermoelectric properties of nanostructured I_2 II IV VI_4 Adamantines

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Keywords:*Thermoelectric materials, chalcogenides*

Abstract:
Thermoelectrics has long been considered a very attractive technology for cooling and waste heat recovery. A promising strategy to improve the efficiency is the use of complex crystal structures allowing large electrical conductivities in thermally isolating materials [1]. On the other hand, the reduction of the crystal domains to the nanoscale allows increasing the material's thermoelectric figure of merit, mainly by further reducing its thermal conductivity. Moreover, the narrow electron energy bands of quantum confined structures usually have associated high effective masses and therefore large Seebeck coefficients.

We present here a novel colloidal synthetic route to prepare quaternary adamantine nanocrystals with controlled size, shape and composition. We put special effort in designing a cost-effective and scalable process susceptible of being implemented in real applications. The synthetic route presented here is applied to the preparation of grams of the quaternary chalcogenide $Cu_{2+x}Cd_{1-x}SnSe_4$ ($0 \leq x \leq 0.5$) with accurately controlled composition and narrow size distributions. The electrical and thermoelectric properties of these materials were characterized over a wide temperature range. We will show how these materials have high Seebeck coefficients (150-300μV/K), electrical conductivities up to 14000 S/m, and thermal conductivities down to 0.3 W/mK, leading to ZT values up to 0.5 at 700 K. [2]

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Thermoelectric Properties of Solution-Processed Chalcogenide Nanocomposites

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Keywords: *nanostructures; Thermoelectrics; solution processing.*

Abstract:
It has been shown that the family of bulk cubic compounds with complex composition and general formula $Ag_nPb_mM_nN_{m+2n}$ (M = Sb,Bi, N= Te,Se), as well as the ternary compounds $Ag(Sb/Pb)_2Te$ exhibit remarkable thermoelectric properties[1,2]. On the other hand several works have been reported on the improved thermoelectric properties of nanostructured materials [3, 4].

In this work we propose multicomponent nanostructures made of $Ag_2N_nM_m$ (N=Te, Se, M= Bi, Pb, Sb) as potential thermoelectric materials. These materials combine a set of desirable features: high crystal symmetry, low thermal conductivity, and the ability to control the carrier concentration, among others, all of them important to obtain high ZT values.

We synthesized the nanostructures in a multistep solution-based synthesis, where pre-synthesized nanoparticles are used as seeds for nucleation and growth of the other material´s phases. The solution processing provides a rather low cost and versatile technique to control the composition and therefore the electronic properties of the resultant material.

The structural and morphological characterization of the obtained nanomaterials was made by means of Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD). We report the measurement of the thermoelectric properties and discuss on the potential of the synthesized nanostructures for improving the thermoelectric efficiency.

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Bismuth-substituted lead-telluride based thermoelectric nanocomposites: solubility-controlled microstructure

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Keywords: *lead telluride; nanocomposite, microstructure*

Abstract:
Ternary and multinary lead-telluride based thermoelectric are among the most efficient thermoelectric materials for the medium temperature range. Important classes encompass LAST-type materials and IV-V-VI compound semiconductors. In the group of IV-V-VI compounds bismuth as a substituent leads reliably to n-type materials, for bulk materials as well as for nanostructured thermoelectric material. We prepared several series of bismuth-containing IV-V-VI nanocomposites applying a ball-milling and compaction approach. Composites of the compositions $(PbTe)_n(Bi_2Te_3)$ with n = 10,15,20 were obtained and compared to samples of the type $(PbTe)_{10}(Bi_{2-x}Sb_xTe_3)$ and $(PbTe)_{15}(Bi_{2-x}Sb_xTe_3)$ (x = 0,1,2). The samples were structurally characterized by high-resolution TEM (HRTEM) analysis, SAED investigations and EDX point analyses. Structural transformations were observed during annealing procedures and their influence on the thermoelectric properties of the different types of compounds was evaluated. The resulting microstructure of the annealed samples and their thermoelectric characteristics seem to be very much controlled by the solubility of the V-VI minority phase in PbTe.

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Thermoelectric transport in PbSe quantum wells

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Keywords: *PbSe quantum wells, thermoelectric properties, temperature, size effects*

Abstract:

For thin film thermoelectric applications, it is necessary to take into account the size effects, which can drastically change the properties. Earlier we have observed thickness oscillations of the galvanomagnetic properties in IV-VI quantum wells and attributed them to the quantum size effects due to electron confinement in the quantum wells [1].

The goal of the present work is to study the dependences of the thermoelectric properties (the Seebeck coefficient, electrical conductivity, Hall coefficient, charge carrier mobility, and thermoelectric power factor) of the (001)KCl/PbSe/EuSe structures on the PbSe quantum well width d (d=5-300 nm) and temperature. PbSe layers were prepared by thermal evaporation of crystals in vacuum, whereas EuSe layers were grown using electron-beam evaporation.

On the basis of the temperature dependences of the kinetic coefficients, thickness dependences of properties were plotted at fixed temperatures. It was established that in the thickness dependences of the thermoelectric properties one can isolate a monotonic and oscillatory components, whose presence is attributed to the manifestation of the classical and quantum size effects respectively. It is found that an increase in the quantum well width up to $d \sim 300$ nm leads to an increase in electrical conductivity and charge carrier mobility as well as to a growth in the exponent in the temperature dependence of charge carrier mobility. This proves that in epitaxial PbSe layers, the classical size effect, connected with the contribution of diffuse scattering by the film surfaces to the kinetic coefficients, takes places.

A theoretical interpretation of the observed dependences is given. The theoretically estimated period of quantum oscillations and the behavior of the monotonic component are in good agreement with the experimentally observed ones.

The observed character of the thickness dependences of the thermoelectric properties should be taken into account for 2D- structures applications in thermoelectricity.

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Half-Heusler superlattices for thermoelectrics

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Keywords: *Half-Heusler; superlattice, thin films*

Abstract:
Due to their exceptional thermoelectric properties Half-Heusler alloys like MNiSn (M=Ti,Zr,Hf) have moved into focus [1,2]. Seebeck and resistivity measurements of thin film TiNiSn and $Zr_{0.5}Hf_{0.5}NiSn$ made by dc magnetron sputtering were performed and their dependence on epitaxial quality is shown. Seebeck coefficient, specific resistivity and power factor for $Zr_{0.5}Hf_{0.5}NiSn$ at room temperature were measured to be 63 μVK^{-1}, 14.1 μm and 0.28 $mWK^{-2}m^{-1}$, respectively. Due to mass fluctuation, superlattices of TiNiSn and $Zr_{0.5}Hf_{0.5}NiSn$ are promising candidates to increase the thermoelectric figure-of-merit by decreasing thermal conductivity perpendicular to the interfaces [3]. The epitaxial growth of superlattices containing TiNiSn and $Zr_{0.5}Hf_{0.5}NiSn$ is demonstrated by measuring satellite peaks in the XRD diffraction pattern originating from the additional symmetry perpendicular to the film surface. Additionally, TEM images give information about interface formation.

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Improved thermoelectric performances in nano-$Co_{0.97}Pd_{0.03}Sb_3$

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Keywords: *skutterudites, nanostructuring, grain boundary scattering*

Abstract:
We synthesized $Co_{0.97}Pd_{0.03}Sb_3$ compacts with grain sizes in the range 200 - 300 nm in order to promote phonon scattering at the grain boundaries. The composition $Co_{0.97}Pd_{0.03}Sb_3$ was chosen because it displays a large power factor (2.5 mW. $m^{-1}K^{-2}$ at 300K) [1]. Powdered samples were initially obtained by ball milling $Co_{0.97}Pd_{0.03}Sb_3$ together with x% (x = 0.5, 1, 2 %) of CeO_2 nanoparticles (~ 8 nm). This additive slows down the grain size growth of the skutterudite matrix which occurs during Spark Plasma Sintering (Zener effect) [2] and it contributes to phonon scattering. X-ray powder diffraction confirmed the nearly single phase character of the matrix. Scanning electron microscopy shows that grains in the ~ 200 nm range are obtained in samples with 1, 2% CeO_2 while grains in the ~ 300 nm range are obtained in samples with 0, 0.5% CeO_2. The inclusions of oxide are dispersed at the grain boundaries. $Co_{0.97}Pd_{0.03}Sb_3$ samples with nanosize grains display larger resistivity values in the temperature range [300 – 800K] than the micron-size grains reference material. But the nanosize grains samples also display a larger Seebeck coefficient (- 220 □V.K^{-1} at 300K), possibly arising from electron energy filtering, which partially compensate for the power factor reduction by the resistivity increase. The lattice thermal conductivity is decreased in nano-$Co_{0.97}Pd_{0.03}Sb_{12}$ and its room temperature value correlates not only with the grain sizes but also with the amount of CeO_2 nanoparticles. This results in an enhanced (+20%) average ZT value (300 – 650K) in nano-$Co_{0.97}Pd_{0.03}Sb_{12}$ + 0.5% CeO_2.

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Effect of Fe doping on thermo oxidation behaviors of filled $CoSb_3$-based skutterudite

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Keywords: *$CoSb_3$-based filled skutterudite, oxidation, pesting, thermoelectric material*

Abstract not presented

Benificial effect of Se substitution on the thermoelectric properties in $Co_4Sb_{12-x-y}Te_xSe_y$ skutterudites

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Keywords: *Skutterudite*, *$Co_4Sb_{12-x-y}Te_xSe_y$*, *Nanostructure*, *Thermoelectric*

Abstract:

Skutterudite-based compounds, $Co_4Sb_{12-x-y}Te_xSe_y$ (x = 0.4, 0.5, 0.6 and y = 0, 0.1), are synthesized by the solid state reaction and spark plasma sintering methods , of which the structure and the thermoelectric properties have been investigated systematically. It is found that doping of Se resulted in a decrease in the lattice parameter and a refinement in the grain size compared with that of single Te-doped samples. Some localized wavy patterns with a diameter about 10-20 nm embedded in the matrix are discovered in all of the samples. The samples doping of Se do not yield a certain increase in the power factor due to the reduced electrical conductivity, but it shows a significant depression in the lattice thermal conductivity because of the enhanced point-defect scattering owing to the larger mass fluctuations and strain field fluctuations. Besides, the effect of reduced grain size and nanoprecipitates on lattice thermal conductivity should not be neglected. The highest dimensionless thermoelectric figure of merit ZT = 1.09 is achieved at 800 K in the $Co_4Sb_{11.3}Te_{0.6}Se_{0.1}$ compound, which is improved by 15% as compared with that of single Te-doped $Co_4Sb_{11.4}Te_{0.6}$ compound at the corresponding temperature.

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Thermoelectric Enhancement in $CoSb_3$ skutterudite compounds with double and triple filling of In, Yb, Ce

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Keywords: *Thermoelectric properties, skutterudites, triple filled, thermal conductivity*

Abstract:
Yb atom is one of the most effective species to fill the voids in the skutterudite structure in order to reduce the thermal conductivity and thus enhance the thermoelectric performance of skutterudite compounds. In this work, we aim to find the best filling partners for Yb using different combinations of Ce and In. All samples were prepared by the traditional method of synthesis relying on melting-annealing and followed by spark plasma sintering. The thermoelectric properties of four samples of $Yb_{0.2}In_{0.2}Co_4Sb_{12}$, $Yb_{0.2}Ce_{0.15}Co_4Sb_{12}$, $Yb_{0.2}Ce_{0.15}In_{0.2}Co_4Sb_{12}$, and $Yb_{0.3}Ce_{0.15}In_{0.2}Co_4Sb_{12}$ (nominal) were examined based on Seebeck coefficient, electrical conductivity, thermal conductivity, and Hall coefficient. Hall coefficient and Seebeck coefficient signs indicate that all samples are n-type skutterudite compounds. Electrical conductivity increases with the increasing Yb+Ce content. A high power factor value of 59 $\mu V/K^2$-cm for $Yb_{0.2}Ce_{0.15}Co_4Sb_{12}$ and a lower thermal conductivity value of 2.82 W/m-K for $Yb_{0.2}Ce_{0.15}In_{0.2}Co_4Sb_{12}$ indicate that Ce may be a good partner with Yb and it is more effective than In to enhance the thermoelectric performance of skutterudites. The highest ZT value of 1.43 was achieved for $Yb_{0.2}Ce_{0.15}In_{0.2}Co_4Sb_{12}$ triple-filled skutterudite.

Thermoelectric properties of magnesium silicide prepared by self-propagating high-temperature synthesis

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Keywords: *magnesium silicide, SHS, thermoelectric materials*

Abstract:
Magnesium silicide doped with bismuth, silver or boron was produced from elemental powders by self-propagating high-temperature synthesis (SHS) [1,2]. Additionally, the effect of Sn- and Ge-doping on thermoelectric performance of Mg_2Si binary compounds was investigated. The reaction was carried out under dynamic vacuum in the temperature range 713 – 873 K. Powder products were densified by a hot pressing technique. Phase composition of the materials was investigated by XRD, morphology and chemical composition by TEM/SEM and EDS analyses. Netzsch LFA instruments were used for thermal property measurements. The Seebeck coefficient and resistivity were determined in the temperature range 300 – 900 K using a home-made set-up. The obtained results were reproducible and comparable with the data reported by other laboratories. Thermoelectric properties of doped magnesium silicide obtained by SHS were discussed with reference to the synthesis parameters and dopant type.

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Solid State Synthesis of Magnesium Silicide Based Materials

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Keywords: *Low Temperature Synthesis, Thermal Analysis, Transmission Electron Microscopy*

Abstract:
The Mg2Si compound is a promising material with significant advantages as its already high ZT, its high melting point and low density and encourages growth of light and economically advantageous systems. Based on the literature, the synthesis of Mg2Si material presents difficulties mainly due to the large difference in the melting points of Mg and Si. Mechanical alloying has been considered as an advantageous solid state synthesis technique but there are also difficulties due to the severe agglomeration of the material that is known to be major problem; the dry milling is practically not possible under various conditions [[1]]. Therefore, Mg2Si –based materials have been synthesized by a variety of methods, including induction melting [2], vertical Bridgman growth [3], spark plasma sintering [4], and mechanical alloying [5]. In this work, the synthesis of magnesium silicide based compounds at low temperatures, through solid state reaction, will be presented.

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Encouraging thermoelectric properties and durability of residual metal-Mg free Mg_2Si prepared by an all molten process

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Keywords: *Thermoelectricity, Magnesium silicide, Doping, Electrode material*

Abstract:
Mg_2Si is a promising candidate for practical thermoelectric power generation; however, concerns about it degrading due to oxidation has until now prevented its use in practical applications. Nevertheless, it has several promising features, such as the abundance of its constituent elements, its non-toxicity, and the facts that it is light weight and has the capability of generating power. These features have motivated the development of Mg_2Si for several years now. We have attempted to synthesize stoichiometric and single phase Mg_2Si sources initiated from molten materials in order to reduce the possibility of oxidation owing to residual metal-Mg. This is because the remaining metal Mg in Mg_2Si has been known to disturb the reproducibility of the sintering processes and consequently undermine the aging characteristics of Mg_2Si.

In this report we show the present status in the development of residual metal-Mg free Mg_2Si, focusing on the material synthesis, the doping characteristics, the sintering adaptability, the metal electrode compatibility, and the durability at elevated temperatures. Commercially available Mg_2Si is fabricated at 1378 K, beyond the congruent melting point of Mg_2Si at 1358 K. It is initiated from a mixture of pure Mg and Si, while waste Si sludge and recycled Mg-alloys, such as those from the Mg-Al-Zn-Mn system, can also be used as sources. For the dopants, Bi, Al and Sb give n-type conductivity, while Ag gives p-type, and Cu amphoteric characteristics. The ZT values obtained were 1.08 for Bi-doped n-type and 0.12 for Ag-doped p-type Mg_2Si. The atmospheric durability of Mg_2Si, with the hot-side at 873K and the cool-side at 373K, was more than 11,000 h when doped with Sb, while degradation was observed with some of the dopants. The plasma activated sintering (PAS) method allowed sintered pellets as large as 40 mm in diameter to be made. Metal electrodes, such as Ni, and transition-metal silicides, such as $CoSi_2$, $CrSi_2$, NiSi and $TiSi_2$, were formed simultaneously during the sintering process. Since sintered Mg_2Si exhibits a lack of residual metal-Mg, wet post-processes even with hot water can be used with no significant degradation.

Nanocrystallization of amorphous M-Si thin film composites (M=Cr, Mn) and their thermoelectric properties.

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Keywords: *Transition metal silicides, thin film, nanocrystallization, transport properties*

Abstract:
We report on electrical resistivity and thermoelectric power of Cr-Si and Mn - Si composite films at temperatures from 100 K to 1000 K. The films were deposited on unheated Si/SiO_2 substrates by magnetron sputtering from composite targets. The as-deposited films have amorphous structure. We use annealing with in-situ transport properties measurements to transform the films into nanocrystalline (NC) state with continuous monitoring their state. Nanocrystallization is considered as a promising way to improve thermoelectric efficiency $ZT=\alpha^2 \sigma/\kappa$, primarily due to reduction of lattice thermal conductivity κ. Among variety of methods for preparation of NC materials, crystallization from amorphous state has features which are crucially important with respect to their electronic transport properties: since the crystallites and their interfaces are formed in this method via solid state reaction, the NC samples are dense and the interfaces are clean. This removes additional factors affecting properties of a nanocrystalline composite, such as contamination of nano-crystal interfaces by elements from environment or nano-crystal lattice distortion during nanocrystallization. Depending on the initial film composition, the films are transformed during annealing into single phase or multi-phase NC composites with average grain size of 10 nm to 20 nm. We study the crystallization kinetics, stability of NC state and relation between transport properties and structural state of the composites.

Thermoelectric properties of hot-pressed $CrSi_2$ samples.

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Keywords: *chromium disilicide*

Abstract:
Technology is developed and a series of $CrSi_2$ pure and doped samples obtained by hot pressing. Mo, Ge and Al were used as the dopants. Electrical conductivity, Seebeck coefficient and thermal conductivity were measured in the wide temperature range (300-1000 K).

Al impurity addition allows to change the hole concentration. Mo and Ge dopants result in significant reduction in thermal conductivity. The measured thermoelectric parameters were used for the estimation of the thermoelectric power parameter and dimensionless figure of merit.

Frequency Dependent Electron Damping in n-type PbSe

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Keywords: *Thermoelectric PbSe, Infrared Reflectivity, Free carrier effective mass*

Abstract:
The cubic semiconductor PbSe has attracted scientific attention for more that seven decades now, mainly due to its optical properties [1], and lately as a thermoelectric material in the temperature range 600 – 900 K [2, 3]. Recently theoretical and experimental reports have pointed out the appealing characteristics of PbSe in the advancement of thermoelectrics, as the lattice thermal conductivity is lower than that of PbTe [3] and Se is 50 times more abundant than Te in earth. PbSe has a higher melting point (1355K) than that of PbTe (1253K) and it can be used at higher temperatures. Therefore, both high temperature applications, as well as solar thermal energy conversion, could benefit from the development of PbSe based thermoelectric generators.
Important parameters to consider when selecting or designing material systems for thermoelectric applications are the band-gap size, the shape and width of the bands near the Fermi level, the carrier effective masses and also the carrier relaxation time. In this work we study the infrared (IR) optical properties of n-type PbSe samples doped with Cl exhibiting an electron carrier density in the range 7.5×10^{18} cm^{-3} - 3.8×10^{19} cm^{-3}. The IR reflectivity spectra, measured in the 100-3000cm^{-1} spectral region, in room temperature, are dominated by free carriers giving rise to blue-shifted reflectivity minimum in the region > 700cm^{-1}. Effective mass was found to increase with increasing carrier concentration supporting the non-parabolicity of the band model for PbSe, in accordance with the results extracted from thermopower measurements [4]. The analysis of the experimental reflectivity spectra showed that the conventional Drude model with a constant carrier relaxation time, failed to describe the behaviour in the whole frequency range. It was found that the lineshape of the reflectivity spectra can be better described by a frequency dependent electron damping parameter with resonant-like behaviour similar to the one observed in the case of resonant electron scattering off potential wells [5].

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Growth, electrical and thermal properties of doped mono and polycrystalline SiGe-based Quantum Dot SuperLattices

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Keywords: *nanostructures, quantum dots superlattices, SiGe*

Abstract:
SiGe materials present several advantages such as their compatibility with microelectronic techniques and non toxicity, but present a low figure-of-merit at room temperature. However it was shown theoretically that the figure of merit *ZT* could be highly increased by embedding nanoparticles in SiGe offering new potential applications.

We report here the growth of different monocrystalline and polycrystalline SiGe-based quantum dot superlattices (QDSLs) on Si (001) substrate.

The QDSLs were grown using an industrial Reduced Pressure Chemical Vapor Deposition tool (RPCVD). In this work, SiGe spacer width as well as Ge dots sizes and densities have been controlled. The SiGe layers were highly doped during the growth. Electrical and thermal properties of such structures have been measured and compared to standard SiGe thin films, showing notably a considerable thermal conductivity decrease.

Seebeck Coefficients in Silicon Nanowire Arrays

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Keywords: *silicon nanowire; Seebeck coefficient; thermoelectricity*

Abstract:
In recent years, there has been great interest in the fabrication of thermoelectric devices using nanostructured materials [1, 2]. In particular, this approach raises the possibility of the fabrication of thermoelectric devices in silicon, allowing compatibility with large-scale integrated device fabrication techniques. The use of silicon nanowires (SiNWs) [2] may allow an increase in the thermoelectric figure-of-merit $ZT = S^2\sigma T/k$. Here, S is the Seebeck coefficient, σ the electrical conductivity, k the thermal conductivity, and T the absolute temperature. A reduction in k in the NWs can increase ZT without affecting the power factor $S^2\sigma$.
In this work, we measure S in n- and p- type SiNW arrays, with doping concentration 10^{15} – 10^{16} cm^{-3} and lengths from ~10 µm to ~90 µm. The SiNW arrays (Fig. 1) were created using a metal-assisted chemical etching (MACE) process. The NW diameter in an array varies from 30 – 200 nm. Figure 2 shows S measured in p-SiNW arrays, with NW lengths from 33 - 87 µm. In the 37 µm sample, S = 914 µV/K, an increase from the bulk value of 642 µV/K. For longer arrays, S reduces in value and for the 87 µm array S becomes negative, implying carrier inversion for majority carrier holes to electrons. This behaviour is similar to SiNW transistors fabricated using MACE [3]. The measurements suggest a strong influence of the NW surface on the Fermi level pinning influencing the band bending at the surface of the NWs.

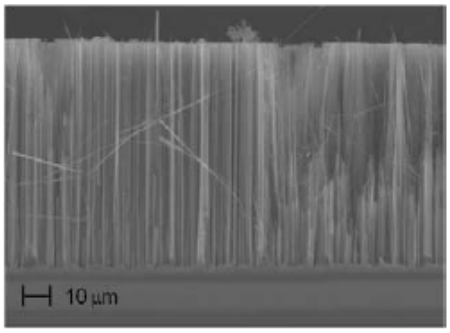
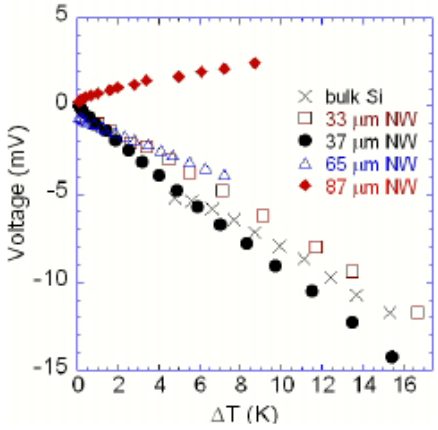


Fig. 1: SEM image of SiNWs array



Sample	S (µV/K)
Bulk	642
33µm	676
37 µm	914
65 µm	457
87 µm	-250

Fig. 2: Voltage as a function of temperature difference ΔT in bulk Si, and p-SiNW arrays of lengths 33, 37, 65, and 87 µm. Table shows measured S.

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Dielectric relaxation in Sb_2Te_3 thin films

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Keywords: *Thermoelectric materials, novel materials*

Abstract:
Sb2Te3 thin films were prepared in thickness range of 230-3500Å by thermal evaporation technique. The dielectric properties and ac conductivity of the Sb_2Te_3 films were investigated in the frequency range of 25 Hz- 100 kHz at various temperatures (293-373K). The relaxation time in structure calculated from ac conductivity results and cole-cole diagrams. The relaxation time is obtained as $\approx 10^{-5}$ s. The relaxation time values were evaluated and a good agreement between the relaxation time values obtained from ac conductivity and cole-cole diagram methods were observed. Film thickness, temperature, frequency dependence of the relaxation time were also investigated. The temperature coefficient of the capacitance (TCC) and permitivity (TCP) were determined as a function of the film thickness.

Formation and homogeneity range of the clathrates type-I in the ternary systems (Sr, Ba)-(Ag, Au)-(Si, Ge)

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Keywords: *clathrate type-I, thermoelectric properties, phase equilibria, crystal structure*

Abstract:
Formation and homogeneity range of the ternary clathrates of type-I, $Ba_8T_xGe_{46-x-y}\square_y$ and $Ba_8T_xSi_{46-x}$ (T = Ag or Au and □ is a vacancy; space group type Pm-3n) at 800°C (600°C) and phase relations concerning this region have been investigated. Furthermore, the existence of type I clathrates has been investigated in the homologous systems Sr-T-(Si,Ge). For all the ternary systems, Ba-Ag-Ge, Ba-Ag-Si, Ba-Au-Ge und Ba-Au-Si, partial isothermal sections have been derived at 800°C for the region of 0 to 33 at% Ba. For characterization of the clathrates and other ternary compounds existing at 800°C, X-ray powder diffraction, electron probe microanalysis (EPMA) and X-ray single crystal diffraction were used. Thermoelectric properties (thermopower S, electrical resistivity ρ and thermal conductivity λ) have been measured for clathrate compositions

$Ba_8Ag_xGe_{46-x-y}\square_y$ (x, y = 2.1, 2; 3.4, 1.1; 4.8, 0; 5.3), $Ba_8Ag_5Si_{41}$, $Ba_8Au_{5.1}Si_{40.9}$ and $Ba_8Au_6Ge_{40}$ between 4.2 and 900 K from which a thermoelectric figure of merit has been evaluated. These studies evidenced the closeness of the systems to a metal to isolator transition.

Composition Dependence of Thermoelectric Properties in Polycrystalline Type-I $Ba_8Ga_xSi_{46-x}$ (Nominal x=14-18) Clathrates Prepared by Combining Arc Melting and Spark Plasma Sintering Methods

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Keywords: *Silicon clathrate; gallium composition dependence; carrier concentration dependence; thermoelectric properties*

Abstract:
The gallium composition dependence of thermoelectric properties in polycrystalline $Ba_8Ga_xSi_{46-x}$ compounds with the type-I clathrate structure is presented. Polycrystalline *n*-type samples with various nominal gallium compositions (nominal x=14-18) were prepared by combining arc melting and spark plasma sintering (SPS) techniques. Results of Rietveld refinement of powder x-ray diffraction data and electron probe microanalysis (EPMA) show that the type-I clathrate phase with the stoichiometry (x=16) is not formed even though the gallium rich compositions (nominal x=17, 18) and the solubility limit of gallium composition is about 15. The lattice constant a increases monotonically with increasing x in the nominal composition range of x=14-16 but is saturated in x>16. The Hall carrier concentration n at room temperature decreases from about 2×10^{21} cm^{-3} to about 4×10^{20} cm^{-3} with increasing x. The magnitude of Seebeck coefficient S increases and the electrical conductivity $\boldsymbol{\sigma}$ decreases with increasing x at room temperature due to the decrease in n. The room temperature Hall mobility $\boldsymbol{\mu}$ increases with decreasing n. The thermal conductivity $\boldsymbol{\kappa}$ decreases with increasing x due to the decrease in the electronic contribution. The reduced Fermi energy, the effective mass m^*, and the Lorentz number L are determined from an analysis of experimental data on a single parabolic band model with the acoustic phonon scattering as the predominant scattering mechanism. The lattice thermal conductivity $\boldsymbol{\kappa_L}$ determined by $\boldsymbol{\kappa_L=\kappa-LT\sigma}$ relation is as low as 1.1 $Wm^{-1}K^{-1}$ for nominal x=16. The dimensionless thermoelectric figure of merit ZT is estimated to be 0.55 at 900 K for nominal x=16. The calculation of ZT using the determined parameters at room temperature $\boldsymbol{\mu}$=10 $cm^2V^{-1}s^{-1}$, m^*/m_0=2, and $\boldsymbol{\kappa_L}$=1.1 $Wm^{-1}K^{-1}$ predicts the maximum ZT=0.8 (900 K) at the optimum carrier concentration of 2×10^{20} cm^{-3}.

Evaluation of the thermoelectric potential in the clathrate-I $Ba_8(Zn,Ni)_xGe_{46-x}$

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Keywords: *clathrate-I; thermoelectric potential*

Abstract:
Although the clathrate-I formation in the Ba-Zn-Ge-system was already studied in details concerning the crystal structure, phase relations at 800°C and physical properties [1] as well as host-guest coupling and thermoelectric properties of a single crystalline sample [2], the thermoelectric potential (figure of merit ZT) in this system, which should show a maximum close to the Zintl-balanced composition $Ba_8Zn_8Ge_{38}$, was not yet evaluated.

Thus samples with compositions close to the metal-semiconductor transition have been synthesized using ball-milling and hot pressing. Moreover the influence of substituting Zn partially by another transition metal, namely Ni, was investigated. All samples were characterized by x-ray powder diffraction (XRD) and electron microprobe analysis (EMPA). The thermoelectric properties, electrical resistivity, Seebeck-coefficient and thermal conductivity, were measured in a temperature range from 4.2 – 700 K.

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Zn Migration in Spark Plasma Sintering of Zn_4Sb_3

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Keywords: *Zinc antimonide, Spark Plasma Sintering, Synchrotron powder diffraction*

Abstract:
The phase homogeneity of Spark Plasma Sintering (SPS) pressed thermoelectric Zn4Sb3 pellets in the direction of the press axis has been studied by Potential Seebeck Microprobe Scanning (PSM). A significant difference in the Seebeck coefficient indicates the changes of the starting phase. High resolution synchrotron powder diffraction patterns were recorded to investigate the compositions of the phases. The emergence of the ZnSb phase in one end of the pellet and Zn impurity in the other explains the difference in the Seebeck coefficients. Spatial phase distribution along the axis in the cross section of the pellet was depicted from the refinements of the X-ray diffraction patterns. They reveal the migration of the highly mobilized Zn atoms under the direct current applied when pressing by SPS.

Crystal structure and XPS analysis of In-doped β-Zn_4Sb_3

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Keywords: *β-Zn_4Sb_3; indium doping; Rietveld refinement; X-ray photoelectron spectroscopy*

Abstract:
β-Zn_4Sb_3 is a promising candidate thermoelectric material with extraordinary low lattice thermal conductivity and high dimensionless figure of merit. In the paper, X-ray diffraction (XRD) patterns and X-ray photoelectron spectroscopy (XPS) of In-doped β-Zn_4Sb_3 compounds with nominal composition $Zn_4Sb_{3-m}In_m$ ($0 \le m \le 0.18$) were investigated to reveal the effect of indium doping on the crystal structure and binding characteristics. The Rietveld refinement based on the XRD data indicates that the indium impurity preferentially occupies the 12*c* Sb(2) site in $Zn_4Sb_{3-m}In_m$. The lattice parameter *a* increases and *c* decreases with the increasing *m*, accompanying with lattice distortion and bond length and angle modification. Indium doping leads to an increment in the occupancy of Zn at the 36*f* Zn(1) and interstitial Zn sites, whereas the total occupancy of Sb and In maintains constant. XPS analysis shows that the valence of Sb decreases and that of Zn increases with increasing indium doping in $Zn_4Sb_{3-m}In_m$. This implies that negative charge might transfer from In and Zn to Sb atoms. Curve-fitting of Sb 3d photoelectron peaks prove that only the Sb atom at the 12*c* Sb(2) site is charged to more negative with the increasing *m*. Thus more Zn^{2+} ions near the 12*c* Sb(2) site are needed to maintain the charge balance, which is why the occupancy of electropositive Zn increases in the compound. The asymmetric Sb-In ionic bond forms by In substituting Sb at the 12*c* Sb(2) site, which changes the vibration behavior of Sb-Sb dimer and leads to more dynamical disorder of the localized dumbbell vibrations in β-Zn_4Sb_3. These new lattice disorders in β-Zn_4Sb_3, introduced by the substitution of In for Sb, result in an much low lattice thermal conductivity of 0.49 $W \cdot m^{-1} \cdot K^{-1}$ of $Zn_4Sb_{2.96}In_{0.04}$.

High electron mobility in Cu-doped ZnSb containing particles of Zn_3P_2

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Keywords: *Zinc Antimonides*

Abstract:
Partly motivated by the excellent figure of merit of Zn_4Sb_3, efforts have recently been made to optimize the thermally more stable ZnSb phase. Adding copper as the dopant in ZnSb resulted in a maximum carrier concentration of $8x10^{18}$ cm^{-3} [1]. Using the single parabolic band approximation, this study estimated a maximum figure of merit at a carrier concentration of about $2x10^{19}$ cm^{-3}.

We have now prepared samples of ZnSb containing particles of Zn_3P_2. These particles are formed by adding small amounts of phosphorus and additional zinc to a melt of ZnSb [2]. When these samples where doped with copper, a carrier concentration of $2.0x10^{19}$ cm^{-3} was achieved. At high carrier concentrations a lower mobility is usually observed due to impurity scattering introduced by the dopants. Surprisingly, even if the carrier concentration was increased an order of magnitude compared to ZnSb, these samples had a higher mobility.

The increased electrical conductivity resulted in a higher dimensionless figure of merit in the temperature range from 300 K to 700 K and surpassed 0.9 above 550 K.

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Comparison of the structural and thermoelectric properties of ball-milled and co-reduced $Bi_{1-x}Sb_x$ Nanoalloys

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Keywords: *BiSb-alloys, synthetic conditions, pressing conditions*

Abstract:
$Bi_{1-x}Sb_x$ nanoparticles of different compositions were synthesized in order to investigate the effect of nanostructuring on the thermoelectric figure of merit. Two synthesis pathways, one top down and one bottom up, were carried out and each compared with the bulk material. The top down approach was done by ball-milling and the bottom up synthesis by reduction of the metal precursors in organic solvent. Both pathways led to nanosized alloy particles with the rhombohedral crystal structure $R\bar{3}m$. The influence of the reaction and pressing conditions on the structure and the thermoelectric properties was investigated for both pathways. In addition, the influence of the composition on the thermoelectric properties was studied and compared with the bulk material.

An investigation of thermoelectric properties of the Bi-Sb-Te thick films relative to different thermal annealing process

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Keywords: *thermoelectrical property; the electric current assisted annealing process; BiSbTe thick film*

Abstract withdrawn

Anomalous Seeding Effect of Vanadium Diboride on the Thermoelectric Properties of Higher Borides

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Keywords: *seeding; borides; high temperature thermoelectrics*

Abstract:
Seeding of highly conductive metallic boride particles has been found to be a way to significantly improve the thermoelectric properties of higher borides. Previously we have discovered that seeding of small amounts of RB_4 and RB_6 metallic borides into sintered bodies of $RB_{22}C_2N$ and $RB_{17}CN$ could lead to significant increases of the power factors and figure of merits [1]. $RB_{22}C_2N$ and $RB_{17}CN$ are among a series of homologous compounds hoped to be the long awaited n-type counterparts to boron carbide. The increase of the power factors of the seeded materials was mostly the result of resistivity reduction, and it is possible this metallic boride seeding method can be effectively applied to other thermoelectric materials also.

At the same time it is an obvious fact that the figure of merit is much more sensitive to a Seebeck coefficient change. From previous experiments we have found that introducing a certain amount of CoB into $YB_{22}C_2N$ samples leads to an increase in the absolute value of the thermopower. In the current work we report on an anomolous seeding effect we have discovered for vanadium diboride. The thermopower of seeded samples have shown a large dependence on temperature. Besides this, effects of thermal treatment on both resistivity and Seebeck coefficient of VB_2 seeded $YB_{22}C_2N$ samples were observed. An increase in the maximum absolute value of the Seebeck coefficent of close to 2 times could be achieved, simultaneously accompanying an increase in the electrical conductivity of more than 100 times. Analyses of the influence of VB_2 amount in the sample, initial additive and thermal treatment on the thermoelectric properties will be presented.

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Classical and quantum size effects in Bi-Sb thin films

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Keywords: *Bi-Sb solid solutions, thin films, thermoelectric properties, size effects*

Abstract:
Recently, bulk crystals of the Bi-Sb solid solutions and low-dimensional structures based on them have attracted much attention as promising low-temperature thermoelectric and magnetoelectric materials for refrigerating devices at temperatures below ~ 200 K. The possibility of enhancement of the thermoelectric figure of merit in low-dimensional structures [1] has stimulated studies of Bi-Sb films. Besides, Bi-Sb solid solutions are interesting materials for solid states physics, which have extremely low effective electron masses, an anomalously high charge carrier mobility and mean free-path. In thin films one can observe two types of size effects: the classical one, which takes place when the film thickness is comparable with the mean free path of charge carriers in the material, and the quantum size effect, when the film thickness and the de-Broglie wavelength of charge carriers are of the same order of magnitude. Due to their unique electronic properties, Bi and Bi-Sb solid solutions are convenient objects for observation of both classical and quantum size effects, as well as for using these effects for controlling their thermoelectric properties.

The room-temperature dependences of the electrical conductivity, Seebeck coefficient, Hall coefficient, and thermoelectric power factor on the thickness (d=10–400 nm) of thin films grown on mica substrates by thermal evaporation in vacuum of Bi-Sb solid solutions crystals with 9.0 at.% Sb were obtained. It was established that an increase in d up to ~ 200 nm leads to a change in kinetic coefficients, and in the d - dependences of the thermoelectric properties, quantum oscillations were observed. It was shown that the monotonic component of the d-dependences can be satisfactorily approximated by theoretical calculations based on the classical Fuchs - Sondheimer theory. The theoretically estimated period of oscillations is in good agreement with the experimentally observed period.

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Thermoelectric properties of nanostructured Bi-Sb-Te doped with C_{60}

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Keywords: fullerene, nanocomposite, bismuth-antimony-telluride, thermoelectrics

Abstract:
In the present study, a new concept of nanocomposite material composed of nanocrystallites of Bi-Sb-Te alloys with a size of 10-35 nm which are covered by approximately one-molecule thick C_{60} layer is reported. C_{60}-decorated grain boundaries and ultrahigh elastic modules of the molecules give a possibility of an effective phonon blocking in nanoparticles of semiconductor which decreases the lattice thermal conductivity. Moreover, the molecules of C_{60} act as electron traps, and thus have acceptor effect: decrease the concentration of free electrons in *n*–type semiconductor and increase hole concentration in *p*-type material. The concentration of free charge carriers depends nonmonotonically on the concentration of fullerene in the composite. Using the new nanocomposite concept with C_{60}, we can vary and optimize transport properties of the thermoelectric materials.

The nanocomposites Bi-Sb-Te-C_{60} were synthesized using a procedure of mechanical alloying of nano-powdered Bi-Sb-Te with C_{60} in a planetary mill. $Bi_{0.5}Sb_{1.5}Te_3$ was used for the nanocomposite synthesis with *p*-type electrical conductivity and Bi_2Te_3 was used for the *n*-type nanocomposite. The concentration of C_{60} in mixed powder was varied in the range of 0 to 6 vol.%. After the treatment in the planetary mill, Bi-Sb-Te-C_{60} powder was loaded in a piston-cylinder cell in Ar atmosphere, compressed and sintered. The presence of C_{60} in the samples prevents from re-crystallization of Bi-Sb-Te nanocrystals during sintering and subsequent annealing and crystalline size in nanocomposite Bi-Sb-Te-C_{60} does not change. The thermal conductivity *k* of Bi-Sb-Te-C_{60} samples depends strongly on the temperature and concentration *C* of C_{60} fullerene in the samples. At room temperature, *C* decreases by a factor of up to 1.7 depending on initial value of *k*. The decrease of *k* with the increasing of *C* can be attributed to the additional C_{60}, because the mean crystalline size in the sintered samples does not depend on C_{60} concentration. The electrical resistivity of both *p*-type and *n*-type material increases as compared with pristine material.

The thermoelectric figure of merit ZT has increased as compared to starting material by 30% and equals to 1.16 for the optimized thermoelectric nanocomposite of *p*-type.

Thermoelectric properties of BiTeBr and BiTeI Single crystals and composites of BiTeI with BiI_3, CuI and superstochiometric Bi

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Keywords: *bismuth-iodine-bromide, thermoelectrics, nanocomposites, BiTeI, BiTeBr*

Abstract:
The single-crystalline BiTeI and BiTeBr were grown by the Bridgman method. Thermoelectrical properties of BiTeI and BiTeBr single crystals are investigated. Temperature dependence of conductivity, Seebeck coefficient and thermal conductivity are measured in the temperature interval 5<T<300 K. Both semiconductors have *n*-type conductivity. The figure of merit for BiTeBr is much higher than that of BiTeI, which is related mainly to a larger Seebeck coefficient for the former compound. We calculated the electronic structure of the both crystals in the context of the band model using the density-functional theory (DFT) and the hybrid functional B3LYP (the exchange part is the functional Becke 3, and the correlation part is the Lee–Yang–Parr GGA functional); for the description of chemically inert electron internal shells, we used the quasi-relativistic pseudo-potentials: the Stuttgart–Dresden groups (known as the Stoll–Preuss potentials for the Te and I atoms and the Hay–Wadt potentials for Bi and Br. The valence shells of atoms were described by the basis sets of DZ quality recommended for the corresponding pseudopotentials. The calculations were carried out using the software package CRYSTAL98. It is shown that both compounds are semiconductors with an indirect energy band gap. Composites of BiTeI with BiI_3, CuI and Bi are synthesized. Influence of BiI_3, CuI and superstohiometric Bi on there galvanomagnetic and thermoelectric properties are investigated. Seebeck coefficient of composite of BiTeI with CuI essentially increases while thermoconductivity decreases. The same is observed for samples with BiI_3. Superstohiometric Bi decreases thermoconductivity and electroconductivity and has almost no influence on thermopower. We got high values of Seebeck coefficient of composite of BiTeI with CuI and the high figure of merit of single-crystalline BiTeBr whose are comparable to that for crystals of bismuth telluride, which now is the base thermoelectical material at temperatures close to 300 K. The new data obtained in this study are very important to open prospects for increasing the efficiency of existing thermoelectric devices.

Thermoelectric Performance of PEDOT:PSS/SWCNT Nanocomposite

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Keywords: *Thermoelectric, PEDOT:PSS, SWCNT, Organic Thermoelectric.*

Abstract:
This paper reports the fabrication and thermoelectric performance of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/single-walled carbon nanotubes (SWCNTs) nanocomposite. PEDOT:PSS which is a conductive and electrochemically, thermally stable polymer has been synthesized as a main matrix polymer with single-walled CNTs (SWCNTs) as fillers to give more electrical conductivity for high thermoelectric figure of merit, ZT.
Typical thermoelectric materials have been inorganic semiconductor materials in which there are trade-offs between the electrical conductivity and the Seebeck coefficient so that a lot of efforts are required to find the optimized concentration of carriers. And also those materials are so toxic and too expensive to be utilized for the mass production. Therefore, polymers have been tried as thermoelectric materials because of their low cost and high processability.[1,2] Considering the thermoelectric figure of merit, $ZT = S^2\sigma T/k$ where S denotes the Seebeck coefficient, σ is the electrical conductivity, k is the thermal conductivity, and T is absolute temperature, polymers have a potential for good thermoelectric material due its low thermal conductivity of polymers. Especially PEDOT:PSS which has good electrical conductivity is proper material for thermoelectric applications.
In this experiment, SWCNT are dispersed by a solution of sodium dodecyl sulfate (SDS) and mixed with PEDOT:PSS. Thermoelectric properties which consist of electrical conductivity, Seebeck coefficient, and thermal conductivity were measured as a function of SWCNT concentration at room temperature. Concentration of SWCNT was from 40wt% up to 90wt%. The electrical conductivity was increased from 590 S/cm to 1871 S/cm by increasing SWCNT concentration up to 80wt%, while the Seebeck coefficient and thermal conductivity remained insensitive to SWCNT concentration. The Seebeck coefficient is around 20 μV/K and thermal conductivity is 0.25~0.4 W/mK. Maximum thermoelectric figure of merit (ZT) is 0.003 for PEDOT:PSS and 0.07 for PEDOT:PSS with SWCNT concentration of 80wt%.

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Thermoelectric properties of ScN thin films

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Keyword: *thin film, transition metal nitrides, thermoelectric properties*

Abstract:
Transition metal nitrides are promising for high temperature thermoelectric materials because of their high thermal stability, corrosion resistance, and their electrical properties which vary over a wide range from semiconducting to metallic depending on the transition metal elements. However, they are relatively unexplored to date for this purpose. Here, we have investigated the thermoelectric properties of ScN thin films grown by reactive dc magnetron sputtering in Ar/N_2 on a single crystal $Al_2O_3(0001)$. All films exhibit n-type behavior. High purity ScN films show high Seebeck coefficient ~90 μV/K and low electrical resistivity ~2.94 μΩ·m yielding a remarkably high thermoelectric power factor of ~2.5×10^{-3} W/(m·K^2), corresponding to an estimated thermoelectric figure of merit of ~0.2 at 800 K, using the thermal conductivity of ScN thin film material. We also demonstrate that the thermoelectric properties are highly sensitive to composition and impurities. Different Ar/N_2 flow rate ratios, gas pressure and target conditions were tested resulting in films with various crystal qualities, composition and impurities of for instance oxygen. All films contain trace amounts of F originating from the Sc target. It is found that the impurity level and crystal quality of the ScN tend to have very limited effect on the Seebeck coefficient while the electrical resistance is strongly affected. Generally, increased nitrogen flow in sputtering gas resulted in increased resistivity. However it was also found that the electrical resistance tends to increase with increased crystal imperfections related to defects and impurities.

Preparation routes and thermoelectric properties of $FeGa_3$

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Keywords: *$FeGa_3$, grain boundaries, spark plasma sintering, thermoelectric*

Abstract:
New studies on the thermoelectric properties of $FeGa_3$ have been reported recently. The investigations of several groups showed a relative low thermoelectric efficiency for the pure binary compound [1-3]. Our investigations on tuning the charge carrier concentration in $Ru_{1-y}In_3$, isostructural to $FeGa_3$, revealed a significant improvement of the figure of merit *ZT* by substitution of indium by tin or zinc [4]. For this reason we reinvestigated $FeGa_3$ and developed different preparation routes to achieve single-phase materials, which can be used for further substitution experiments.

A liquid-solid-reaction with subsequent SPS treatment was performed, according to the reported procedure for $RuIn_3$ [5], yielding polycrystalline materials. Crystal growth experiments with gallium as flux medium were carried out and yield crystals of high quality. The influence of the grain boundaries on the thermoelectric properties can be determined by comparing the measurements on the poly- and single-crystalline materials. Furthermore we developed a fast direct synthesis route via SPS in two steps, involving first the reaction and second the compaction of the the resulted product. Elemental gallium was handled for the first time for reactions inside the SPS equipment.

X-ray powder diffraction, chemical and metallographic analysis were performed in order to determine the exact composition. The different synthesis methods lead to different amount of grain boundaries, their influences on the thermoelectric properties is discussed.

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Surface state effects on the thermopower of 30- to 200-nm diameter bismuth nanowires

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Keywords: *topological; surface, Rashba*

Abstract:
Many thermoelectrics like Bi and Bi(2)Te(3) exhibit Rashba spin-orbit surface bands [1] for which topological insulator behavior consisting of ultrahigh mobilities [2] and enhanced thermopower for solid-state energy conversion has been predicted. Most of the experimental evidence comes from angle resolved photoemission spectroscopy. There are few experimental realizations that demonstrate this behavior in electronic transport. Bi nanowires realize surface-only electronic transport since they become bulk insulators when they undergo the bulk semimetal-semiconductor transition as a result of quantum confinement for diameters close to 50 nm. We have studied 20-, 30-, 50- and 200-nm trigonal Bi wires via coupled measurements of resistance and thermopower from 4 K to 300 K.[3] In this work, the wires were also studied via low temperature magnetoresistance for fields up to 9 T. Shubnikov-de Haas magnetoresistance oscillations caused by surface electrons and bulklike holes enable the determination of their densities and mobilities. For 50 nm, a high degree of suppression of the bulklike contribution is achieved; in other words in 50-nm nanowires the surface conduction dominates over holes. Surface electrons are observed to have high mobilities exceeding 2 $m^2sec^{-1}V^{-1}$ and to contribute strongly to the thermopower, dominating for temperatures $T<$ 100 K. The surface thermopower is $-1.2\ T\ \mu V/K^2$, a value that is consistent with theory raising the prospect of developing nanoscale thermoelectrics of high figure of merit based on surface bands. In this presentation, we will review electronic transport including thermopower in topological insulators and also present our recent work where, using the same procedures as in [3], we test Te and Sn doped Bi nanowires in order to further improve the thermoelectric properties of the nanowires.

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Synthesis and Thermoelectric Properties of layered CdI_2 type compounds

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Abstract:
Thermoelectricity is nowadays considered as a plausible way to produce "clean" electrical energy from virtually any kind of waste heat. However, the need for always higher devise efficiency combined with the mandatory lowering of the cost of the watt thermoelectrically produced, help maintaining upstream material research. Material development thus passes by the discovery of novel phases. In fact, the past few years have witnessed the emergence of new families of compounds, some of which are now regarded as promising thermoelectric materials. Development of new materials with higher efficiency is thus one of the main current interests in thermoelectric research. Narrow band gap semiconductors are good candidates for thermoelectric applications, because such materials have large Seebeck coefficient, reasonably high electrical conductivity and low thermal conductivity. Keeping this in consideration we have chosen to investigate systems having a CdI_2-type hexagonal layered structure. This layered structure is flexible and ideal for intercalating various chemical species, mostly because of the weakly bonded layers. Moreover, there are numerous compounds crystallizing in such a structure type and we have decided to focus our investigation on transition metal selenides for their rather semiconducting properties capable of generating promising thermoelectric properties at medium temperatures. We therefore embarked in the systematic study of $CrSe_2$ and $TiSe_2$ type systems with different intercalated species as well as different substitutions in the CdI_2 type layers. Our first results show the potential of such structure for generating potentially efficient thermoelectric materials.

Semiconducting Glasses: A New Class of Thermoelectric Materials?

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Keywords: *Thermoelectric materials; Semiconducting glasses, Thermoelectric glasses*

Abstract:
The development of the "Phonon Glass and Electron Crystal" (PGEC) idea led to a better understanding of the mechanisms affecting the phonon propagation, without altering the electrical charge propagation. Several general rules to increase the thermoelectric efficiency were launched, the most important ones being the use of compounds with complex crystal structures, the presence of heavy atoms weakly bounded to the structures, the existence of inclusions and/or impurities, the formation of solid solutions and the existence of a large number of grain boundaries.

Glasses can have most of these characteristics. However, the high degree of disorder usually produces broad electronic bands (leading to low Seebeck coefficients) and large electron scatterings (implying low electrical conductivities) and, consequently, low power factors. Therefore, the question if there is any type of glasses suitable for thermoelectric applications must be raised.

We have recently showed that some semiconducting glasses can have interesting thermoelectric properties [1,2]. In this contribution a review on semiconducting glasses for thermoelectric applications will be made, being presented several examples of semiconducting glasses showing high Seebeck coefficients, very low thermal conductivities and tunable electrical conductivities. In particular, the case of chalcogenide glasses will be stressed, pointing for this family of glasses as a good candidate for high-performance thermoelectric materials.

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Advanced High Temperature Thermoelectric Materials for Space and Terrestrial Power Generation Applications

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Keywords: *Thermoelectric, Energy Conversion, Power Generation*

Abstract:
In addition to the well-established need for highly reliable space power systems, there has been recently renewed interest in developing practical new materials capable of efficient thermal-to-electric conversion of high grade heat sources (up to 1300 K), generated through fossil fuel combustion or as a waste exhaust stream. Proven state-of–practice $Si_{0.8}Ge_{0.2}$ alloys have a combined dimensionless figure of merit (ZT) value of only 0.55 when averaged over operating temperatures of 1275 K to 575 K. In addition, the significant Ge content precludes their use for large scale terrestrial applications due to cost considerations.

We present an overview of collaborative research efforts to identify and characterize advanced bulk thermoelectric materials capable of tripling average ZT values while maintaining reliable operation for more than 15 years at temperatures up to 1300 K. The first research area concerns two families of very low lattice thermal conductivity refractory rare earth compounds, based on n-type $La_{3-x}Te_4$ and p-type $Yb_{14}MnSb_{11}$. We report on recent experimental results, guided by first principle electronic structure calculations, in tuning the properties of these rare earth compounds through suitable chemical substitutions and discuss the potential for other refractory materials to generate high ZT values. The other main research area focuses on engineering state-of-the-art materials such as Si-Ge alloys, PbTe, skutterudites and silicides by forming bulk homogenous and composite 3-D nanostructures. Such materials present orders of magnitude increases in the density of interfaces, thus scattering phonons very effectively and leading to very large reductions in lattice thermal conductivity values, even though it has proven difficult to truly decouple thermal and electrical transport effects. Other mechanisms leading to significant improvements in electrical properties are also discussed.

An assessment of the maturity of selected materials for potential integration into high efficiency long life and thermally stable thermoelectric power generation devices is presented.

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Overview: German Priory Program on Nanostructured Thermoelectric Materials

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Keywords: *nanostructures, priority program, thermoelectric characterisation*

Abstract:
The purpose of the scientists within this Priority Program SPP 1386 „Nanostructured Materials" will be the development of new thermoelectric systems by using nanostructured materials funded by the German Science Foundation (DFG) until 2015. Since June 2009 finical support has been provided for 18 cluster projects including the nationwide participation of 36 German groups with a total amount of 14 M$. Within this Priority Program scientific issues concerning physics, nanotechnology and micro system technology, measurement and energy technology as well as material sciences are connected with each other. This priory program has reestablished the fundamental research oriented activities on thermoelectric nanostructures and materials at universities in German and is one of the largest research networks on thermoelectricity in Europe. In the presentation we will give an overview about the concept and goals of this priority program and present a summary of recent research highlights originated from the SPP 1386 activities.

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Synthesis, characterization and thermoelectric properties of fine grains Gd-doped ZnO

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Keywords: *thermoelectric, ZnO oxide, sol-gel, SPS*

Abstract:
Oxides, composed of nontoxic, naturally abundant, light, and cheap elements, are expected to play an important role in extensive thermoelectric applications.[1] Among them, ZnO-based materials are considered one of the best n-type thermoelectric oxides, with a thermoelectric figure of merit that reaches ZT = 0.65 at high temperature.[2] Our group is interested in improving the thermoelectric properties via doping with rare earth ions.

In this study, we report on the preparation of $Gd_xZn_{1-x}O$ (nominal x = 0.0005 to 0.03) nano-size powders by using the modified-Pechini method. Experimental data (XRD, FEG-SEM) indicate that Gd incorporates into the ZnO wurzite structure as well as the diminution of the grain size with increasing of Gd nominal concentration (down to 20 nm for x = 0.03). Attempts to dope higher Gd quantity (nominal 5 at. %) revealed unsuccessful with the formation of Gd_2O_3. The powders are then densified into pellets via Spark Plasma Sintering (SPS), with an increase of the grain size up to 50-180 nm. We observed Gd_2O_3 phase segregation after SPS step for high Gd doped concentrations (starting from 1 at. %). Temperature-dependent thermoelectric properties have been measured with two distinct conditions: as-obtained after SPS; and with a post-SPS annealing in air. The obtained results suggest the formation of defects, during SPS process. After a post-SPS heat treatment, the best properties at room temperature are observed for nominal 0.2 - 0.3 at. % Gd-doped ZnO, with an electrical resistivity of about 1.10^{-2} ($Ohm.cm^{-1}$) and Seebeck coefficient of -160 $\mu V.K^{-1}$, corresponding to a power factor ($S^2.\sigma$), ~ 0.28 $mW.m^{-1}.K^{-2}$. Therefore, this family of materials is promising and is worth being studied in more detail.

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Controlling Microstructure of Metal Oxides for Efficient Thermoelectric Materials for Energy Harvesting

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Keywords: *nanocomposite; ZnO; phonon scattering; thermal conductivity*

Abstract:
Thermoelectric (TE) conversion is one of the most promising energy options for better overall energy efficiency, which is attracting much more attention after the nuclear power plant crisis in Fukushima, Japan, caused by the massive tsunami attack on March 11. The threat of radioactive substances realized by the crisis is likely to shift the energy policy of Japan and also several European countries more to renewable energies. However, conventional TE materials such as Bi_2Te_3 and PbTe based on Bi, Te, and Pb are unlikely to prevail for wide commercialization because of the toxicity, poor heat durability, and low abundance of the comprising elements, particularly for those containing Te.

In terms of durability and safety at high temperature in air, metal oxides are most attractive. In fact, several oxide materials such as In_2O_3, $CaMnO_3$, ZnO, $SrTiO_3$, $NaCoO_2$, and $Ca_3Co_4O_9$ have been reported to show promising thermoelectric performance. Nevertheless, the light constituting element, oxygen, in oxide materials results in a high sound velocity of acoustic phonons carrying heat, leading to high thermal conductivity of oxides particularly at around room temperature.

Microstructure control is one of the prospective ways to effectively reduce the thermal conductivity with maintaining a sufficiently high electrical conductivity. In this paper, microstructure control of ZnO-based oxides by multinary doping and nanovoid formation will be reported. Upon the binary doping of ZnO with Al and Ga [1], the amount of a Ga-related impurity phase is revealed to show an excellent quantitative agreement with the decrease in the thermal diffusivity. Furthermore, multinary doping with Al, Cu, and Ga results in a substantially low thermal conductivity values just 2–3 times higher than the theoretical minimum of the thermal conductivity [2], showcasing an effective thermal conductivity reduction by a nanocomposite structure in bulk oxides. The phonon scattering will be discussed in terms of the mean free path and microstructure in the oxides.

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Chemical peculiarities of layered sodium cobaltates

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Keywords: *sodium cobaltate, stability, exfoliation*

Abstract:
The research of oxide materials as candidates for thermoelements in thermoelectric modules was spurred by the discovery that single-crystalline semiconducting $NaCo_2O_4$ exhibits a large thermoelectric power, which was reported by Terasaki et al in 1997 [1]. Since then several scientific papers, mostly dealing with electronic structure, transport properties and magnetism of $NaCo_2O_4$ have been published. It appears, however, that its chemical properties have somewhat been neglected.

In the literature the $NaCo_2O_4$ and related $Na_xCo_2O_4$ compounds have been described as possible candidates for the p-type branch in oxide thermoelectric modules. It is argued that, compared to for instance binary tellurides, the advantage of oxide-based thermoelectric modules would be their thermal stability which would enable energy harvesting from "waste heat" generated by systems that operate at high temperatures.

Issues such as high oxidation state of Co and volatility of Na-containing compounds render sodium cobaltates prone to decomposition at elevated temperatures. Furthermore layered crystal structure of $Na_xCo_2O_4$ enables interacalation of molecules such as water, which can lead to exfoliation and thus degradation of the material. We have systematically studied the formation of $Na_xCo_2O_4$ compounds and their chemistry under atmospheric conditions with respect to high-temperature and long-term stability.

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Influence of processing conditions on the thermoelectric properties of $La_{1-x}Sr_xCoO_3$ (x=0, 0.05)

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Keywords: *sintering temperature*

Abstract:
In the search for new thermoelectric materials, the metal transition oxides have received significant attention recently because of their inherent chemical and thermal stability especially at high temperatures. Among the thermoelectric oxides, a promising one is the Sr-doped LaCoO3 (x~0.05) compound which has been reported to exhibit one of the highest ZT values at room temperature [1]. The high ZT value is related to the high thermopower value that has been reported by several groups. Androulakis *et al*. have reported S_{RT} =710μV/K for $La_{0.95}Sr_{0.05}CoO_3$ prepared via citrate-gel and sintered at 1000°C [1], Kobayashi *et al*. have reported S_{280K} =710μV/K for single crystal $La_{0.95}Sr_{0.05}CoO_3$ [2]. On the other hand, several other groups have reported significantly lower thermopower values, for example, Zhang *et al*. have reported S_{RT}=250μV/K for $La_{0.95}Sr_{0.05}CoO_3$ prepared via citrate gel and sintered at 1000°C [3]. This discrepancy in the value of measured thermopower for apparently similar materials is most likely related to microstructure issues. In order to clarify the effect of processing conditions on the thermoelectric properties of $La_{1-x}Sr_xCoO_3$, $LaCoO_3$ and $La_{0.95}Sr_{0.05}CoO_3$ pellets sintered at different temperatures have been investigated.

$LaCoO_3$ and $La_{0.95}Sr_{0.05}CoO_3$ powders were prepared using the citrate-gel (Pechini) process. The obtained powders were pelletized and then were sintered at 800°C, 1000°C, 1100°C and 1300°C. All samples were characterized by means of X-Ray Diffraction and Scanning Electron Microscopy in order to investigate their structural and morphological properties.

The thermoelectric and magnetic properties were measured in a wide range of temperatures (2- 350K). We will present the influence of the processing conditions on the magnetization as well as on the thermoelectric properties.

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The thermoelectric compound $Ca_3Co_4O_9$– synthesis and characteristics

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Keywords: *oxide thermoelectric materials, $Ca_3Co_4O_9$, synthesis, characteristics*

Abstract:
In the global search for renewable, green energy sources, thermoelectric (TE) materials, with their ability to convert heat directly into electrical energy, promise the only route to effectively overcome the problems of utilizing waste heat, which is widely dispersed and varies a great deal in intensity.

In recent years, increasing attention has been given to oxide thermoelectric materials, which exhibit a high thermal and chemical stability, are oxidation resistant and non-toxic. Furthermore, they are made of abundantly available and low-cost elements. Among the oxide TE materials the Co-based oxides with a misfit layered structure, such as $NaCo_2O_4$, $Ca_3Co_4O_9$, $Ca_3Co_2O_6$, and $Bi_2Sr_2Co_2O_y$, appear to be very promising.

In this work we studied the synthesis and characteristics of the $Ca_3Co_4O_9$ compound, which shows, according to the literature data, a good thermoelectric performance. This can be further improved through a microstructure optimization, texturing and the control of the carrier density and mobility by the incorporation of selected dopants.

The solid-state formation of single-phase, dense and homogenous samples of the $Ca_3Co_4O_9$ and $Ca_3Co_2O_6$ compounds at relatively low temperatures is rather slow and complicated, so the methods for the preparation, pre-treatment and pre-reaction of the mixtures are critical for a successful synthesis.

The samples were prepared with a classical ceramic procedure from oxide powder of $CaCO_3$ and Co_3O_4 in various molar ratios ranging from 8:4 to 17:4. Part of the as-prepared mixtures was mechano-chemically activated by high-energy ball milling for 2 to 10 hours. Starting powder mixtures with the same compositions were also prepared from fine, attrition-milled powders of $CaCO_3$ and Co_3O_4. Part of the samples from attrition-milled powders was subsequently mechano-chemically activated. The samples were then sintered at different temperatures in the range from 760°C to 920°C.

The morphology of the starting powder mixtures, their thermal behaviour, phase compositions and the microstructures of the sintered samples were analysed using granulometric analysis, DTA/TG analysis, x-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDXS). The microstructural characteristics, phase composition of the differently prepared samples and the influence of the preparation on the formation of the $Ca_3Co_4O_9$ phase will be presented and discussed.

Modulated crystal structure of layered cobaltate α'-Na_xCoO_2 (x~ 0.75)

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Keywords: *sodium cobaltates, incommensurate structure, superspace group*

Abstract not presented

Growth and characterization of high-quality thermoelectric $Na_{0.65}CoO_2$ thin films

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Keywords: *Thermoelectric, oxide, epitaxial, thin film*

Abstract:
Nanostructured materials and superlattices have attracted a lot of attention for thermoelectric research because of the significantly lowered thermal conductivity, due to enhanced phonon scattering at interfaces. Although most of these studies focused on traditional thermoelectric materials, such as Bi_2Te_3, several alternatives are available such as the skutterudites, clathrates and oxide materials.
We present the growth and characterization of thin films of Na_xCoO_2, which is one of the most promising thermoelectric oxide materials. Single oriented thin films with a low surface roughness are grown by Pulsed Laser Deposition (PLD) on various substrates, such as Al_2O_3, $LaAlO_3$ and $DyScO_3$. Depending on the substrate material a preferred in-plane orientation is observed, indicating that the films are not only single oriented, but also in-plane strained to the substrate. Based on X-Ray Diffraction (XRD) analysis, the expected composition of the samples is $Na_{0.65}CoO_2$.
Time-dependent electrical transport measurements and X-ray Photoelectron Spectroscopy (XPS) have shown that those samples are chemically unstable in ambient conditions. Due to a reaction of Na from the sample with moisture (from air) NaOH is easily formed, which in turn reacts with CO_2 into Na_2CO_3. We present a method to obtain chemically stable $Na_{0.65}CoO_2$ thin films, in ambient conditions, by the growth of an in-situ Al_2O_3 capping layer, which stops the reaction of Na from the sample and stabilizes the intrinsic properties.
Electrical transport properties and the thermopower of these samples have been studied. At room temperature a resistivity and thermopower of respectively 1.3mΩcm and 70.5 μV/K are measured. Based on an estimated thermal conductivity of 4 W/mK for thin films, a ZT value of 0.027 at room temperature is calculated. This is comparable to values reported for single crystals, demonstrating the effectiveness of our growth method to fabricate high-quality thermoelectric thin films of oxide materials.

Thermoelectric characteristics of SiGe nanowire arrays as a function of Ge concentration

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Keywords: *SiGe nanowire; Seebeck coefficient; Thermoelectricity*

Abstract:
Nanostructures have been proven to greatly enhance the thermoelectric figure of merit (ZT) of semiconductors in comparison with their bulk. This improvement is due to the increased phonon scattering at the interfaces that reduces the thermal conductivity. It has been shown [1] that single Si nanowires (NWs) exhibit a 60 times higher ZT than Si bulk. In addition to the use of nanostructures to boost ZT, the introduction of alloys can further reduces the thermal conductivity via alloy scattering without deteriorating the other performance parameters such as Seebeck coefficient and electrical conductivity. Notwithstanding the promising results obtained on single NW, their thermoelectric application is complex and has not yet been widely investigated. In this work, we propose to use an array of vertically upstanding SiGe/Si NWs for the thermoelements.

$Si_{1-x}Ge_x$ layers were grown on lowly doped p-Si substrates using RP-CVD. A linearly graded relaxed $Si_{1-x}Ge_x$ layer was deposited first to overcome the lattice mismatch between Si and SiGe, followed by a 3 µm thick constant composition layer. Three different Ge concentrations of x = 20%, 30% and 40% are available. Arrays of NWs were prepared using metal assisted electroless chemical etching [2]. The etching process is optimized to avoid the removal of the SiGe layers during the chemical etching. SEM and EDX techniques are used to characterize the SiGe containing NWs.

The Seebeck coefficient and thermal conductivity of the SiGe NWs are measured via a comparative technique. A known p-Si control sample is used to estimate the temperature drop across the Cu/sample interfaces in the set-up and is subsequently used to estimate the heat flux entering the sample-under-test. These measurements show that the SiGe containing NWs exhibit higher Seebeck coefficient than the bulk material. The longer SiGe NW array gives a higher Seebeck coefficient. At the same time we observe that the maximum temperature difference that can be maintained across the sample increases with increasing Ge concentration and with increasing NW length. This indicates that the thermal conductance is decreasing with increasing Ge concentration and NW length.

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Lattice dynamics on low dimensional chalcogenides

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Keywords: *phonon scattering; texture, nanowires*

Abstract:
Lattice dynamics plays a crucial role in the operation of room temperature thermoelectric materials, such as chalcogenide compounds. To retain the operating thermal gradient, a low thermal conductivity is required which leads to enhanced thermoelectric efficiency.

A way to decrease thermal conductivity is by introducing phonon scattering mechanisms, e.g. nanostructuration. In parallel, theoretical studies on the effects of dimensionality [1] predict an enhancement of the figure of merit for dimensions in the ~10 – 50 nm range.

On one hand, lattice dynamics measurements on free standing ensembles of low dimensional structures can only be realized by scattering methods. On the other hand, a hindering parameter in understanding the lattice dynamics on such ensembles is related to the inherent high texture of many tellurides.

Measurements of phonon assisted nuclear resonance absorption of γ-rays [2] on Bi_2Te_3 nanowires with diameter between 30 and 200 nm will be reported. The extracted tellurium specific density of phonon states as well as the corresponding thermodynamical parameters, e.g. speed of sound, force constants, atomic displacement parameters, show a dimensionality dependence. Comparison with previously measured bulk Bi_2Te_3 [3] will be discussed.

Synchrotron radiation data will be presented for the same nanowires and an overview of the texture distribution will be given.

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Influence of Hot Uniaxial Pressing process parameters on microstructure and thermoelectric properties of N-type Silicon-Germanium alloy

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Keywords: *Hot Uniaxial Pressing (HUP), thermoelectricity, microstructure, porosity*

Abstract:
The optimization of powders preparation and consolidation process leads to the achievement of a high thermoelectric figure of merit (ZT=1.3 at 1050K) in an n-type silicon-germanium (SiGe) alloy hot pressed at low heating rate. Our powder has been prepared by high-energy ball milling and then uniaxially hot pressed in a vacuum graphite furnace. A parametric study has been performed to investigate the temperature, stress and dwelling time influence on the densification rate and thermoelectric performances. It has been experimentally observed that pressing conditions can considerably limit nanograin growth. Preserving nanostructuring ensures an increase of the phonon scattering due to grain boundaries effect, and so reduces the lattice thermal conductivity. Unfortunately, the electric conductivity decreases by the same order and finally the same figure of merit has been obtained for samples with different grain size prepared at different process temperatures (between 1050°C and 1220°C). Working on grain boundaries engineering to enhance charge carriers mobility or nano particles incorporation seems to be a promising way in addition to limiting nanograin growth with a densification process control.

We also investigated the effect of porosity on the figure of merit. Porous samples have enhanced Seebeck coefficients due to energy filtering and low thermal conductivity. However, the bulk one remains thermoelectrically better due to a significant degradation of electrical and thermal conductivity ratio in porous samples. Once more, it is expected that grain boundaries quality plays a major role on transport properties which could be enhanced with an adapted thermal treatment.

Microstructure for the Determination of the Seebeck Coefficients of Doped Poly-Si Thin Films

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Keywords: *Seebeck Coefficient, Poly-Si, Microstructure, Thin Films*

Abstract:
For commercial, integrated thermoelectric sensors and transducers, poly-silicon (poly-Si) thin films are of particular interest due to their availability in standard microfabrication processes. Methods for the local determination of material properties are needed, e.g., in view of the homogeneity over the substrate or the self-calibration of integrated microsystems [1]. We report a simple planar microstructure for the determination of the Seebeck coefficients of doped poly-Si thin films against aluminum (Al).

The test structures are fabricated from a phosphorous (n) or boron (p) doped LPCVD poly-Si and an Al metal layer separated by a dielectric layer of Si_3N_4 on Si substrates. The structures consist of single poly-Si/Al-thermoelements used for the measurement of the thermopower while a temperature gradient is applied by an integrated poly-Si heater. The temperatures of the hot and cold contact of the thermoelement are monitored by integrated resistive poly-Si temperature sensors adjacent to the contacts.

Finite element (FE) simulations are used for the modeling of the temperature distribution in the contact area of the thermoelement and within the temperature sensors. Based on the simulations, an appropriate design of the device was identified. The design is capable of compensating temperature differences between the contacts of the thermoelements and the temperature sensors. The FE simulations show a temperature difference between the sensor and the contact of less than 0.1 K.

The thermopower of n- and p-doped poly-Si is measured in a temperature range from 300 K to 350 K which is typical for room temperature applications. Thermopowers of −78 µV/K and 186 µV/K were determined for n- and p-doped poly-Si at 300 K. The results are in good agreement with the Seebeck coefficients reported for similar thin films [2, 3].

Furthermore, an alternative type of the test structure is fabricated using additional bulk micromachining by anisotropic KOH-etching of silicon. The alternative type enables the application of higher temperature gradients along the thermoelement and thus provides a higher output voltage.

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Anisotropy analysis of thermoelectric properties of $Bi_2Te_{2,9}Se_{0,1}$ prepared by SPS method

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Keywords: *bismuth telluride, thermoelectric properties, anisotropy, scanning thermoelectric microprobe, SPS method*

Abstract:
The *n*-type $Bi_2Te_{2,9}Se_{0,1}$ materials were synthesized by the direct fusion technique. The polycrystalline samples have been fabricated by the uniaxial pressing of powders by spark plasma sintering (SPS) method. The materials were subjected to the heat treatment in H_2-Ar atmosphere at 480 K, for 24 h.

The influence of preparation conditions on the anisotropy of electrical and thermal properties was thoroughly studied for the direction perpendicular and parallel to the pressing force. The microstructure and the chemical composition of both types of samples were examined using a scanning microscope (SEM) equipped with an X-ray energy dispersion detector (EDX). The XRD method was applied for the phase analysis of materials, as well as, for determination of preferred orientation of $Bi_2Te_{2,9}Se_{0,1}$ grains. The Seebeck coefficient distribution was studied by the scanning thermoelectric microprobe (STM). Temperature dependences of thermoelectric properties (thermal and electrical conductivities, Seebeck coefficient) were measured over the temperature from 300 K to 550 K.

The statistical analysis of results has shown strong influence of pressing force direction both on structural and transport properties. The applied heat treatment of materials significantly improves their thermoelectric figure of merit. Particularly, it was found that annealing in H_2-Ar atmosphere leads to enhancement of the ZT three times up to ~0.7 at 370 K in direction perpendicular to the pressing force.

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Temperature-controlled formation of microstructure of n-type bismuth telluride with SPS method

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Keywords: *bismuth telluride, microstructure, spark plasma sintering*

Abstract:
Bismuth telluride due to its great ratio c/a of the crystal unit cell physical properties demonstrate strong inhomogeneity. Additionally the thermodynamics of crystallite growth depends on growing process method and parameters and is not fully clear yet. The microstructure of produced material determines its electric and heat transport properties and therefore is subject of interest as potential way for introducing improvements.

In this work, bismuth telluride was synthesized by mechanical alloying of stoichiometric quantities of Bi and Te powders. The phase purity, crystallite and particle size of the powder were analyzed by XRD, SEM, EPMA and laser diffraction methods. To determine the influence of temperature on microstructure, disk-shaped samples where produced with spark plasma sintering (SPS). The sintering was performed with the same pressure (16MPa) but different temperatures in the range from 240^{o}C to 450^{o}C which corresponds to 0.6 – 0.85 of melting temperature (absolute scale) and interval of ~45^{o}C. The sintering time, heating and cooling ratio were the same for each sample. The microstructure of samples was then studied by XRD and SEM showing that the crystallite growing ratio and then changes of morphology is not a monotonic function of sintering temperature. Analysis of peaks width corresponding to lattice planes (00.6) and (11.0) confirms that crystal growing ratio along and perpendicular to hexagonal axis depends on process temperature and is not homogeneous. The temperature dependencies of electric resistivity and absolute Seebeck coefficient were also measured from room temperature up to 200^{o}C for all samples excluding one sintered at 240^{o}C due to its fragility. The resistivity of sample produced at 290^{o}C exhibits negative temperature coefficient. The resistivity of the others increases with temperature and the thermal coefficient of resistance is higher for samples sintered at higher temperatures. The highest value of the Seebeck coefficient equal to -142uV/K at 175^{o}C was achieved for the sample prepared at 450^{o}C.

Basing on the obtained results the second stage of investigation was devoted to preparation of samples with structure suitable for further hot-press deformation. Two-steps procedure with initial sintering at 290^{o}C and then at 410^{o}C with accompanying increase of pressure up to 50MPa was found to give material consisting of well formed flake-shaped grains.

Thermal Analysis Methods for the Characterization of Thermoelectric Materials

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Keywords: *Thermal Analysis, IV-VI semiconductors, thermoelectric, thermophysical properties*

Abstract:
The figure of merit $ZT = (S^2\sigma\lambda^{-1})T$ describes the efficiency of thermoelectric materials, with S = Seebeck coefficient, σ = electrical conductivity, λ = thermal conductivity and T = absolute temperature . Another aspect for the application of thermoelectric materials is their thermal and chemical stability during operation.

Classical Thermal Analysis methods like Dilatometry, Differential Scanning Calorimetry (DSC) and Laser Flash Analysis (LFA) deliver the thermal expansion, specific heat and thermal conductivity of materials. With these data, the thermal conductivity can be calculated by means of the formula: $\lambda(T)=a(T)*c_p(T)*\rho(T)$ with c_p = specific heat and ρ = density

To study the thermal stability of materials, a thermobalance or thermogravimetric analyzer (TGA) is often employed. Simultaneous combination of TGA and DSC (which is called STA, Simultaneous Thermal Analysis) and a mass spectrometer (MS) increases the information content exponentially. Phase transitions (solid-state transitions, melting, etc.) can be detected together with the mass change. With the help of an MS coupling, the evolved gases can be identified and often quantified simultaneously with the corresponding mass changes and caloric effects.

Last but not least, the Seebeck coefficient can be determined by commercially available Seebeck measuring devices which measure the temperature-dependent electrical conductivity and the thermoelectric voltage.

In this contribution, the above-mentioned thermal analysis methods and a new Seebeck instrument are explained together with examples related to IV-VI semiconductor materials.

Thermoelectric Characterization of Si/Ge Superlattices

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Keywords: *Si/Ge superlattice cross plane, thermal conductivity, electrical conductivity*

Abstract not presented

Impact of internal thermal bypasses in high temperature TE-modules

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Keywords: *Thermal bypass; high temperature TE-modules; convection; thermal radiation*

Abstract:
High temperature thermoelectric generators (TEG) enable elevated conversion efficiencies, but require suitable materials and smart packaging. However, internal thermal bypasses given by the setup of the modules may reduce the efficiency as compared to the theoretical prediction. In a classical TE-module two ceramic plates are separated by the thickness of the p- and n-doped semiconductor legs. A bypass heat current can flow through the gaps between the semiconductor legs, carried by convection as well as thermal radiation. The significance of both contributions scales with the temperature difference. We present experimental results to evaluate the impact of either bypass.

The influence of convection losses is determined by changing the atmospheric pressure while recording the TE-module conversion efficiency. Thermal radiation losses are extracted from measured emissivity values for a given module geometry.

Based on our results we propose optimized module geometries, encapsulation and altered material surfaces. Depending on temperatures and geometries the electrical output power could be increased by a factor of more than 1.25.

Preparation and characterisation of contacts for high temperature thermoelectric modules

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Keywords: *high-temperature, thermoelectric module, fabrication, contact*

Abstract:
Thermoelectric devices have been identified as promising converters for energy harvesting due to their capability to convert heat into electricity. A great amount of heat is released from internal combustion engines, which are nowadays fairly abundant in the industrial and automobile sectors and is considered an important application for thermoelectric devices, especially heat recovery from automobile exhausts. Materials able to work in the temperature range required for these applications, (up to 850 K) are available in a laboratory-scale, however they have to be assembled when fabricating a thermoelectric device (module), what implies the creation of contacts with suitable electrical and thermal properties. Due to the high temperature range, diffusion of metallic atoms occurring at the junctions producing poisoning and degradation of the materials, and differences in the thermo expansion coefficients that can lead to the appearance of cracks, can be more accentuated, resulting in poor efficiency modules.

In this paper we report the use of high temperature solder alloys that allow the fabrication of high temperature thermoelectric modules. As an initial approach, well-known Bi_2Te_3 thermocouples were fabricated using a ~ 300 ^{o}C melting point solder alloy. Secondly, junctions of promising thermoelectric materials for high temperatures were prepared employing a ~ 700 ^{o}C solder. The properties of the junctions are evaluated and the experimental procedure to obtain good contacts is described, providing a methodology for the fabrication of high-temperature thermoelectric modules.

Preparation and fabrication of film thermoelectric materials and micro-thermoelectric power generator by electrodeposition and MEMS technology

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Keywords: *electrodeposition, film thermoelectric materials, MTEG, performances*

Abstract:
p-type $(Bi, Sb)_2Te_3$ and n-type $Bi_2(Te, Se)_3$ film thermoelectric materials were prepared by electrodeposition from the solutions either containing Bi^{3+}, $HTeO_2^+$ and SbO^+ or containing Bi^{3+}, $HTeO_2^+$ and H_2SeO_3. XRD analyses show that the electrodeposited films possess a preferential crystal orientation along (015) after annealing at 250ºC for 12h. Based on the electrodeposited TE films, two micro-thermoelectric power generators (MTEG) with different thickness of the thermoelectric legs were fabricated by MEMS technology. The characteristics of the MTEG are its high packing density of thermoelectric legs and the thermal transferring direction along the legs, which are benefit for the MTEG to get higher output power and output voltage. The fabricating process involves mainly the following two steps: 1) Fabricating film thermoelectric components with thermoelectric legs connected electrically in series; 2) Integrating the film thermoelectric components together layer by layer and electrically in series. The maximum output power of the two MTEGs are 770μW/cm^3 and 357μW/cm^3 with the size of 30mm (length) × 2mm (width) × 1mm (thick) under a temperature difference of 20K condition at room temperature, separately. The results reveal that the thickness of the legs affects the output power and output current remarkably.

Acknowledgments: This work is co-supported by International Cooperation Project of Chinese Science and Technology Ministry (2009DFA62700) and Doctorial Fundation Project of Chinese Education Ministry (200800560002).

Reduced Energy Consumption by Massive Thermoelectric Waste Heat Recovery in Light Duty Trucks

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Keywords: *Heat recovery; Thermoelectric generator; Energy consumption; CO_2 emissions*

Abstract:
The main objective of the EC funded HEATRECAR project is to reduce the energy consumption and curb CO2 emissions of vehicles by massively harvesting electrical energy from the exhaust system and re-use this energy to supply electrical components within the vehicle or to feed the power train of hybrid electrical vehicles.

HEATRECAR is targeting light duty trucks and focuses on the development and the optimization of a Thermo Electric Generator (TEG) including heat exchanger, thermoelectric modules and DC/DC converter. The optimization is driven through the simulation of the energy flow including powertrain, thermal systems, electrical board net and auxiliaries.

The main objective of the project is to design, optimize and produce a prototype system to be tested on a 3t diesel truck. The base case is a Thermo Electric Generator (TEG) producing 1 KWel at 130 km/h.

We present the system design and simulation results such as energy efficiency and thermal power to be generated by the system. We discuss key drivers for the optimization of the thermal-to-electric efficiency, such as materials, thermo-mechanical aspects and integration. Based on the assessment result, the optimized TEG prototype design, which will be integrated into the Iveco Daily for final vehicle test runs, is presented.

Acknowledgments: Acknowledgements to the HEATRECAR project partners contribution : V.Monnet (Valeo), L.Holmgren (Thermo-Gen AB), Kilian Bartholomé (Fraunhofer –IPM), Miroslaw Brzoza (Robert Bosch GmbH), J. Reinschke and M. Honsberg-Riedl (Siemens).

Processing flexible thermo-generators based on Bi_2Te_3 nano-powders by the Spark Plasma Sintering SPS technique

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Keywords: *Thermoelectricity, Nano-powder, Sintering, Thermo-generator*

Abstract:
The fabrication of current thermoelectric generator (TEG) is a multi-steps process which requires the cutting and hand-assembling of very small thermo-elements and is time consuming. We report on a new and rapid way to build efficient thermo-generator based on n-type and p-type Bi_2Te_3 nano-materials embedded in a polymer matrix via one step Spark Plasma Sintering (SPS) process. n-type and p-type Bi_2Te_3 nano-powders are obtained through a mechanical alloying process leading to particle size of about 50 nm [1]. The flexible thermo-generator is assembled in one step by Pulsed Current Electrical Sintering (PECS) from a stacking of: 1) p-type powder, 2) special design of an electrical insulating polymer matrix and 3) n-type powder. The sintering temperature was 320°C under 50MPa and 5 minutes soak time [2]. After polishing the two sides of the thermo-generators in order to reveal series of n-type and p-type thermo-elements, electrical connections of these plots are made. Due to the fast sintering treatment by SPS, the nanostructure of thermo-elements is preserved. Flexibility has been tested by mechanical measurements. The thermoelectric characterizations of such TEG have been investigated leading to a generated output voltage of 51mV for 34 thermocouples in a temperature gradient $\Delta T \sim 14°C$.

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Acknowledgments: This work has been supported by the French National Agency (ANR) in the frame of its programme "Recherche Technologique Nano-INNOV/RT" (THERMOINNOV project n°ANR-09-NIRT-007). We thank Jean-Christophe Sangleboeuf from LARMAUR, University of Rennes 1, France for mechanical measurements.

Improving the conversion efficiency of thermoelectric generator through pulse mode operation

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Keywords: *thermoelectric modules, device performance*

Abstract:
This paper proposes a novel approach for improving the conversion efficiency of thermoelectric generators through "pulse model" operation. The theoretical outline for a thermoelectric generator operating under pulse model is presented. A calculation based on a material with ZT =1.5 shows that an increase in the conversion efficiency by ~ 40% can be obtained through pulse model operation. This is equivalent to a substantial increase of ZT from 1.5 to 2.7.

Interface contact resistivity and diffusion at high temperature of Al/Sb/Bi_2Te_3 element

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Keywords: *Bismuth telluride; interlayer, electrode, contact resistivity*

Abstract:
Currently the widely used thermoelectric module is based on Bi_2Te_3. In principle the module must work at temperatures lower than 180 °C due to the limitation of solder served as part of electrode, the relatively low temperature difference across the module would leads to low output and efficiency of converting heat energy into electricity. In this paper, we have developed a new high temperature electrode material for Bi_2Te_3. Al/Sb/Bi_2Te_3 element was fabricated by hot-press technique, in which Sb acts as interlayer. The interface as well as electrode was evaluated by SEM observation, EPMA, measurement of contact resistivity and shear strength. The electrode was found to be bonded well with Bi_2Te_3 material. The contact resistivity at Sb/Bi_2Te_3 interface is 3 μΩ-cm^2, which increases to 6 μΩ-cm^2 after aging at 300 °C for 20 days. The related microstructure change along with composition analysis will also be reported.

Exergetic analysis of a thermo-generator for automotive application: a dynamical approach of the efficiency.

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Keywords: *waste heat recovery, thermoelectric power generation, modelling, exergy*

Abstract:
It is well known that, when using car combustion engines, only a fraction of the burnt fuel energy actually contribute to drive the vehicle. Typical passenger vehicle engines run about 25% efficiency while a great part of the remaining energy (about 40%), is lost through the exhaust gases. This latter has a significant energy conversion potential since the temperature (more than 300°C) and the mass flow rate are high enough. Thus, direct conversion of heat into electricity is a credible option if the overall system is optimized.

This point is crucial since the heat conversion into work process is very sensible to any mismatching of the different parts of the system, and very sensible to the possible varying working conditions. All these effects constitute irreversibility sources that degrade the overall efficiency.

The exergetic analysis is an efficient tool for finding the root causes of theses irreversible processes. In order to investigate the performance of our automotive thermo-generator we propose an analysis of the exergy flow through the system under dynamic conditions. Taking into account the different irreversible sources such as thermal conduction and Joule effect, we are able to localize and quantify the exergy losses. Then in order to optimize the thermoelectric converter for a given vehicle, correct actions in term of design and working conditions can be proposed.

Performance characterization of high-efficiency segmented $Bi_2Te_3/CoSb_3$ unicouples for thermoelectric generators

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Keywords: *segmented thermoelectric unicouples, power generation, performance characterization, numerical modeling, skutterudites, bismuth telluride*

Abstract:
High efficiency segmented thermoelectric unicouples STUs made of Bi_2Te_3 and $CoSb_3$-based alloys have been developed. The performance parameters of elements were tested on the constructed set-up for selected temperatures ranging from 288 to 673K. Characterizations of electrical resistances of contacts and materials were made by scanning thermoelectric microprobe (STM). The extended numerical model of STU, which assumes i.e. thermal resistances and thermoelectric effects at junctions, as well as, inside segments (Thomson effect) was developed and its predictions were compared with experimental data. Calculations of the effects of thermal, electrical contact resistances and side heat losses on the performance of these STUs are presented and discussed.

The results of investigations indicate that constructed elements exhibit very high experimental maximal efficiency η_{max} = 9.3% and power density of 1.48 $W \cdot cm^{-2}$ for temperatures T_H = 673 K at hot shoe and T_C = 288 K at cold shoe. Measurements made by STM show very low electrical resistances of junctions from 16 to 22 $\mu\Omega \cdot cm^2$ which effect in excellent load parameters for STUs: I_{max} = 60 A (at $U_{out} \rightarrow 0$) and I_{opt} = 26 A for maximum power condition.

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Effective power factor and thermoelectric figure of merit

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Keywords: *classical thermoelectric theory; device modeling and simulation, effective performance parameters*

Abstract:
The work reviews and calculates effective values for the figure of merit and the power factor of a thermoelectric (TE) element which are obtained in the optimizing process of the performance parameter (power output and efficiency) of the element. Especially the difference to the classical Ioffe theory [1] is highlighted if a temperature and/or spatial dependence of the TE material coefficients (Seebeck coefficient, electrical and thermal conductivity) are taken into account.

The basis of the calculation is delivered by Domenicali's equation [2] which is valid in the framework of the classical Onsager-de Groot-Callen theory of thermoelectricity which is a kind of field theory for the electric field $\vec{E}(\vec{r},t)$ and the temperature field $T(\vec{r},t)$. In this theory of continua the particular case of chemically and physically constant material properties (CPM), first treated by Ioffe, is widely used for the determination of the performance parameters of TE systems. Ioffe's theory [1] is a good approximation for small temperature difference and/or small length of the TE element. Otherwise, especially for high temperature differences, the temperature dependence (physical inhomogeneity) and/or the spatial dependence (chemical inhomogeneity) of the material properties have to be considered in the calculation. These inhomogeneities are leading to different optimal performance parameters in comparison to the CPM due to e.g. the Thomson effect.

Analytical models either revisited from the literature or developed in previous work [3,4] especially for functionally graded materials (FGM, spatial dependence) and numerical calculations for real material data are given and are compared with the CPM to find effective values for the power factor and the figure of merit, respectively. The results are used to gain a better understanding how to prepare TE in a manner that optimal performance parameters are achieved under specific working conditions.

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Impact of novel thermoelectric materials on automotive applications

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Keywords: *Automotive; lightweight non-toxic materials; skutterudites; magnesium silicide*

Abstract:
Despite the fact that thermoelectric (TE) devices are compact, quiet, rugged, stable and very reliable, thermoelectrics have found only niche applications because they are also inefficient (less that 5% conversion efficiency is typical) and costly. The key to more widespread acceptance of thermoelectric is the development of materials that are capable of much higher conversion efficiency, but other fundamental materials parameters play a role not less important to open to large applications and markets. In particular the automotive sector requires low materials density, materials made from widely-available pure elements with very large supply chains, non-toxicity of elements and potential compliance with REACH and RoHS obligations and low raw material cost combined with low manufacturing costs.

The impact of novel TE materials on automotive application will be described focusing on promising nano magnesium silicide and skutterudites. Centro Ricerche FIAT activities both on thermoelectric waste heat recovery and interiors cooling will be presented.

CFD Modeling of Thermoelectric Generators in EGR-coolers

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Keywords: *thermoelectricity, heat transfer, CFD, EGR*

Abstract:
A large amount of the waste heat in the exhaust gases from diesel engines is removed in the exhaust gas recirculation (EGR) cooler. If this energy partially could be converted to useful electric energy using thermoelectric elements it would give a significant environmental and economical impact [1]. Introducing a thermoelectric generator (TEG) in an EGR cooler requires a completely new design of the heat exchanger and to achieve that, a good model is essential for this development.

The temperature varies both inside the thermoelectric elements and along the heat exchanger [1]. Since the TE materials has different optimal working temperature a combination of materials would increase the performance of the TEG [2].

In this work, a transient CFD model for gas flow and heat transfer has been used together with an in-house code for predicting the thermoelectric performance during a vehicle test cycle. The CFD model was validated using published data [3] and used to identify design requirements for new TEG-EGR systems. Besides the prediction of heat transfer, Seebeck potential, Peltier effect, Joule heating and thermoelectric power generation, the simulations also gave detailed insight to the temperature gradients in the gas-phase and inside the TE elements. The results show that the greatest heat transfer resistance is located in the gas phase and it is of high importance to reduce this in order to achieve a large temperature difference over the thermoelectric elements.

For an EGR application it is also of great importance to maintain a low pressure drop in the gas which contradicts the requirement of high heat transfer. When developing new TEG systems it is therefore important to focus also on the heat transfer and not only on improving the materials. This work shows how advanced simulations method can be used to obtain the insight and optimize the design with respect to all these design requirements.

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Thermoelectric Exhaust-Gas Energy Recovery: An Integrated Approach

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Keywords: *skutterudites; energy recovery, modelling*

Abstract:
Thermoelectric devices are attractive candidates for a system to recover waste heat from a vehicle exhaust gas stream. In a modern high-efficiency vehicle engine, around 30% of the energy is released to the atmosphere in the form of hot exhaust gases. A second law analysis [1] indicates that an appreciable fraction of this waste heat may be recovered as useful work. A thermoelectric energy-recovery system capable of achieving a 10% improvement in fuel consumption would have a significant impact on efforts to reduce the level of CO_2 emissions to the levels of European legislative targets. Implementation of thermoelectric technology in automotive heat recovery requires developments in materials, module fabrication and understanding of the system-wide impact of a thermoelectric generator on the engine performance.

In seeking to address the scientific and technical challenges associated with the design and construction of a thermoelectric energy-recovery system, we have adopted a holistic approach involving collaboration between materials chemists, thermoelectric specialists and automotive engineers. Here, we will provide an overview of the project and outline progress to date. Our efforts have focused on the skutterudite family of materials as the basis for an energy recovery system. We will describe the synthesis and characterisation of a range of skutterudite materials, $R_xM_4Sb_{12}$ (R = rare earth; M = Fe, Co, Ni), with particular emphasis on the production of dense oxide-free samples, together with measurement of their thermoelectric properties. Investigation of the high-temperature stability of these materials has been carried out by X-ray diffraction. The skutterudite materials resulting from the synthetic program form the basis of newly-designed thermoelectric modules. Module fabrication, including the identification of suitable contact materials and the development of methods to electroplate and solder the thermoelements with minimal contact resistances, will be described. The thermoelectric performance of the resulting module is evaluated under conditions of large ΔT. In parallel with the materials synthesis and module fabrication, computational studies have been conducted on candidate heat exchanger designs, a key component of the thermoelectric generator. In addition, simulations of thermoelectric generator performance under the conditions of a standard NRTC running cycle have been performed using the GT-Power package.

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Self-cooling on power MOSFET using n-type Si wafer

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Keywords: *Self-cooling device; Peltier effect, thermal conduction; n-type Si wafer*

Abstract:
When we use power devices in the electrical equipment incorporating Si devices, the heat removal is one of the most important issues because Si devices must be less than the temperature of 150℃ not to affect the performance of Si devices and the equipment. Yamaguchi *et al*. have proposed a new scheme for cooling Si devices called the self-cooling devices [1]. However, it has yet to be shown that a comprehensive understanding of the self-cooling device is still lacking. To determine whether the self-cooling device remove the Joule heat from Si devices such as a power MOSFET under high current, we studied the temperature distribution measurement by using the infrared thermography. Figure 1 shows the temperature distribution of the upper side when the power MOSFET without n-type Si wafer generate the Joule heat ($R_{On}I^2$=5.40W, where R_{On}=1.5mΩ), where the current of I=60A flowed from the drain to the source. The temperature distribution in the upper side has a maximum at 41.4℃. On the other hand, it is clearly shown that the temperature distribution of the upper side shifts about 2℃ to the low temperature when the power MOSFET with n-type Si wafer, i.e., the self-cooling device generate the Joule heat (RI^2=9.00W, where R=2.5mΩ) as shown in Fig.2. The temperature distribution in the upper side has a maximum at 39.4℃. This fact indicates that the n-type Si wafer removes the heat from the upper side to the water cooled heatsink by both the Peltier effect due to the self-current of I=60A (|S|TI=12.4W, where |S|=688μV/K at T=300K) and the thermal conduction. These observations indicate that n-type Si wafer cools down the power MOSFET by using both the Peltier effect and the conventional thermal conduction. These results provide new insight that the self-cooling device is one of the efficient means to remove the heat from Si devices.

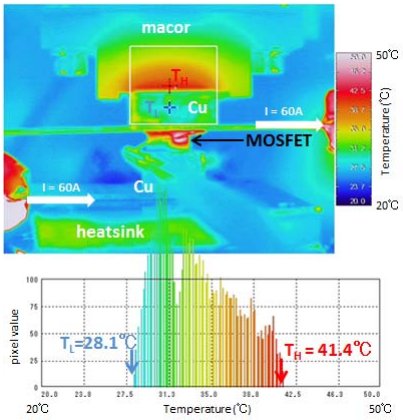

Fig.1 Temperature distribution (MOSFET only)

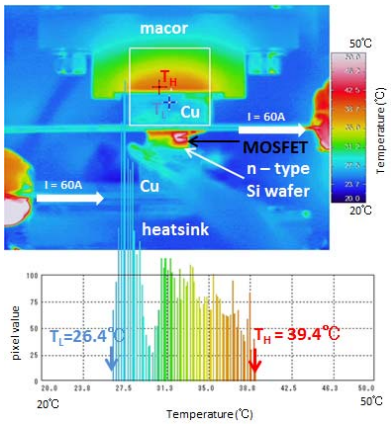

Fig.2 Temperature distribution (MOSFET + Si wafer)

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Prospects for Improvement in LED Performance Using Thermoelectrics

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Keywords: *LED; Thermoelectric cooling, Temperature control*

Abstract:
Light emitting diodes (LEDs) become the most usable lightning devices which have good prospects to replace traditional light sources. Such LED characteristics as lifetime, brightness and color stability are greatly depend on operating temperature. Therefore, thermal management is one of the most important aspects when using LED lighting systems.

In this paper the thermal parameters of modern LEDs and efficiency of existing LED thermal management systems are reviewed and analyzed. Dependence of LED performance on its operating temperature is presented.

The thermal model of the cooling system containing LED with its internal thermal resistance, thermoelectric cooler (TEC) and a heat sink is proposed. The problem of optimal matching of the system's components is solved with consideration of 3-dimensional heat spreading in the TEC top substrate. It is shown that the use of thermoelectric cooling makes it possible to increase LED performance considerably, especially at elevated ambient temperatures.

Using loop heat pipe to increase the power generation efficiency of thermoelectric generator

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Keywords: *System & industrial applications, generator applications*

Abstract withdrawn

Modeling and Optimization of a Triple Tube Heat Exchanger: Thermoelectric Generators Applications

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Keywords: *Thermoelectric generator, Power generation, Numerical simulation, Waste heat recovery*

Abstract withdrawn

A 1 kW_{el} thermoelectric stack for geothermal power generation — Modeling and geometrical optimization

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Keywords: *thermoelectric, stack, geothermal, modeling, optimization;*

Abstract:
A thermoelectric stack composed of arrays of state-of-the-art Bismuth-Telluride alloy thermoelectric converter (TEC) modules is considered for geothermal heat conversion. The TEC modules consist of Al_2O_3 plates with surface 30x30 mm^2 and 157 *p*-type $(Bi_{0.2}Sb_{0.8})_2Te_3$ and *n*-type $Bi_2(Te_{0.96}Se_{0.04})_3$ thermoelement pairs, each having a cross-section of 1.05x1.05 mm^2. The TEC modules have a figure-of-merit of ~1 and a theoretical heat-to-electricity conversion efficiency of ~5% when operated at the stack's design conditions (T_{hot} = 120 °C, T_{cold} = 20 °C). Hot and cold fluid channels are arranged in a counter-flow configuration for the heat transfer medium, water. The cold channel temperature is assumed to have a constant temperature of 20°C. The effect of varying hot water inlet temperatures (100 – 120 °C), temperature drop along the hot channel (10 – 20 °C), number of TEC modules per array (10 - 30), thermoelement length (1 – 4 mm) and hot channel height (0.5 – 2 mm) on heat-to-electricity efficiency and stack volume is investigated.

A heat transfer model coupling heat convection between the TEC plates and the water flow in the channels, heat conduction, and electric currents in the thermoelements is formulated. The calculated open-circuit voltage is compared to that resulting from the mean temperature differences across the TEC modules computed by a CFD model simulating heat transfer and flows of the thermoelectric stack. The validated heat transfer model is then applied to maximize the heat-to-electricity efficiency of the stack and minimize its volume. These two criteria are optimized simultaneously by varying the hot water inlet temperature, the temperature drop along the hot channel, the number of TEC modules per array, and the hot channel height, whereas for the optimum thermoelement length, a trade-off between them has to be found.

An optimized 1 kW_{el} stack consists of 100 arrays, each containing 15 TEC modules, and is of dimensions 0.45x0.3x0.1 m^3. It is operated with 1 kg/s of hot water at 120°C and a temperature drop of 20°C along the hot channels with a height of 0.5 mm and shows a heat-to-electricity conversion efficiency of ~2%.

Study of a thermoelectric system equipped with a maximum power point tracker for distributed electric generation.

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Keywords: *thermoelectric generator, maximum power point, MPPT, Power generation*

Abstract:
According to the International Energy Agency, 1.4 billion people are without electricity in the poorest countries and 2.5 billion people rely on biomass, such as wood fuel, charcoal, agricultural waste and animal dung, to meet their energy needs for cooking in developing countries. The use of cooking stoves equipped with small thermoelectric generator to provide electricity for basic needs (LED, cell phone and radio charging device) is probably a solution for houses far from the power grid. The cost of connecting every home with a landline is a lot higher than dropping thermoelectric generator and/or solar panel in each house. Thermoelectric generators have very low efficiency but with distributed power grid, they might become really competitive.

Our laboratory works in collaboration with planète-bois (a non governmental organization) which has developed energy-efficient multifunction (cooking and hot water) mud stoves based on traditional stoves designs. A prototype of a thermoelectric generator ((Bismuth Telluride) has been designed to convert a small part of the energy heating the sanitary water into electricity. This generator can produced up to 10 watts on an adapted load. Storing this energy in a battery is necessary as the cooking stove only works a few hours each day and as the working point of the stove varies a lot during the use it is also necessary to regulate the electrical power.

An electric DC DC converter has been developed with a maximum power point tracker (MPPT) in order to have a good efficiency of the electronic part of the thermoelectric generator. The theoretical efficiency of the MMPT converter is discussed. First results obtained with a hot gas generator simulating the exhaust of the combustion chamber of a cooking stove are presented in the paper.

Thermoelectric Generating System attached to a Carburizing Furnace at Komatsu Ltd., Awazu Plant

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Keywords: *Bi-Te, TEG, Carburizing, MPPT*

Abstract:
At the end of October 2009, KELK Ltd. started a field test of the thermoelectric generation (TEG) system at a carburizing furnace of Komatsu Ltd., Awazu Plant. Residual carburizing gas based on CO, N and H_2 is burned resulting that 20-30 kW range of flame constantly heats up the hot side of TEG.

A single unit of TEG consists of 16 of the Bi-Te modules, each of which has a size of 50 × 50 × 4.2 mm^3 and can generate 24W under the circumstance of 280 °C and 30 °C of hot side and cold side temperature, respectively [1]. 16 modules are separated into 4 groups and they are connected electrically depending on design concept, namely in case of focusing on reliability, parallel connection are used and in case of on simplicity and high-voltage transmission, series connection is preferably employed.

The module is being life-time tested at various conditions. For instance, 10,000 of heat cycling under the hot side temperature between 250 and 50 °C with a constant cold side temperature at 30 °C gives within a few percent degrade.

Both buck- and booster-type DC/DC converters controlled by one chip computer were set up and Maximum Power Point Tracking (MPPT) was well facilitated to search for the maximum output power depending on the hot and cold temperature.

The electric output power from the 16 modules is summed up to charge 4 lead storage batteries (12V-65Ah) and then through DC/AC inverters electricity goes to fluorescent light tubes inside the factory. Typically 220 W can be generated and 180 W is delivered to the batteries.

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Acknowledgments: The authors would like to express their gratitude to Prof. Kajikawa who was the Project Leader of the national project on the development for Advanced Thermoelectric Conversion Systems. The aid of this research by the New Energy and Industrial Technology Development Organization (NEDO) is gratefully acknowledged.

Thermoelectric Generator Hidden in a Shirt with a Fabric Radiator

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Keywords: *Thermoelectric generator; thermopile; wearable device; fabric radiator*

Abstract:
The body-area network of wireless sensors for monitoring chronic deceases and vital body parameters requires integration of these devices in clothing. They must function for the service life of a piece of garment with no technical service and no need for battery replacement or recharging. Therefore, thermoelectric generator (TEG) is quite competitive to batteries in such applications.

The experiments performed in this work on people have shown that textile has insignificant impact (either negative, or positive) on heat transfer from a thermopile. Based on obtained results, the TEG with sixteen one-stage thermopiles from Thermix (with about two thousand BiTe thermocouples in total) has been designed, fabricated and integrated into an office-style shirt. It is hidden between two cotton layers and invisible from either side. Unlike devices reported in the literature earlier, the new TEG does not require any modifications of garments. The thermopiles are mounted on one cotton layer that is sewed from inner side to a shirt. The cold plates are glued to carbon fabric heat spreading layer that is glued and sewed to the outer cotton layer of the shirt. The thermopiles with a thickness of buttons (3.5 mm both) are truly unobtrusive because of cotton layer on the skin and a flexible cotton radiator. The carbon fabric occupies 0.075 m^2 on the chest. The shirt with a TEG is indistinguishable from a typical shirt.

Preliminary tests performed on people in the office and outdoors have shown that the average power changes from 1.5 mW at 18°C to 0.6 mW at 26°C, with 1 mW on average, and at 1-1.5 V output. It is an ideal power supply for low-power wearable electronics such as health-monitoring devices. For example, wireless electrocardiography requires 0.4 mW today and in the near future it is going to drop to 0.1 mW. The thermoelectric shirt produces more energy during 9 months of use (while being worn 10 hrs per day) than the energy stored in alkaline batteries of the same thickness and weight. The shirt can be handled in the same way as other clothing, i.e., with periodic machine washing and ironing.

Architectural innovation foresight of thermoelectric generator charger integrated portable power supply for portable consumer electronic device in metropolitan market: the case study of Thailand

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Keywords: *Thermoelectric Generator (TEG);Portable Consumer Electronic Device (PCED); Portable Power Supply; Innovation; Foresight*

Abstract not presented

Design and Development of a TEG Cogenerator Device Integrated in Self Standing Gas Heaters!

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Keywords: *cogeneration, combustion, gas, TEG*

Abstract:
A wide range of technical solution based on gas combustion are available for heating of both residential and industrial environment. While in most cases the gas combustion is localized in a central heating unit (the boiler) and the generated heat is transferred to an intermediate fluid (e.g. water) which is circulated through heat radiators located in the rooms of the controlled environment; in some relevant cases each heat-radiating unit includes the gas combustor and operates autonomously with local gas and electrical feeding. This approach more frequently applies to industrial or commercial environments, where localized heating may be more effective than uniform heating of the whole environment and the use of autonomous units is characterized by higher flexibility of design and operation. For such autonomous gas heaters, the cogenerating thermoelectric generator (TEG) is integrated within the heater and would permit its installation and operation without the need of a connection to the electrical grid and would eventually increase their overall efficiency, through the reduction or elimination of any electrical power consumption from the grid for fans (or pumps), safety , monitoring and control devices and accessory functions (illumination).

A self standing gas heater for heat radiation in outdoor commercial environments has been selected as a test case for verifying feasibility and profitability of such technical solution. A TEG device is integrated in the heater, cogenerating an amount of electrical power which is dedicated to its autonomous operation from electrical connection to grid and for accessory functions (high efficiency LED illumination).

Approaches for the design and structure of the TEG are discussed, as well the constraints for integration in the existing self-standing gas-heater design. Based on the design and aiming to optimization of performance, design features of the general TEG components are examined:
- heat capturer/collector for capturing heat from the flame and transferring it to the hot side of the TEG!
- TEG module technology choice and selection,
- natural convection radiator for dissipating heat from the cold side of the TEG,
- analysis and optimization of the thermal chain,
- TEG assembly and its design as a whole.

A prototype has been built and tested and its functional behaviour has been modeled through multiphysics numerical simulation, to allow design optimization and extrapolation of the results towards larger or more complex designs.

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Electric Power Output Optimization in Seebeck Generators: Beyond High *ZT*

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Keywords: *Figures of Merit, Efficiency, Economic impact*

Abstract:
Over the last years a large interest has showed up for the possibility of enhancing the thermoelectric figure of merit *ZT* by damping the material thermal conductivity (*e.g.* by quantum confinement) rather than by increasing its power factor. Actually, while *ZT* is an appropriate performance index when optimizing the rate of heat conversion over small temperature differences, when used as a general criterion to qualify material−system performances it may turn out to be somewhat misleading. Actually, while high conversion rates are quite obviously desirable when TEGs are expected to convert limited low-enthalpy heat flows, other criteria have to be considered when thermoelectric generators (TEGs) are to be deployed for bulk energy production.

It has been shown [1] that, under fixed heat flow conditions, the optimization of *ZT* may actually proceed only by maximizing the power factor, since materials with low κ may be unable to duly dissipate heat. Perhaps more surprisingly, also when operating between sources at fixed temperature the highest electric power that a TEG can output may be obtained by increasing κ, not decreasing it [2]. In addition, the effect of large temperature differences on the thermodynamic efficiency, the coefficient of performance and on the maximum power output will be re-analyzed in this view.

Optimization of electric power output instead of the conversion rate will be shown to impact on the economic factors concurring to define mature scenarios of application for TEGs. Possible criteria to evaluate economic sustainability of thermoelectric large-scale energy production will be advanced and discussed with reference to actual settings.

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POSTER
PRESENTATIONS

Optimisation of the efficiency of nanowire array based thermoelectric generators

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Keywords: *silicon nanowire array, thermoelectricity, simulations*

Abstract:
The steady state heat conduction equation is solved for a thermocouple where each leg consists of combinations of bulk Si and Si nanowire based materials. The configuration and material properties of this thermocouple are optimised using general, constrained optimisation techniques. Three different configurations of thermoelectric legs were optimised. It was found that, under specified fabrication restraints, the maximum efficiency of a bulk Si thermocouple is h = 0.00026 while the efficiency of a nanowire/bulk and nanowire/bulk/nanowire thermocouple is h = 0.009 and h = 0.012 respectively.

The one-dimensional heat conduction equation used includes Joule heating but excludes the Thomson effect. The first boundary condition assumes that the junction thermal resistance is zero and thus the temperature is continuous across the junction. The second boundary condition states that the thermal power leaving a material junction is the sum of the thermal power entering it and the thermal power generated as a result of the Seebeck effect. The solution is found using a matrix formalism based on these boundary conditions. Defining the thermoelectric conversion efficiency as the fraction of the input power which is converted to electrical power, the optimisation problem is then solved using general, constrained optimisation techniques. The problem is formulated by:

$$P = \begin{cases} \min \eta(x) \\ g(x) = 0 \\ h(x) \le 0 \end{cases}$$

where x is the design vector, consisting of all the design variables, h*(x)* is the objective function and *g(x)* and *h(x)* are the constraints based on fabrication limitations. Material parameters as a function of doping density are taken from textbooks while material parameters related to nanowire arrays are taken from recently published experimental results on single wires assuming the arrays behave similarly. Three structures were simulated, a bulk Si thermocouple, a thermocouple where each leg consists of an array of nanowires on bulk Si and a thermocouple where bulk Si is sandwiched between two nanowire arrays. The result of the efficiency versus current simulation for D*T* = 10K and a nanowire array length of 100 µm is given in fig.1. When neglecting the thermal resistance between metal contact and semiconductor, the possible efficiency improvement obtained by introducing an array of vertically upstanding nanowires in each leg of the thermoelement can be a factor of nearly 50.

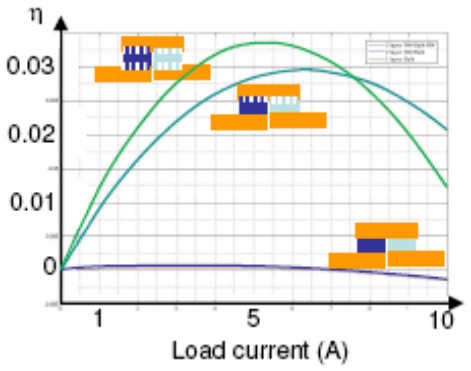

Figure 1: Efficiency versus load current for three thermocouple configurations.

Influence of hole- and phonon-nanoparticle scattering on the transport coefficients in $Bi_xSb_{1-x}Te_3$ bulk nanostructures

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Keywords: *thermoelectrics, semiconductors, nanostructures, nanocomposites, heat conductivity, electric conductivity, thermoelectric power, phonon scattering*

Abstract:
Investigations of nanostructured materials have already lead to an increase of the thermoelectric figure of merit. Probably a high figure of merit can be reached in bulk nanostructures fabricated by melt spinning with subsequent hot pressing. In the present work possible ranges of the transport coefficient modification due to the scattering of holes and phonons by nanoinclusions in such p-$Bi_xSb_{1-x}Te_3$ bulk nanostructures are theoretically estimated. The dependence of the power factor on parameters of potential barriers or wells and on the carrier density was analyzed. The estimations showed that the reduction in lattice thermal conductivity (about 10%) for nanoinclusions of $(Bi,Sb)_2Te_3$ solid solution with different composition is much greater than the change in the power factor. Therefore corresponding increase of the thermoelectric figure of merit for this case is determined by phonon scattering. The influence of the nonlinearity of the phonon spectrum on the thermal conductivity change was analyzed, e.g. it was shown that in the case of sine-shaped instead of linear phonon spectrum the estimations gave two times higher thermal conductivity reduction.

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Enhanced thermoelectric efficiency of a weakly coupled quantum dot

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Keywords: *thermoelectric efficiency; Coulomb blockade; quantum dot*

Abstracts:
In the present work we investigate the thermoelectric properties of a multi-level quantum dot weakly coupled to two electron reservoirs in the Coulomb blockade regime. The heat current through the dot is calculated within a master equation approach when weak temperature and voltage differences are applied between the two reservoirs [1,2]. Detailed calculations and analytical derivations for the power factor (S^2G) and the dimensionless figure of merit (ZT) are presented. We confine our interest in the limit where the energy separation between successive energy levels is much larger than the thermal energy. We find a giant enhancement of ZT due to the violation of the Wiedemann-Franz law when the phonon contribution to the thermal conductance is ignored. Quite interestingly, we show that both the electronic and the phononic contributions to the thermal conductance exhibit a similar activated behavior. As a result large values of ZT (2.4-8) are reported when phonons are taken into account. Our findings suggest that both electron- and phonon-blocking structures have improved thermoelectric performance.

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On the Semimetal-Semiconductor Transition in Thin Bi Films

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Keywords: *Bi thin films, thickness, semimetal–semiconductor transition, theoretical model*

Abstract:
Quantum size effects in thin semimetallic Bi films can manifest themselves in the form of a semimetal–semiconductor (SMSC) transition, which occurs with decreasing Bi layer thickness *d*. The theoretical prediction of a possible significant enhancement of the thermoelectric figure of merit in Bi quantum wells due to the SMSC transition [1] stimulates studies in that direction. According to the model proposed in [2], the formation of the energy gap takes place when electron and hole first subbands intersect the Fermi level simultaneously, and the critical thickness of such a transition corresponds to ~ 25-30 nm. However, a significant difference in electron and hole effective masses in Bi, the presence of the surface acceptor states, as well as the appearance of new experimental data [3] require a model adjustment.

In the present work, a model taking into account the above-mentioned factors is proposed. The difference in the values of the effective masses of electrons and holes determines the fact that the degeneracy of the electron gas disappears before the lowest electron and hole subbands overlap. Using the proposed model, we give a more accurate interpretation of the experimental results [3]. It follows from our analysis that at thicknesses *d* between 20 and 30 nm we observe not a SMSC transition, as was predicted in [2], but rather a semimetal – degenerate semiconductor transition. As far as a semimetal – nondegenerate semiconductor transition is concerned, even if it is possible under the presence of acceptor surface states, it occurs at *d* between 5 - 7 nm.

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Quadrupole Method Applied to a Thermoelectric Leg

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Keywords: *Thomson effect, Laplace, Quadrupole, COP*

Abstract not presented

Spin-dependent thermoelectric effect in magnetic tunnel junctions

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Keywords: *Seebeck, tunnel junction*

Abstract:
We report thermovoltage measurements performed on CoFe/Al_2O_3/CoFe like tunnel junction[1]. The temperature difference is obtained from laser heating of one of the 2 leads. A very large voltage of about 1mV is obtained as well as a magnetic configuration independent off diagonal Onsager coefficient. A temptative model based on a non magnetic resonance close to the Fermi level is proposed to explain both of these peculiar behaviors.

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KKR-CPA study of Mg2*X* (*X*= Si, Ge, Sn) thermoelectric materials

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Keywords: *electronic structure, disorder, formation energy, thermopower*

The magnesium Mg2*X* compounds, where *X* is an element as Si, Ge or Sn, crystallize in a simple antifluorite-type structure. Undoped alloys as e.g. Mg2(Si-Sn) exhibit a figure of meritzT~1, which makes them extremely promising materials for thermoelectric power generation (also due to low volume density). Alloying and doping (including specific electronic states of impurities) are well established ways to improve thermoelectric efficiency related to electrons as electrical conductivity and Seebeck coefficient. In this perspective it is of particular importance to investigate density of states and electron parameters near the Fermi surface in order to better understand thermoelectric properties of these systems.

Electronic structure calculations were performed using the Korringa-Kohn-Rostoker method with the Coherent Potential Approximation (KKR-CPA) [1,2] allowing to account for disorder effects in self-consistent way. The charge conductivity type (electron or hole) was determined from the Fermi level position with respect to the conduction or valence band edges. Moreover, the total energy determined from the KKR-CPA method gave unique advantage to study phase stability in terms of the formation energy of compounds. The site preference of illustrative dopants is also discussed by taking into consideration limiting conditions of magnesium and silicon chemical potentials. The sign and the magnitude of the Seebeck coefficient in *n/p* type doped Mg2(Si-Sn) and Mg2(Si-Ge) alloys were studied from the Mott's formula based on the Fermi surface transport coefficients or on simplified analysis of density of states [3].

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Phonon self energy in transition metals

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Keywords: *phonon calculation, anharmonicity, self energy*

Abstract:
We present ab initio calculations of the phonon self energy of transition metals obtained using second order many body perturbation theory [1, 2].

The code we have implemented use the symmetry properties of the phonon-phonon interactions to express the self energy as a sum over irreducible triplets. It is analogous to the reduction of integration to the irreducible part of the Brillouin zone for one particle properties.

The self energy of transition metals is then calculated. We show that the Peierls approximation[3] is in fact reasonable for bcc and fcc metals, but fails for the hcp. The decays paths of phonons producing the self energy is finally analyzed using surfaces of reciprocal space defined by conservation law.

The calculations of the self energies and relaxation time presented here are the necessary first steps toward an ab-initio calculation of the phonon thermal conductivity.

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Transport properties calculated from complex Fermi surface with Boltzmann approach on the example of $TiFe_{1-x}Ni_xSb$ half-Heusler compound.

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Keywords: *thermoelectric, complex Fermi surface, Boltzmann approach, half-heusler*

Abstract:

The Green function Korringa-Kohn-Rostoker methodology [1,2] with the coherent potential approximation was used to calculate complex energy band structure in disordered alloys. Using Boltzmann approach on one hand, and life-time and velocity of electron determined on Fermi surface on the other, thermoelectric-related electron transport properties as temperature dependent Seebeck coefficient, electrical residual resistivity, and carrier concentration, were investigated. Calculation were performed in selected series of half-Heusler compounds (e.g. $TiFe_{1-x}Ni_xSb$) within several approximations for relaxation time leading to partly different results. Interestingly, these materials experimentally revealed tunable electron transport properties, manifested by thermopower switching from positive to negative values at the metal-semiconductor-metal crossover, when varying number of valence electrons in the system [3].

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Effect of temperature gradient on high-frequency dielectric permittivity in quantum-well superlattice structures

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Keywords: *quantum well superlattice; thermoelectromagnetic waves*

Abstract:
At present, quantum well superlattice structures have the highest thermoelectric figure of merit due to the reduced lattice thermal conductivity and enhanced power factor (see, for example, [1-3] and citations therein). On the other side, it is well known that semiconductor superlattices, like various periodic multilayer metamaterials, under certain conditions possess unusual electromagnetic properties such as negative refraction and near field focusing due to opposite direction of the phase and group velocities of the waves [4-7].

In this work, for the first time to our knowledge, an attempt is made to examine the effect of the temperature gradient on electromagnetic properties of the quantum-well semiconductor superlattices such as GaAs/AlAs or BiTe/SbTe. We present the results of this study and indicate a model for the tuning of the refraction index in the superlattice structures using the temperature gradient as a tuning parameter. First, we present a charge carrier transport analysis based on the Boltzmann kinetic equation at relaxation time approximation, in the presence of the temperature gradient and electromagnetic fields of the propagating wave. Assuming that the period of the structure is much smaller than the wavelength of interest and using the method of effective anisotropic medium, we calculate high-frequency tensor of electrical conductivity and obtain an analytical expression for the complex dielectric permittivity. We show that temperature gradient leads to the appearance of an additional part in the expression for the permittivity tensor and has the potential to change significantly the refractive index, polarization and dispersion properties of the material. Both the quantity and the direction of the alternating thermoelectric field depend considerably on the scattering mechanism of 2D charge carriers. In addition, the temperature gradient leads to the appearance of the girotropy (optical activity) of the structure due to linear dependence of the complex dielectric permittivity on the wave vector.

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Analytical and Experimental Studies on an Innovative Composite Approach for Enhanced Thermoelectric Performance

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Keywords: *Composite, Thermoelectric, Indium, Bi_2Te_3—Sb_2Te_3 compound*

Abstract:
Despite having zero emissions, solid state reliability, and precision, thermoelectric modules have long been reserved for specialty applications due to their low efficiency. One of the main causes of this low efficiency is the relatively high electrical resistance of semiconductor materials such as bismuth (II) telluride and antimony telluride (Bi_2Te_3—Sb_2Te_3**)** compound material typically used to conduct the electric current necessary in thermoelectric cooling. However, this project showed that replacing major sections of Bi_2Te_3—Sb_2Te_3 compound material with indium metal greatly increases efficiency of the thermoelectric module without changing the nature of the Peltier Effect. The indium was sandwiched between 2 slices of Bi_2Te_3—Sb_2Te_3 compound material and then the three components were fused with diffusion bonding. A noninvasive high precision infrared temperature detection system was employed to measure the temperature distribution. The temperature distribution of the composite structure was analytically derived and compared with experimental results. The analytic results agreed with experimental results for verifying the concept of the composite thermoelectric structure.With this innovative technology, we were able to use fewer amounts of Bi_2Te_3—Sb_2Te_3 compound material and raise the efficiency of the thermoelectric devices (TEDs), thus reducing the cost of the TED modules due to the greater cost of Bi_2Te_3—Sb_2Te_3 compound material. These results also propose a flexible framework that can potentially be combined with the discoveries of new semiconductor materials with higher Seebeck coefficients, quantum well effect as well as thin film configurations. This method of increasing efficiency, by retaining all the advantages of traditional thermoelectric technology and bettering price and efficiency, has the potential to ultimately replace vapor compression technology altogether.

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Enhancement of thermoelectric properties by high rate magnetron sputtering

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Keywords: *Sputtering; Thin-Film, Bismuth Telluride*

Abstract not presented

Characterization of thermoelectric materials deposited by electrochemical technique

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Keywords: *Electrodeposition, Bi-Sb-Te thin films, thermoelectrical/electrical properties*

Abstract:
A thermoelectric converter is a solid-state heat engine in which an electron gas serves as the working fluid, converting the flow of heat into electricity. This energy converter type has no moving components, making it silent, totally scalable, and extremely reliable. Binary thermoelectric compounds such as Sb_2Te_3, Bi_2Te_3, and Bi_2Se_3 have been extensively studied because of their potential applicability in efficient thermoelectric conversion devices.[1-3] Electrodeposition of such thermoelectric materials, including binary and ternary compounds, has attracted much attention because it offers many advantages, including cost-effectiveness, rapid deposition rate, and ease in controlling the microstructure and crystallinity by adjusting the electrodeposition parameters.[3] In the present study, we performed systematic studies on Bi-Sb-Te thin films electrodeposited from acidic nitric acids at room temperature and correlated their material/structural properties to their thermoelectrical/electrical properties.

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Nanostructured $Ag_{0.86}Pb_{22}SbTe_{20}$ Thermoelectric Materials

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Keywords: *AgPbSbTe; thermoelectrics*

Abstract:
Nanostructured $Ag_{1-x}Pb_{18+m}SbTe_{20}$ (x = 0 ~ 0.2, m = 0 ~ 4) thermoelectric materials have been prepared using ball milling and spark plasma sintering (SPS) to investigate the effect on microstructure and thermoelectric performance. Our experiments are focused on $AgPb_{18}SbTe_{20}$ and expected to get high ZT value according to published report [1], but the LAST system is very unstable with p-type and n-type behaviors. To ensure our sample undergoing n-type behavior, the composition is modified by adding more Pb. The Seebeck coefficient changes from positive to negative values, which is following the same behavior with previous report [2]. Electric properties of the sintered samples with different amount of Ag contents were measured from room temperature to 750 K. The maximum power factor of 1.43 mW/m-K^2 was obtained at 718.9 K for the $Ag_{0.86}Pb_{22}SbTe_{20}$ sample with ZT = 0.6. In order to reduce resistivity, the sample was grinded by ball mill and consolidated by SPS under different conditions. A high ZT value of 1.1 at 737.8 K had been achieved for our sample by SPS at 400 ℃ for 5 min under a pressure of 50 MPa.

The investigation of the $Ag_{1-x}Pb_{18}MTe_{20}$ (M = Bi, Sb) (x = 0, 0.14, 0.3) system with substitution of Bi to Sb on the thermoelectric properties has been published [3]. The ZT value decreases dramatically as changing the composition from Sb to Bi. They attributed the different values of thermal conductivity for this system due to the differences in mass contrast of Bi and Sb with Pb, respectively. Therefore, we investigate other elements to replace Ag and Sb, and expect ZT value of PbTe derived system can be enhanced.

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Roles of Twin Structure on Thermoelectric Property in Ag added $Bi_{0.5}Sb_{1.5}Te_3$ compound

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Keywords: *twin, $Bi_{0.5}Sb_{1.5}Te_3$ compound, Ag adding*

Abstract:
The thermoelectric properties of the Ag-added $Bi_{0.5}Sb_{1.5}Te_3$ compounds were investigated in the temperature range from 323 K to 573 K. The temperature dependence of the Seebeck coefficient and the electrical conductivity for the Ag-added compound is of the degenerate semiconductors, which is fairly different from the conventional ternary $Bi_{0.5}Sb_{1.5}Te_3$ alloy.

It was confirmed that the twin was formed with Ag addition in $Bi_{0.5}Sb_{1.5}Te_3$ alloy and the twin acts similarly as 'nano phone scatter'. A population of the twin of the nanoscale increased with Ag addition and the lattice thermal conductivities minimized. The carrier concentration increased efficiently by the formation of substitutional defects with Ag addition. The power factor maximized, then the value is observed as 3.31×10^{-3} W/m·K^2 in 0.05 wt. % doped compound. It observed that the effects of Ag addition on thermoelectric properties were optimized in 0.05 wt. % doped compound. The maximum ZT value is achieved as 1.2 at 373 K, while that of the ternary $Bi_{0.5}Sb_{1.5}Te_3$ alloy is only 0.88. Each of the maximum peak ZT shifts to a higher temperature region with Ag addition, Specially.

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Reinvestigation of the Se impurity influence on the structural and thermoelectric properties of $AgSbTe_2$

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Keywords: *thermoelectric properties, structural properties, $AgSbTe_2$,*

Abstract:
Recently the $AgSbTe_2$-$AgSbSe_2$ alloys were thoroughly investigated due to their very promising thermoelectric properties [1,2]. However, conclusions of researchers differs significantly on chemical and structural stability of lightly doped $AgSbTe_2$ during long-term temperature treatment.

In order to reinvestigated results samples with nominal composition $AgSbTe_{2-x}Se_x$ (x=0.0, 0.01, 0.02, 0.04, 0.1) were prepared. The structural properties were investigated by X-ray diffraction and SEM microscopy. The electrical conductivity, thermal conductivity and Seebeck coefficient have been measured as a function of temperature in the range from 300 to 675K. Heat capacity and phase transitions were studied by DSC method in the temperature range from 300 to 675K. The investigation was made on samples after hot pressing (SPS) 5min, 725K, 30MPa and after annealing in quartz ampoules in temperature 610K for one week. To analyze the homogeneity of Seebeck coefficient on the surface before and after annealing the special measurement was made using scanning thermoelectric microprobe. The influence of doping and annealing on thermoelectric properties was analyzed.

It was found that annealing of Se doped $AgSbTe_2$ samples leads to slight changes in chemical composition of materials and their thermoelectric properties. The maximum figure of merit ZT = 1.13 was measured for sample with x = 0.01 at 600K and was lower than reported value of 1.4 [1].

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Highly Crystalline and Perfectly Stoichiometric Bismuth Antimony Telluride Compoundsby Pulsed Electrochemical Deposition Technique and Annealing

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Keywords: *Bi2Te3 and related materials, pulsed electrochemical deposition and nanowires*

Abstract:
High performance materials of n-type Bi_2Te_3 and p-type Sb_2Te_3 and $(BiSb)_2Te_3$ has been deposited onto stainless-steel and Au-substrates from aqueous electrolytes based on nitric acid with optimized compositions and degree high of crystallinity. In order to optimize the thermoelectric performance, the films have been annealed under inert atmosphere with in-situ XRD- and electrical conductivity measurement. The stoichiometry of the films has been determined for a wide range of deposition potentials. The morphology of films has been optimized by means of pulsed potentiostatic deposition technique. Structural analysis of the composition has been performed by ICP-OES, TXRF and SEM-EDX-measurements. Homogeneity of the deposited films (x- and z-direction) has been proved by GD-TOF-mass-spectrometry. Seebeck values up to 160 µV/K have been observed and power-factors of about 2.5 mW/K^2*m at 500K could be achieved – what is actually three times higher than best reported previously electrochemically deposited thermoelectric films .

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nano-Bi_2Te_3 for Printing Thermoelectric Generators

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Keywords: *bismuth telluride, nanoparticles, printing, thermoelectric generators,*

Abstract:
Printing is probably the easiest way to produce large quantities of cheap and scalable macroscopic devices. With lots of printing technologies available today thermoelectric inks are still very rare.[1] In cooperation with other institutions the development of a complete thermoelectric printing process is investigated. For a printing process certain specifications of the printer have to be fulfilled so the first step is to find appropriate thermoelectric particles of efficient materials in the desired temperature range. For room temperature applications the most common material is bismuth telluride. By nanostructuring the materials figure of merit can even be enhanced significantly.[2] Chemical production of nanoscale bismuth telluride and the corresponding alloys has gained significant interest among lots of researchers during the last years. Many novel synthetic approaches[3] lead to a even bigger variation in morphology e.g. very small nanoparticles[4] or microspheres composed of aggregated nanoplates[5]. Some synthetic approaches where reproduced, varied and compared with respect to the printing process. The best synthesis was selected and improved to produce thermoelectric material in reasonable quantity and suitable morphology. Some thermoelectric data and first printing tests are shown.

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Thermoelectric properties of the multilayered Bi_2Te_3 with chalcogenide materials

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Keywords: *multilayered, thermoelectric, chalcogenide*

Abstract:
Chalcogenide materials have been known as good candidates for thermoelectric materials including bismuth telluride and antimony telluride. Especially $Bi_{2(1-x)}Sb_{2x}Te_{3(1-y)}Se_{3y}$ semimetal alloys family has a room temperature ZT value of about 1 [1]. Bismuth telluride based BiTeSb and BiTeSe multilayered thin films have been fabricated using co-sputtering on Si substrate with varying applied power and thermal treatment. Thermoelectric properties have been affected by the texturing, the mobility of charge carriers, and the density of imperfections [2]. In order to confirm the texture of the films we investigated the microstructure through x-ray diffraction and transmission electron microscopy. Carrier density, mobility, and resistivity have been measured by Hall effect measurement system and Seebeck coefficient has been measured using temperature gradient method.

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Features of Growth and Galvanomagnetic Properties of the Bi_2Te_3-based Epitaxial Films

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Keywords: *bismuth telluride based films, epitaxial layer, electro- and magnetotransport*

Abstract:
The $(Bi,Sb)_2Te_3$ films (d = 40 – 5000 nm) were grown by hot wall technique. A system of well in-plain oriented triangle $(Bi,Sb)_2Te_3$ stable islands was detected by AFM at the surface of the mica substrate at the initial stage of the thermoelectric film growth. When the difference of temperature between the $(Bi,Sb)_2Te_3$ powder and substrate was in the range 120-150C, density of the Bi_2Te_3 islands was in the range 10^6 - 10^7 cm^{-2}. A system of an equidistant growth steps was observed at the surface of the grown (d ~ 500 nm) $(Bi,Sb)_2Te_3$ films. The height of the steps was equal to 1/3 of the c-axis unit cell parameter. A separate (11$\underline{0}$5) Bi_2Te_3 grains and screw-like structures were detected at the surface of a thick (d = 5000 nm) films grown at low (T<350C) substrate temperature.

Galvanomagnetic properties of $Bi_{2-x}Sb_xTe_3$ epitaxial films at x=-0.5 were studied in the wide range of the magnetic field from 5 to 14 T through the temperature interval 77-300 K. Tensor components of the magnetoresistivity ρ_{ijlk}, Hall effect ρ_{123}, and electrical resistivity ρ_{11} were measured, and the ratios of the effective-mass tensor components m_i/m_j were calculated in the terms of the many-valley model of energy spectrum with isotropic carrier scattering.

Compression of the constant-energy ellipsoids weakens along bisector and binary axes for films in comparison with bulk thermoelectrics of the same composition. The degeneracy parameter β_d governing the scattering mechanism of charge carriers was higher for films due to additional scattering on grain boundaries. Decreasing the constant-energy surface anisotropy is explained by reduction of carrier scattering anisotropy that leads to increase in thermoelectric efficiency of films.

Synthesis and Characterization of Bulk Nanostructured Bismuth Telluride (Bi_2Te_3).

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Keywords: *Thermoelectrics; Nanostructured materials; Bismuth Telluride (Bi_2Te_3)*

Abstract:
Global energy uncertainty and the limited recourses are increasing the needs for alternative energy sources. Thermoelectric (TE) devices can harvest residual low-grade energy which otherwise is wasted. Bismuth telluride (Bi_2Te_3) is the best-known commercially used TE material in the bulk form for cooling applications at ambient temperature. [1] However, its conversion efficiency, measured by dimensionless figure-of-merit-*ZT*, limits the large-scale industrial applications. Recent studies indicate that nanostructuring can enhance *ZT* while keeping the material format of bulk by employing bottom-up synthetic approach and novel compaction methods.[2] We report on the fabrication of n- and p-type Bi_2Te_3 nanostructures via simple and easily scalable solution chemical synthesis techniques. The developed processing routes allow production of large quantities, ~ 30 g, of TE nanopowder in one batch processing with very high purity. Spark Plasma Sintering (SPS) technique has been used to consolidate these nanoparticles into pellets where nanograin structure is preserved. SPS has very brief exposure time to high temperature and pressure, avoiding excessive grain growth. We investigated and optimized the compaction parameters for nano Bi_2Te_3 powder. Thorough physiochemical evaluations of the TE materials along with thermoelectric transport measurents are reported.

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Enhancement of Seebeck coefficient and figure of merit in Ga-doped single crystal *p*-$BiSbTe_3$

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Keywords: bismuth-antimony-telluride, thermoelectrics, Ga impurity, resonant states

Abstract:
Influence of Ga on temperature dependence (5<T≤300K) of Seebeck coefficient, conductivity, thermal conductivity and figure of merit of the single crystal solid solution semiconductor *p*-$BiSbTe_3$ have been investigated. Shubnikov-de Haas effect in magnetic field B directed along the C_3 axis was used to determine the concentration of holes and their Fermi-energy. The Ga doping causes a decrease in the frequency of Shubnikov-de Haas oscillation and, hence, in hole concentration in the samples. The light-hole concentrations p(SdH) calculated from the SdH effect were compared with the corresponding Hall concentration p(H). The value of p(SdH) is always smaller than the respective value of p(H). This indicates filling of the second, lower valence band at such hole concentrations. Concentration of holes decreases under Ga doping, that is element of the III group of the Periodic table Ga causes a donor effect. The thermal conductivity and the thermopower of single-crystal $BiSbTe_3${Ga} were measured with temperature gradient directed along to the C_2 axis. Ga doping increases Seebeck coefficient insignificantly for the content of Ga 0.3at% and nearly in two times for the content of Ga 2at%. Thermal conductivity in $BiSbTe_3${Ga} mixed crystals changes negligible, resistivity grows. All this implies that the dimensionless thermoelectric figure of merit ZT increases appreciably by gallium doping. Experimentally observed enhancement of the Seebeck coefficient can not be explained by decrease of the hole concentration and pointed out to the remarkable increase in the density of states due to Ga doping. The increase in the thermoelectric power upon gallium doping can be explained by either enhancing the energy dependence of mobility μ or enhancing the energy *E* dependence of the carrier concentration as compared to the conventional dependence characterized by a quadratic dispersion law. This is the case if Ga forms resonance states and locally increases the density of states near the Fermi level, which can be caused by the formation of an impurity band with delocalized states and a large effective mass. This assumption also agrees with the significant (more than twofold) increase in the resistivity at 2at % Ga in $BiSbTe_3$.

Thermoelectric properties of crystals *n*- $Bi_2Te_{3-x}Se_x$ <In> (*x*= 0.15 and 0.3)

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Keywords: *bismuth and antimony chalkogenides, doping with indium, beginning of the intrinsic conductivity, figure of merit Z*

Abstract not presented

Thermoelectric properties of single crystals *p*-$(Bi_xSb_{1-x})_{2-y}Sn_yTe_3$ in wide temperature range

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Keywords:*thermoelectric materials, chalcogenides*

Abstract:
The concept of an impurity-induced resonant state was introduced by Friedel as a bound state with a positive energy with respect to the band edge, i.e. with the same energy as an extended state. An excess density of states arises over a narrow energy range in the band of the host material. Virtual bound states in metals were shown to lead to an increase in thermoelectric power of the host metal by a resonant scattering. Contrasting with the resonant scattering concept, Mahan and Sofo suggest that the thermopower can be boosted intrinsically by the excess density of states itself. Because this mechanism does not involve any scattering, it is in essence temperature independent, and thus suitable for enhancing the figure of merit in thermoelectric materials. The distortion of the density of states by a resonant impurity of Sn was shown to increase the thermoelectric figure of merit *ZT* of the parent semiconductor in the case of Bi_2Te_3 [1]. Here we report the influence of tin doping on the thermoelectric properties of $(Bi_xSb_{1-x})_2Te_3$ single crystals in the temperature range 7 K – 300 K. We studied *p*-type single crystal $(Bi_xSb_{1-x})_2Te_3$ (x=0; 0.25; 0.5) samples both undoped and doped with tin. Temperature dependence of Seebeck coefficient *S*, electrical conductivity, heat conductivity and figure of merit of *p*-$(Bi_xSb_{1-x})_2Te_3$ single crystals were carried out. In order to determine the concentration of light holes and the Fermi energy, we also used the Shubnikov–de Haas effect at $T = 4.2$ K in high magnetic fields. By increasing the Sn content, the hole concentration increases in *p*-$Bi_{2-x}Fe_xTe_3$. The thermal conductivity *k* of the $(Bi_xSb_{1-x})_{2-y}Sn_yTe_3$ crystals decreases due to Sn doping as compared with pristine $(Bi_xSb_{1-x})_2Te_3$, while electrical resistivity increases in the temperature interval 150K<T<300K and decreases at T<150K. The Seebeck coefficient *S* for all compositions is positive and decreases due to Sn doping in the whole temperature range. The main reason for this is an acceptor effect and increase of the hole concentration under Sn doping. Fermi energy increases with Sn-doping and hence Seebeck coefficient decrease.

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Comparison of Water Quench (WQ) process with Mechanical Alloying-Hot Pressing (MA-HP) process for Thermoelectric Properties and Structures of $Bi_2Te_{2.85}Se_{0.15}$.

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Keywords:

Abstract:
$Bi_2Te_{2.85}Se_{0.15}$ is well known to be the best *n*-type materials for the thermoelectric performance at near room temperature [1]. Recently, there has been reported of that Bi_2Te_3 were obtained low thermal conductivity prepared by mechanical alloying and sintered by hot pressing (MA-HP) due to finely grained [2]. However, other thermoelectric properties of those materials are not clarified to except the reduced thermal conductivity. In present study, $Bi_2Te_{2.85}Se_{0.15}$ thermoelectric semiconductors were compared of Water Quench (WQ) process with the MA-HP process for thermoelectric properties and structures.

The raw ingots and sintered compacts of $Bi_2Te_{2.85}Se_{0.15}$ were prepared by two processes. The both processes were prepared nominal compositions of $Bi_2Te_{2.85}Se_{0.15}$ with Bi (5N), Te (6N) and Se (5N). The WQ process was direct melting at 923K for 3h in an evacuated quartz ampoule, and quenching it in the water. The MA was carried out in a planetary ball mill for 30h at a maximum speed of 180rpm. The pulverized powder was then sieved and passed through the size of 150μm in diameter, and the MA-HP samples were obtained by hot-pressing at a sintering temperature of 673K under a mechanical pressure of 147MPa in an argon atmosphere. These process samples were characterized by X-ray diffraction (XRD), differential thermal analysis (DTA), and the measurement of thermoelectric properties.

The XRD patterns of obtained both samples were corresponded to the single phase of $Bi_2Te_{2.85}Se_{0.15}$.The thermal behavior of both samples were the same in the DTA. However, the WQ process and the MA-HP samples were shown *p*-type and *n*-type conduction, respectively. The thermal conductivity of the WQ process sample reached 1.13 $Wm^{-1}K^{-1}$ at room temperature and that of the MA-HP process was 1.07$Wm^{-1}K^{-1}$, respectively. The dimensionless figure merit (ZT) for the WQ and the MA-HP process samples were obtained 0.06 at 353K with *p*-type conduction and 0.85 at 313K with *n*-type conduction, respectively.

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Self-organization processes in $PbTe$-Bi_2Te_3 semiconductor solid solutions and thermoelectric properties

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Keywords: *$PbTe$-Bi_2Te_3 solid solutions, thermoelectric properties, concentration dependences, self-organization processes*

Abstract:
In a large number of solid solutions based on binary compounds, in the range of small impurity concentrations (~0.5-1.0 at.%), we observed anomalies in the property-composition dependences and attributed them to the manifestation of critical phenomena accompanying concentration phase transitions of percolation type occurring under the transition from diluted to concentrated solid solutions [1]. After the impurity continuum is formed, states with spatially correlated distribution of atoms (long- or short-range ordering) corresponding to the minimum in the crystal free energy can be realized. The above mentioned self-organization processes, taking place under increasing concentration of the impurity component, must affect thermoelectric properties leading, on the one hand, to the possibility of qualitative change of properties, and, on the other hand, to the dependence of properties on the preparation conditions.

The objects of the present study are PbTe-based solid solutions in the $PbTe$-Bi_2Te_3 system (0-10 mol.% Bi_2Te_3). The goal of the study is to obtain concentration dependences of structural and thermoelectric properties of samples prepared using different techniques and samples subjected to different types of heat treatment. The dependences of the microhardness, electrical conductivity, the Hall coefficient, thermal conductivity, and the Seebeck coefficient on Bi_2Te_3 concentration were obtained. It was found that within the homogeneity region of PbTe these dependences exhibit unusual for solid solutions non-monotonic behavior, which indicates qualitative changes in the defect subsystem of the crystal occurring under increasing Bi concentration. The experimental results were interpreted taking into consideration complex mechanisms of the defect formation occurring in the PbTe crystal lattice under the introduction of Bi_2Te_3, percolation effects and the possibility of the realization of intermediate ordered structural states in solid solutions. It was established that the type of heat treatment (in particular, aging the alloys) significantly affects the behavior of the concentration dependences of the properties.

From the obtained results it follows that when developing new thermoelectric materials based on multi-component solid solutions, it is necessary to take into consideration both self-organization processes, taking place in a solid solution and caused by an increase in impurity concentration, and relaxation processes.

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Cathodic deposition of BiTe as thermoelectric films using choline chloride based ionic liquids

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Keywords: *bismuth teluride, ionic liquid, electrodeposition, choline chloride–malonic acid mixture*

Abstract:
In recent years a number of chalcogenides were reported as thermoelectric materials in various temperature ranges, being ideally suited to terrestrial cooling and electrical energy generation with applications including waste heat recovery from power plants, in automobile industry and coolers for microelectronics, infrared detectors, laser diodes or computer processors [1-3].

This paper reports electrodeposition of BiTe using ionic liquid based on choline chloride (ChCl) and malonic acid mixture (1:1 moles) in the 25-60^{0}C temperature range. Oxides were introduced as precursors for Bi and Te species. The films of thermoelectric materials were prepared mostly by either potential or current control electrolysis. Pt and Cu foils were working electrodes, platinum plate with a large surface area was auxiliary electrode and Ag wire was quasireference electrode.

The characterization of cathodic process was performed by cyclic voltammetry and electrochemical impedance spectroscopy. Several accelerated corrosion tests as potentiodynamic polarization curves and impedance spectra at open circuit potential were carried out. As corrosive media the 0.5M Na_2SO_4 solutions were used. The corrosion performances are discussed taking into account the applied electrodeposition procedures.

From cyclic voltammetry and impedance experiments carried out using Pt electrode it was possible to predict the potential range at which deposition of BiTe films takes place. The deposition of BiTe from electrolytes occurs on a Te-covered Pt substrate at less negative potentials than for deposition of singular Bi or Te films. Correspondingly, two or three dissolution (stripping) anodic peaks were observed. Nyquist and Bode impedance spectra showed differences in Pt behavior due to its polarization at various cathodic potentials. Equivalent-circuit components providing the best fit to the data were calculated. The morphology and chemical composition of BiTe films deposited on Cu were determined by AFM, SEM and TEM microscopy.

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Synthesis and Characterization of nanostructured PbTe

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Keywords: *PbTe, low temperature synthesis, ball-milling, nanostructured*

Abstract:
PbTe compounds display high structural and chemical stability and low vapor pressure at the operating temperature range (50-600^{o}C). These properties motivated many researchers to study PbTe compounds. It is noteworthy that a large number of these researchers studied nanocrystalline PbTe compounds in order to achieve higher ZT. The fabrication of nanocrystalline materials has been presented as a good method to increase ZT due to the increased phonon scattering at interfaces.

In the present work we have synthesized PbTe and PbTe with Pb precipitates by low temperature synthesis. This technique, which takes place at temperature below the melting point of Te, is preferred since is safer than other techniques and the contamination by impurity diffusion from the quartz could be avoided. Each of the obtained material was divided into 4 parts which was ball milled for different times. The initial materials and the ball-milled powders were characterized by X-ray diffraction technique. In order to estimate the crystalline size of all samples the higher peaks of XRD patterns were analyzed. Their thermoelectric properties were measured on sintered pellets in the temperature range $2 \leq T \leq 350^{o}$K in order to investigate the effect of low temperature synthesis, Pb precipitates and ball milling time on these properties.

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Thermoelectric properties and nonstoichiometry of GaGeTe

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Keywords: *Thermoelectric properties, nonstoichiometry, gallium germanium telluride*

Abstract:
We present original results on transport properties of nonstoichiometric GaGeTe. The polycrystalline samples of composition $Ga_{1+x}Ge_{1-x}Te$ (x = -0.01–0.05) were synthesized from elements of 5N purity using solid state reaction. The products of synthesis were characterized by X-ray diffraction. We observe distortion of hexagonal crystal lattice. While shift of *a* parameter is negligible, *c* parameter drops continuously with increasing Ga content. This fact evidences substitution of Ga for Ge. The samples for transport measurements were prepared using hot-pressing technique. They were characterized by the measurement of electric conductivity, thermal conductivity, Hall coefficient and Seebeck coefficient in the temperature range 80 – 450K. The samples show all p-type conductivity and we observe an increase in hole concentration and electrical conductivity with increasing content of Ga. The influence of Ga/Ge ratio on the properties of GaGeTe is discussed within point defects in crystal lattice of this material.

Thermal, electron transport and far infrared properties of PbTe single crystals doped with Br

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Keywords: *PbTe, thermal diffusivity, electron transport, far infrared reflectivity*

Abstract:
Understanding the properties of PbTe remains in focus as enhancement of thermoelectric efficiency of this material is studied extensively. In this work single crystals of PbTe, doped with less than 1 at % Br, were synthesized using the Bridgmann technique and their thermal, electron transport and far infrared properties were studied. Thermal diffusivity was determined using the photoacoustic method with a transmission detection configuration. Thermal conductivity measurements have been carried out based on laser pulse technique at high temperatures. Electron transport was determined by Seebeck coefficient and Hall effect measurements. IR reflectivity measurements showed that reflectivity in the region of plasma resonance was low. Measured reflectivity diagrams were numerically analyzed -enabling calculation of the carrier concentration and mobility- and compared with the values obtained by Hall measurements.

Sintering Process in Ball-Milled $K_2Bi_8Se_{13}$ Nano-composites

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Keywords: *nanostructured, heat treatment, thermoelectric properties*

Abstract:
$K_2Bi_8Se_{13}$ material has many attractive features for thermoelectric applications. Recently, $K_2Bi_8Se_{13}$ based nanocomposite materials, consisting of nano-crystalline, micro-crystalline and amorphous phases, have been fabricated based on powder technology techniques. The Seebeck coefficient has been enhanced and the thermal conductivity has been decreased, thus presenting interesting behavior.

The study of the behavior of materials under different heat treatment conditions is of interest in terms of reversibility and stability of the structural features, as the application of sintering process is necessary for the development of thermoelectric modules. In this work, structural features, morphology, thermal and thermoelectric properties have been studied in dependence on different heat treatment conditions applied into $K_2Bi_8Se_{13}$ nano-composites.

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A study of dielectric loss mechanisms in $TlSbS_2$ thin films

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Keywords: *Thermoelectric materials, Chalcogenides*

Abstract withdrawn

Influence of electrodeposition additives in the power factor of Bi_2Te_3

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Keywords: *electrodeposition; bismuth telluride, power factor*

Abstract:
Bismuth telluride films were synthesized by electrodeposition techniques. A conventional three-electrode cell, with Ag/AgCl (saturated KCl) as reference electrode, platinum counter electrode, and silicon coated with chromium and gold as working electrode, was used. Films were grown from a nitric acid bath [1], and characterized using SEM, XRD, energy dispersive X-Ray (EDX). Also their transport properties (Seebeck coefficient, S, and electrical resistivity, ρ) were measured.

The main goal of our research was to optimize those bismuth telluride films in order to increase their thermoelectric performance. Our first approach was to modify the growth parameters until the films presented a preferential crystallographic orientation with their c-axis parallel to the surface of the electrode, that is, [1 1 0], which is the most favorable configuration for having the highest thermoelectric performance along the thickness of the film.

In order to further optimize the structure and morphology of the films, the addition of sodium lignosulfonate, as proposed by Kuleshova et al. [2], was studied. In our case, we varied the concentrations of the surfactant, the applied voltages and the type of working electrodes in the electrodeposition process. SEM micrographs showed that those films presented a morphology much denser than in the case of films without additives, and EDX analysis showed no influence of the additive in the composition of the films. As a conclusion of this study, we obtained the most optimized bismuth telluride films from a morphological, structural, and a thermoelectrical point of view: those prepared with 0.09 g/l of additive at -0.04 V of constant potential applied, which exhibited a strong crystallographic orientation along the [1 1 0] axis, as we were looking for, along with an increase of almost 100% in the Power Factor (S2/ρ), compared to those grown without additives, which means an important increase of its efficiency as thermoelectric material.

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Thermoelectric Properties of $Ru_2Ni_2Sb_{12}$ Ternary Skutterudite

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Keywords: *$Ru_2Ni_2Sb_{12}$, ternary skutterudite; thermoelectric properties,*

Abstract:
Polycrystalline samples of $Ru_2Ni_2Sb_{12}$ compound were prepared by powder metallurgy method. The samples were characterized by x-ray diffraction and their structure was refined using the Rietveld technique. Their structure was confirmed to be isostructural with ideal skutterudite structure ($CoAs_3$). The composition of the ternary skutterudite samples was checked by EDX microanalysis. Hot-pressed samples were then characterized by measurements of Seebeck coefficient and electrical conductivity in temperature range 100 – 700 K and by measurement of Hall coefficient in temperature range 90-400 K. The reason of N-type conductivity and possibilities of further improvement of their thermoelectric properties are discussed.

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Alternative route for the preparation of $CoSb_3$ and Mg_2Si derivatives

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Keywords: *$CoSb_3$; Mg_2Si; synthesis*

Abstract:
An alternative route was developed for the manufacturing of cobalt triantimonide and magnesium silicide derivatives for thermoelectric applications [1,2]. The elemental powders were mixed in stoichiometric proportions, cold pressed into cylindrical preforms and heated in oxygen-free environment to initiate the exothermic reaction. According to DTA/TG measurements and observations under high-temperature microscope, the onset of reaction occurred at a temperature not exceeding the melting point of the more volatile component, i.e. antimony in the case of $CoSb_3$ and magnesium in the case of Mg_2Si. The reaction products were additionally heat treated to secure product homogenization. Dense sinters were obtained by hot uniaxial pressing of the obtained powders in moderate temperature-and-pressure conditions. Phase composition, chemical composition and microstructure of materials at consecutive manufacturing stages were systematically analyzed by XRD, TEM, SEM and EDS. Several advantages were identified in the proposed technology: absence of liquid phases, relatively short time of the synthesis, no need of milling for magnesium silicide and easy disintegration into powder for cobalt triantimonide, possibility of in-situ or ex-situ doping and grain size control.

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Oxidation resistant coatings for $CoSb_3$

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Keywords: *$CoSb_3$; protective coatings*

Abstract:
Doped cobalt antimonides, are used as components of thermoelectric devices at temperatures not exceeding 450 ˚C because of poor thermal and chemical stability. In absence of oxygen they degrade by sublimation of antimony, while in air they easily oxidize to form volatile antimony oxides and non-volatile thick double oxide scales [1]. In both cases, protective coatings are indispensable to ensure safe performance of thermoelectric devices over extended times. The most promising solution, reported so far, is a thick aerogel coating, which practically stops antimony loss by sublimation. The assessment of coating effectiveness is generally based on thermogravimetric tests in vacuum, so no conclusion can be drawn about permeability of oxygen and oxidation prevention. The paper presents investigations on the development of protective coatings, which would prevent oxidation of $CoSb_3$. Two types of coatings were applied: magnetron sputtered Cr-Si thin layers [2] and thick enamel layers. Testing involved interrupted oxidation in air for 20-80 h at 500 ˚C and 600 ˚C. The Cr-Si thin layers appeared oxygen-tight at 500 ˚C while the enamel layers - even at 600 ˚C.

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Dependence of microstructure induced with manufacturing parameters and physical properties of compound of skutterudite structure type $Ce_xFeCo_3Sb_{12}$

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Keywords: *microstructure, phase analysis, thermoelectric power factor*

Abstract:
This work is devoted to studies of relations between microstructure and physical properties of the compounds of skutterudite structure from $Ce_xFeCo_3Sb_{12}$ series, where x = 0.3, 0.6, 0.9 and 1. The compounds were produced using powder metallurgy method that combines mechanical alloying and hot pressing. The influence of mechanical alloying parameters, like the duration of the process and the type of protective medium, on microstructural homogeneity and the kind of precipitation was studied. The microstructure investigation performed by X-ray microanalysis (EPMA) technique indicates that increase of alloying duration clearly improves the chemical homogeneity of the compounds in micrometric areas. It is evident especially in case of Ce and Fe distributions. Moreover, the type of protective medium has been found to influence mainly the phase purity of obtained compounds. The process of mechanical alloying was carried out in liquid (acetone) and gaseous (Ar) environments. The diffraction patterns of compounds prepared in argon atmosphere clearly indicate that the precipitations of antimony are smaller in comparison to the compounds prepared in liquid environment. X-ray microanalysis confirms the results obtained with X-ray phase analysis, in microstructure of samples alloyed in acetone there are numerous areas enriched with Sb. The X-ray microanalysis revealed also the existence of various oxide contaminations depending on the type of protective medium used. In the compounds alloyed in acetone distribution of oxygen was evidently correlated with iron in amounts corresponding to Fe_3O_4 phase, whereas in compounds produced in argon cerium is partially oxidized. Performed investigations have shown that full characterization of filled skutterudites should be based not only on XRD analysis, but also microstructural studies. For each synthesized compound temperature dependences of Seebeck coefficient and electrical resistivity were measured in temperature range 300 K - 780 K. Beside the influence of chemical composition of a compound also influence of its microstructure on the values of thermoelectric power factor (PF) and temperature of its maximum has been observed. The compounds prepared in argon exhibit several times larger maximum values of PF. Regardless of the protective medium used, the highest values of PF were obtained for compounds with the lowest Ce content.

Synthesis and thermoelectric properties of the new skutterudites $Yb_xFe_2Ni_2Sb_{12}$ ($0 \leq x \leq 0.24$)

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Keywords: *Skutterudites; Cationic Substitution; Disorder*

Abstract:
Antimonides with the skutterudite structure have been extensively studied with respect to their potential use as thermoelectric materials [1]. The substitution on both framework and transition-metal sites with different atoms as well as the filling the structural voids with electropositive atoms has led to a variety of new compounds. It is now well established that the valence-electron concentration and phonon-scattering effects of the crystalline solids can be tuned by altering accordingly the composition of the skutterudites [2,3]. Characteristic examples of compounds with high *ZT* values such as *n*-type $Yb_{0.19}Co_4Sb_{12}$ (*ZT* = 1 at 600 K) [4] and *p*-type $Ce_{0.9}Fe_3CoSb_{12}$ (*ZT* = 1.1 at 700 K) [5] show partial filling of the cavities with heavy cations. In search of new thermoelectric skutterudites, the substitution of Co with Fe/Ni atoms is also under investigation.

In this study, we report on the synthesis and thermoelectric properties of the new skutterudites $Yb_xFe_2Ni_2Sb_{12}$ ($0 \leq x \leq 0.24$). The compounds have been prepared by melting the pure elements in carbon crucibles under high vacuum and have been characterized by powder X-ray diffraction and Rietveld refinement. Electrical resistivity, Seebeck coefficient and thermal conductivity measurements have been performed on hot-pressed samples. The results indicate that by increasing the Yb content in the skutterudite structure the thermoelectric performance is significantly improved. The physical properties of the title compounds are further discussed in comparison with those of the reported isostructural and isoelectronic $Yb_xCo_4Sb_{12}$ ($0 \leq x \leq 0.19$) system.

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Structural analysis and thermoelectric properties of XNiSn (X= Ti, Zr, Hf) half-Heusler compounds

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Keywords: *half-Heusler; thermoelectric, electron microscopy*

Abstract:
The half-Heusler phases with the general formula XNiSn (X = Ti, Zr, Hf) have drawn our attention due to their potential as thermoelectric materials. They have a narrow band gap of the order of 0.1-0.2 eV at the Fermi level [1] and they show high electrical conductivity and Seebeck coefficient. However, they have a relatively high thermal conductivity of approximately 10 W/Km [2]. In order to reduce the lattice thermal conductivity, mass disorder in X position can be introduced causing additional phonon scattering.

Following this motivation, the effect of different elements at X-site of XNiSn (X = Ti, $Hf_{0.5}Zr_{0.5}$, $Hf_{0.26}Zr_{0.37}Ti_{0.37}$) was studied. A full characterization of the thermoelectric properties was performed in the temperature range from 5 K to 900 K. We show that the thermal conductivity can be reduced up to 60% with a negligible modification of the electrical conductivity and the Seebeck coefficient. The three compositions show n-type behavior and a maximum Seebeck of |S| = 250 μV/K at around 600 K.

The elemental distribution at the microscale was studied by scanning electron microscopy and EDX mapping, while the local structural order by transmission electron microscopy.

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Enhanced Thermoelectric Performance of $(Mn_{1-x}Cr_x)Si_\gamma$ ($\gamma \sim 1.7$) by VEC control

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Keywords: *thermoelectric compounds, higher manganese silicides, chimney-ladder phase, VEC*

Abstract not presented

Formation of electrode materials for sintered n-type Mg_2Si using electroless plating and monobloc sintering methods

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Keywords: *Thermoelectricity, Silicide, Sintering, electrode*

Abstract:
Mg_2Si, the non-toxic and light-weight silicide material, is one of the dominant candidates for a thermoelectric (TE) material with relevant performance in the temperature range from 600 K to 900 K, and one that fits well with the operating temperatures of industrial furnaces, automobile exhausts, and incinerators. In order to realize an Mg_2Si TE power generator, appropriate electrodes are indispensable in terms of the extraction of generated electricity. The requisites for electrode materials to contact to Mg_2Si are: (a) a thermal expansion coefficient matched to that of Mg_2Si, (b) durability and no serious reactions with Mg_2Si at ~ 900 K, (c) low ohmic-contact resistance R_c to Mg_2Si.

Ni has been known to fit to Mg_2Si as electrode material possessing the comparable thermal expansion coefficient to Mg_2Si and stable characteristics such as no reaction and no thermal diffusion to Mg_2Si even at elevated temperature. We have worked with Ni as Mg_2Si electrode and have developed the monobloc electrode formation method, which is simultaneous sintering of electrode material during Mg_2Si sintering. Although monobloc sintering process with Ni electrode provides good ohmic contact even after heat resistance test at operation temperature, it is noted that the monobloc sintering method allows the electrode formation only a vertical plane to the compression direction of the sintering. In order to fulfill the degree of freedom for TE leg fabrication, conventional electroless Ni plating is also adapted to Mg_2Si, although electroless Ni plating to Mg_2Si has believed to be unattainable process owing to the degradation of the matrix during the acidity processes. We report here the two promising Ni electrode formation methods and these electrode properties. For an monobloc Ni sintered Mg_2Si and Ni-plated Mg_2Si samples, the value of R_c with a cross sectional area of 9 mm^2 was 3.46 mW and 3.31 mW, respectively. The output power characteristics and durability of Mg_2Si with both methods will also be discussed.

Mechanical properties of doped n-type Mg_2Si prepared by the plasma activated sintering method

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Keywords: *Thermoelectricity, Magnesium silicide, Mechanical properties,*

Abstract:
One of the more reliable technologies used to help reduce greenhouse gas emissions and the consumption of fossil fuels, and one which is attracting attention, is thermoelectric technology, by which heat can be directly converted into electricity and consequently increase the energy conversion efficiency of power generation by combustion. Magnesium silicide (Mg_2Si) has been identified as a promising advanced thermoelectric material operating in the temperature range from 500 to 800 K. Compared with other thermoelectric materials that operate in the same temperature range, such as PbTe, TAGS (Ge-Te-Ag-Sb) and $CoSb_3$, Mg_2Si has some promising features, such as the abundance of its constituent elements in the earth's crust and the non-toxicity of its processing by-products, resulting in freedom from concern about the prospect of extended restrictions on hazardous substances.

The material quality of Mg_2Si has been improving significantly, and experimental power-generation modules have been fabricated recently. Since the expected operating temperature is up to 900 K, the module suffered from local thermo-mechanically induced stresses due to the differences in thermal expansion coefficients and Young's moduli between the constituent parts, such as the thermoelectric legs and peripheral components. Furthermore, depending on the operating cycle, the module is expected to suffer from heat cycling, which will cause serious durability problems. For these reasons, the design of the module structure should be optimized to adequately relieve the thermo-mechanical stresses in a more sophisticated manner based on the well-defined thermo-mechanical properties of the constituent parts, i.e. the Mg_2Si raw material, the legs for power generation and the integrated modules. Although such an approach is urgently needed to realize robust thermoelectric generators, only a little effort towards this has so far been expended.

Therefore, in this presentation, we present our recent efforts to obtain fundamental thermo-mechanical design data such as Young's modulus, hardness and thermal expansion coefficients of doped n-type Mg_2Si fabricated using a commercial polycrystalline source and the plasma activated sintering technique. It is seen that the fundamental thermo-mechanical characteristics are dependent upon the properties of our initial material, such as the type of dopant and its concentration, and fabrication processes like plasma activated sintering.

Crystal orientation and thermoelectric properties of $MnSi_{\gamma}$ films

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Keywords : *$MnSi_{\gamma}$, film, PLD*

Abstract not presented

Solid-State Synthesis and Thermoelectric Properties of n-type Mg_2Si

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Keywords: *thermoelectric, magnesium silicide, solid state reaction, mechanical alloying*

Abstract:
Mg_2B^{IV} (B^{IV} = Si, Ge and Sn) have a favorable complex of physical and chemical properties and could be a good base for the development of new efficient thermoelectrics. Mg_2Si is a narrow band gap semiconductor with an indirect band gap of 0.78 eV and a promising material for thermoelectric energy conversion at temperatures ranging from 500 to 800 K. Compared to other thermoelectric materials operating in the same conversion temperature range, such as PbTe and $CoSb_3$, Mg_2Si is a non-toxic, and its constituent elements are abundant in the Earth's crust. It is very difficult to prepare Mg_2Si using a melting process due to the large difference in vapor pressure of the constituent elements and lack of solubility, as well as the small difference between the boiling temperature of Mg (1380 K) and the melting temperature of Mg_2Si (1358 K). Therefore, it is difficult to control its composition due to the volatilization and oxidation of Mg. Mechanical alloying has been used to solve the aforementioned problems, which involves the formation of an alloy in the solid phase through repeated mechanical impact during high energy ball milling, and is an advantageous method for the synthesis of semiconducting thermoelectric compounds or solid solutions. However, a ductile-brittle system such as Mg_2Si cannot be fully-transformed to a single phase (Mg_2Si) by mechanical alloying because Mg is so ductile as to stick to the walls of vials and balls, even though a process control agent is used. Therefore, the synthesized Mg_2Si powders have a low yield and non-homogeneous chemical composition. In this study, Group B^{III}(Al, In)-, B^{V}(Bi, Sb)- and B^{VI}(Te, Se)-doped Mg_2Si compounds were synthesized by solid state reaction and mechanical alloying. Mg_2Si powder was synthesized successfully by solid state reaction at 773 K for 6 h and doped by mechanical alloying for 24 h. It was fully consolidated by hot pressing at 1073 K for 1 h. Electronic transport properties (Hall coefficient, carrier concentration and mobility) and thermoelectric properties (Seebeck coefficient, electrical conductivity, thermal conductivity and figure-of-merit) were examined.

Thermoelectric characterization of n-type Mg_2Si doped with transition metal elements

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Keywords: *Thermoelectricity; Magnesium Silicide; Doping; Sintering*

Abstract:
To optimize the thermoelectric (TE) properties of Mg_2Si for practical applications, it needs to be doped, and typical device operating temperatures require that any substitutional element used as a dopant be highly stable. Stable dopant elements in Mg_2Si are needed to ensure long lifetime operation at elevated temperatures. Al, Bi and Sb are well known conventional n-type dopants for Mg_2Si. In terms of the increase in value of the dimensionless figure of merit, $ZT=S^2\sigma T/\kappa$, Bi doping lowers the thermal conductivity, κ, and Al improves the power factor, $S^2\sigma$, derived from the increase in electrical conductivity. These doping effects provide an increase in ZT values as compared with undoped specimens, while an increase in resistivity during aging at ~900 K seems to be a serious problem for Bi- and Al-doped ones. Since first principle calculations suggest that Sb is stable in Mg_2Si, no notable change in resistivity nor surface erosion of the samples was revealed for Sb-doped Mg_2Si during atmospheric durability tests at 873 K for ~11,000 h. Thus, Sb doping is seen to be promising for the fabrication of Mg_2Si TE power-generators; however, incorporation of Sb involves sintering difficulties and toxicity.

To further elevate the TE capability of Mg_2Si, a search for promising dopants should be conducted with a view to finding a substitutional element that gives high electrical activation, thermal stability at elevated temperatures, and is non-toxic for reduced impact on the environment. Of the alternative n-type impurities, we examined Co, Nb, Ta, Nd, and Sm, which possess similar oxidation states to Al, Bi and Sb. Doping was performed during fabrication of polycrystalline Mg_2Si at 1423 K. The polycrystalline Mg_2Si was pulverized to powder with sizes of 75 μm or less and then sintered by a Plasma Activated Sintering (PAS) technique. The thermoelectric properties were measured up to 873 K using an ULVAC-RIKO ZEM-2 and a TC-7000H. With Ta, Nb, and Nd doping the Mg_2Si exhibited comparable or higher ZT values than that of Sb-doped specimens. Ta doping enhanced the power factor by increasing the electrical conductivity, and Nb and Nd reduced the thermal conductivity down to ~2 W/mK at 873 K. The estimated ZT values were 0.69, 0.73, and 0.74 for Ta-, Nb-, and Nd-doped Mg_2Si, respectively. In the presentation, the results of aging tests at 873 K will also be demonstrated.

Development of the method for the preparation of Mg_2Si by SPS technique

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Keywords: *magnesium silicide, thermoelectric materials, SPS technique*

Abstract:
The aim of the study was to develop a fast and simple method for preparation of polycrystalline Mg_2Si. Materials were synthesized by the direct reaction of Mg and Si raw powders. The process was conducted in the graphite dies placed in the chamber of the spark plasma sintering SPS apparatus. The composition of the mixture of powders, as well as, SPS process conditions (temperature, time, pressure) were precisely adjusted for preparation of single–phase materials having good thermoelectric properties.

To determine the phase and chemical composition, the fabricated samples were studied by X-ray diffraction and SEM microscopy coupled with EDX chemical analysis. The uniformity of thermoelectric properties of materials was determined by the scanning thermoelectric microprobe. Thermoelectric properties of samples (thermal conductivity, electrical conductivity and Seebeck coefficient) were measured over temperature range of 300 - 630 K.

The developed method allows easy and efficient preparation of large amounts of undoped Mg_2Si having very low amount of impurities. The analysis by the scanning thermoelectric microprobe (STM) shows that samples have quite uniform distribution of Seebeck coefficient with mean value of 300 [μVK^{-1}]. Prepared materials have intrinsic band gap of 0.32 eV and thermal conductivity λ= 7.5 [$Wm^{-1}K^{-1}$] at room temperature.

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Fabrication of large size sintered pellets of n-type Mg_2Si using a plasma activated sintering method

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Keywords: *Thermoelectricity; Silicide; Doping; Sintering*

Abstract:
Magnesium silicide (Mg_2Si) is a candidate for use as a thermoelectric (TE) material at operating temperatures ranging from 600 to 900 K. Mg_2Si has some appealing features, such as the abundance of its constituent elements in the earth's crust and the non-toxicity of both Mg_2Si and its processing by-products. This suggests it is safe to handle and can be used in practical devices, and results in freedom from concern with regard to the increasing regulations on hazardous substances. Recently, some groups have fabricated TE generators (TEG) consisting of n-type Mg_2Si and p-type $MnSi_x$ with the conventional π (pi)-leg structure and single n-Mg_2Si for a uni-leg structure. In the preparation of Mg_2Si legs using a plasma or conventional sintering method, however, it is known that there is a very narrow process window for the sintering parameters; as a result, the largest sintered sample size exhibiting sufficiently good TE properties and durability was ~15 mm in diameter. So, the establishment of a reproducible and scalable leg sintering process is needed in order to take Mg_2Si TEGs into production.

To obtain better electrical conductivity and phonon scattering, impurity doping is relevant and effective for Mg_2Si. Al, Bi and Sb are well-known n-type dopants in Mg_2Si. Bi can minimize the thermal conductivity, and Al enhances the electrical conductivity, while both dopants exhibit local precipitation and/or unstability at elevated temperature operation and consequential degradation. Sb is the most stable element in Mg_2Si and provides excellent thermal and electrical conductivities. However, making reproducible sintered pellets from the Sb-doped Mg_2Si causes cracks to form during sintering. In order to improve this for Sb-doped specimens, we have developed a metallic binder for the sintering process. A remarkable further benefit of the binder is that it enables us to reproducibly fabricate large size sintered Sb-doped Mg_2Si pellets up to 30 mm in diameter with no internal cracks. For a binder of a given content, the observed power factor and thermal conductivity were identical to that of conventional Sb-doped samples, while excess binder degrades the TE properties. The binder mixture also plays a part in increasing the yield in the production of TE legs up to 82%, as well as improving the hardness of the sintered sample.

Synthesis and characterization of Bi-doped Mg_2Si thermoelectric materials

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Keywords: *magnesium silicide, bismuth, thermoelectricity*

Abstract:
The Mg_2Si-based alloys are promising candidates for thermoelectric energy conversion for the middle-high range of temperature. They are very attractive as they could replace lead-based compounds due to their low cost, non-toxicity [1, 2] and low density. They could also result in thermoelectric generator weight reduction (a key-feature for the automotive application field [3, 4]). The high value of thermal conductivity of the silicide-based materials could be reduced by increasing the phonon scattering in the presence of nanosized crystalline grains. This does not heavily interfer with the electrical conductivity of the thermoelectric material [5-6].

Nanostructured dense materials were obtained under inert atmosphere through ball milling, thermal treatment and spark plasma sintering processes. In particular, the role of several bismuth doping amounts (1 at%, 2 at% and 4 at%) in Mg_2Si were investigated. The morphology, the composition and the structure of the obtained samples were characterized by FE-SEM, EDS and XRD analyses during the different process steps.

Moreover, the Seebeck coefficient analyses at high temperature and the electrical and thermal conductivity (obtained by Laser Flash analysis) of the samples are presented in this work. With the aim of further increasing the scattering phenomena by interface or boundary effect, carbon nanostructures named Single Wall Carbon Nanohorns were added to the Mg_2Si in order to produce a nanocomposite material. The influence of the nanostructured filler on the material thermoelectric properties are also discussed.

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Nanostructured multilayered thin film barriers for Mg_2Si thermoelectric materials

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Keywords: *thin film, magnesium silicide, thermoelectricity*

Abstract:
The Mg_2Si-based alloys are promising candidates for thermoelectric energy conversion in the middle-high temperature range in order to replace lead compounds. The main advantage of silicide-based thermoelectrics is the nontoxicity and the abundance of their constituent elements in the earth crust [1, 2].

The drawback of such kind of materials is their oxygen sensitivity at high temperature [3] that entails their use under vacuum or inert atmosphere. In order to limit the corrosion phenomena, nanostructured multilayered molybdenum silicide-based material were deposited via RF magnetron sputtering onto stainless steel, alumina and silicon (100) to set up the deposition process and then onto Mg_2Si pellets. .

XRD, EDS, FE-SEM and electrical measurement at high temperature were carried out in order to obtain, respectively, the structural, compositional, morphological and electrical characterization of the deposited coatings. At the end, the mechanical behavior of the system thin film/Mg_2Si-substrate as a function of temperature and the barrier properties for oxygen protection after thermal treatment in air at high temperature were qualitatively evaluated by FE-SEM.

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Thermoelectric properties of Mg_2Si-based compounds synthesized partially using magnesium alloy

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Keywords: *dimagnesium silicide; magnesium alloy, solid-liquid phase reaction*

Abstract:
Mg_2Si compounds are promising eco-friendly thermoelectric materials because both constituent elements of Mg and Si have no toxicity and exist richly in earth crust. We have a plan to use the compounds in the applications that convert waste heat in the temperature range (300-600 ^oC) into electric power. However, the thermoelectric performance of the compounds has not yet reached to the practical use level. In addition, the compounds don't have durability in the thermoelectric performance under atmospheric circumstances in the temperature range of 500-600 ^oC. These issues have to be solved for the practical use. In our previous work, we obtained knowledge that Al doping in Mg_2Si lower the electrical resistivity and improved the thermoelectric performance. We newly attempted to use a magnesium alloy (AZ61) that includes the main three elements of aluminum (5.8-7.2 wt%), zinc (0.4-1.5 wt%) and manganese (0.15-0.35 wt%) in order to synthesize the Mg_2Si-based compounds. The Mg_2Si based compound powder was synthesized from the mixture of silicon powder, AZ61 chips and Mg powder by the liquid-solid phase reaction method. The compound powder was sintered by the pulse discharge sintering method. The influence of mixing ratio of two metals of AZ61 and pure Mg on the thermoelectric properties was investigated. Addition of AZ61 greatly decreased the electrical resistivity as well as Al-doped Mg_2Si and the thermoelectric performance had improved most in the 50wt%AZ61 mixing sample.

Formation of Mg_2Si thick films on Si substrates using pack cementation process

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Keywords: *thermoelectric materials, chemical vapour deposition*

Abstract:
Magnesium silicide (Mg_2Si) is a prospective narrow gap semiconductor for thermoelectric energy conversion at high temperatures. It has low density (1.99g/cm^3), high melting point (1085ºC), is mechanically stable and environmentally friendly as it consists of non-toxic elements in the earth's crust. These features, along with its ZT make Mg_2Si a good candidate material for thermoelectric applications. Many attempts have been made to produce Mg_2Si films on Si substrates. However, the easy oxidation and volatilisation of magnesium are the two main obstacles to obtain pure high-quality crystalline Mg_2Si films.

In this work, chemical vapour deposition by pack cementation process was used, for the first time, for the formation of Mg_2Si compound. For this process Si substrates were cut in 1x1 cm pieces, placed in porcelain crucibles filled with powder mixtures composed by 25-50% wt. laboratory grade Mg (320-mesh), 3% wt. halide activator and Al_2O_3 as filler. The crucibles were sealed with porcelain lids and placed in a tubular argon-purged electric furnace. A series of experiments were carried out at temperatures 450^{o}C to 650^{o}C with deposition times at 15, 30, 60 and 180min. Thick films, with thickness varying from 5μm to 85μm have been prepared, depending on growth temperature and deposition time. Mg_2Si was formed as a result of the Mg diffusion into the Si matrix. SEM observations showed that the film thickness is increased with the deposition time, and at the higher temperature (650^{o}C) films have significantly bigger thickness, which is attributed to the higher diffusion rate of Mg at that temperature. Films were studied with X-ray diffraction and FTIR to determine the structure and phase identification. Results indicate the presence of pure Mg_2Si phase without any MgO phase.

Electrodeposition and characterization of p-type Bi-Te-Sb-Ag film thermoelectric materials

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Keywords: *electrodeposition; film thermoelectric material; Bi-Te-Sb-Ag; power factor*

Abstract withdrawn

Influence of Film Thickness and Annealing Temperature in Growth of Mg_2Si Thin Films

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Keywords: *Thermoelectric Mg_2Si films, Dual Cathode Magnetron Sputtering, XRD*

Abstract:
Thermoelectric (TE) materials can provide electricity when subjected to a temperature gradient or cooling when electrical current is passed through it. Although the efficiency of thermoelectric materials has been significantly improved over the last decade, major advances are still needed to meet the future requirements. Magnesium based compounds have been proposed as good thermoelectric materials for high temperature range. Magnesium silicide (Mg_2Si) is a prospective narrow gap semiconductor for thermoelectric energy conversion. It has high ZT, low density (1.99g/cm^3), high melting point (1085ºC), is mechanically stable and environmentally friendly as it consists of non-toxic elements in the earth's crust.

In this work we examine the influence of film thickness and annealing temperature on the growth of Mg_2Si thin films. Films were grown by dual cathode magnetron sputtering (DCMS) at room temperature. Two series of films were grown one with thickness about 0.96μm (films-A) and another with 1.99μm (films-B). Sputtered films were subsequently annealed in Ar gas atmosphere at temperatures 250°C, 300°C (films-B) and 380°C, 500°C (films-A). Results indicate that growth in films-A proceeds with the formation of two phases, a cubic (Fm-3m) and a strained (compressed) cubic with smaller lattice constant. When film thickness is doubled (films-B) material transforms into unstrained cubic phase. Annealing films-B at 300°C transforms films into the same compressed cubic phase that was observed in films-A. Further annealing of films-A causes a strain relieve and at 500°C films are single phase.

Spark plasma sintered Half-Heusler compounds with high Figure-of-Merit

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Keywords: Half-Heusler, Spark plasma Sintering

Abstract:
Half-Heusler compounds exhibit very promising thermoelectric properties for high temperature applications, combined with several additional advantages such as environmental friendliness, low production-costs and future availability of raw materials. The high thermoelectric potential can be mainly attributed to the high Seebeck coefficient and the low electrical resistivity values found recently in several half-Heusler alloys. The main drawback is still their relatively high thermal conductivity. The most common approach for reduction of the thermal conductivity is by phonons scattering due to mass fluctuations obtained upon atomic substitution of the involved elements. Yet, it is well known that the microstructural aspects such as solidification defects, the degree of ordering and phase separation can also drastically reduce the thermal conductivity and thereby would allow a significant increase in ZT. In this study, *n*-type $Ti_{0.3}Zr_{0.35}Hf_{0.35}NiSn$ half-Heusler alloy was prepared by the spark plasma sintering method and followed several heat treatment conditions. High *ZT* values with a maximal value of 0.82 at 450^{o}C, were found for this composition. The effect of the microstructure on the transport properties will be described in details.

Comparison of transport properties of type I germanium clathrates $A_8Ga_{16-x}Ge_{30+x}$ (A- K, Ba) with band structure calculations.

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Keywords: *clathrates, band structure calculations*

Abstract:
Samples of germanium clathrates $A_8Ga_{16-x}Ge_{30+x}$ filled with Ba and K were prepared using standard powder metallurgy methods. Electronic band structure calculations were performed for the obtained compositions based on the DTF theory. The structure and phase composition of the prepared samples were analyzed by powder x-ray diffraction XRD. The microstructure and chemical composition were examined by scanning electron microscope SEM and EDS analysis. Electrical conductivity, Seebeck coefficient and thermal conductivity were measured in the temperature range 20 - 400°C.

The observed properties were compared with the preliminary electronic band structure calculations, showing good qualitative correlation between measured transport properties and theoretical predictions.

N type thermoelectric recycled carbon fibre sheet with electrochemically deposited Bi_2Te_3

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Keywords: *Recycled carbon fibres, Seebeck coefficient, Electrical resistivity, Bismuth telluride*

Abstract:
An N-type thermoelectric recycled carbon fibre sheet with bismuth telluride coating has been successfully synthesised through the electrodeposition technique. The Seebeck coefficient and electrical properties of the combine recycled carbon fibre sheet and bismuth telluride films are reported. Classification of the crystal structure, surface morphology and the elemental composition of the resulting deposits are methodically characterised by XRD, SEM and EDX correspondingly. Cyclic voltammetry is also carried out in nitric acid solutions to investigate the right range of deposition potential. An N-type thermoelectric sheet is successfully synthesis with the highest attainable Seebeck coefficient of -54 μV/k with an electrical resistivity of 2.95×10^{-5} Sm^{-1}. The results shows slight differences in morphologies and thermoelectric properties for the films deposited at varying deposition potential. The increase in thermoelectrical properties of the recycled carbon fibre is inline with the development of a flexible yet robust cooling fabric.

Thermally induced decomposition of acrylic acid grafted luminescent silicon quantum dots in ultrahigh vacuum

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Keywords: *Silicon, quantum dots, thermogravimetric analysis, X-ray photoelectron spectroscopy*

Abstract not presented

High Figures of Merit in Degenerate Semiconductors. Energy Filtering by Grain Boundaries in Heavily Doped Polycrystalline Silicon

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Keywords: *Degenerate Silicon, Energy Filtering, Grain Boundaries*

Abstract:
Heavily doped *p*-type silicon has been reported by the present authors [1-2] and by other investigators [3] to be characterized by somewhat unexpectedly high power factors, up to 12 mW K^{-2} m^{-1}. Also, in the case of polycrystalline films phonon scattering at grain boundaries (GBs) dumps thermal conductivity κ, leading to a quite remarkable *ZT* value of ≈ 0.2 at room temperature. While low κ values are likely and already reported in polycrystalline silicon, high Seebeck coefficients are unexpected in materials with high carrier densities.

A semi-quantitative model has been proposed [2], showing that the potential barrier structure at GBs, along with the nanometric grain size, leads to an unusual mechanism of carrier filtering, named adiabatic energy filtering. Actually, the presence of potential barriers associated to segregated boron disables charge transport by holes in the band deep tail. This leads to a decrease of the actual carrier density, as in the case of standard energy filtering. However, the nanometric grain size along with the inefficiency of the hole-hole relaxation mechanism in degenerate semiconductors prevents carriers from relaxing, causing an increase of the average (macroscopic) drift mobility. Thus, in spite of the decrease of drifting hole density the electrical conductivity is found to increase. At the same time, the formation of exponential band tails leads to an increase of the energy derivative of the density of states (DOS) around the Fermi energy, resulting in high thermoelectric coefficients.

In this communication experimental evidence will be presented on polysilicon films deposited onto oxidized silicon substrates, doped by high-current implantation to an average boron density of 4.4×10^{20} cm^{-3} and then annealed to promote boron segregation. Hall mobility was measured as a function of temperature from 20 to 300 K, along with Seebeck coefficient and electrical resistivity.

A fully quantitative model of charge transport will be presented, encompassing a detailed analysis of the DOS shape and of the relaxation mechanisms in this class of system. The model will be discussed and corroborated with the experimental results gathered on degenerate polycrystalline silicon.

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Preparation and thermoelectric properties of B_4C-Si-B composites

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Keywords: *boron carbide; composite; thermoelectric properties*

Abstract:
Ceramic thermoelectric materials are receiving increased attention for energy conversion from waste heat because they are cost-efficient, environmentally friendly and thermally stable at high temperature. Recent investigations on boron carbides show that boron-rich carbides with large Seebeck coefficient, moderate electrical conductivity and low thermal conductivity are promising candidates for high temperature applications [1]. Furthermore, preparation of B_4C-based composite, e.g. B_4C-SiC composites has proved to be a useful approach to modify the thermoelectric properties of boron carbide [2,3].

In this work B_4C-Si-B composites have been prepared by spark plasma sintering (SPS) using different amount of B_4C, B, and Si powders. The composition and the microstructure of the dense composites are characterized by means of XRD, SEM and EDX, the studies show that the composites contain B_xSi_yC and SiC phases with a homogenous structure. Moreover, the structure of the B_xSi_yC Phase is studied by Raman spectroscopy. The thermoelectric properties are investigated up to 1000 K. All the samples are p-type semiconductors and high Seebeck coefficient >300 μV/K has been achieved at temperatures above 500 K. The electric conductivity of the composites increases with the temperature and reaches a level > 15 S/cm. The formation of the ternary phase in the composite is found to decrease the thermal conductivity to < 10 W/mK.

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Switching effect in transverse thermopower in single-crystal Bi microwires

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Keywords: *Bi microwire; transverse thermopower; switching effect*

Abstract:
In the thermoelectric-anisotropic media there is transverse to the temperature gradient electric field. We investigated at room temperature the transverse thermopower in thin single-crystal bismuth microwires. The single-crystal nanowire samples in the diameter range 5 - 15 μm were prepared by the high frequency liquid phase casting in a glass capillary using an improved Ulitovsky technique [1]; they were cylindrical single-crystals with (10$\underline{1}$1) orientation along the wire axis. In this orientation, the wire axis makes an angle of 19.5° with the bisector axis C_1 in the bisector-trigonal plane. Bismuth microwire was placed between two polished aluminum plates, which were at different temperatures. At relative displacement of the plates the microwire was rotated around its axis. Transverse thermoelectric power varied by rotating microwires. The maximum thermoelectric power (S_{max} ~ 200 – 600 μV/K at the length of the plates L = 4.5 cm) occurred at the direction of the transverse temperature gradient along the C_3 axis. For the first time significant difference was found in the values of the thermoelectric power after turning micrwires at 180 degrees (i.e. when the direction of the temperature gradient is reversed). The value of this switching effect, defined by us as (S_{max}-S_{min}) / (S_{max} + S_{min}), depends on the diameter d microwire and varies from 0.4 (for microwires with d = 14 μm) to 0.75 for microwires with d = 5 μm. Different assumptions about the nature of the observed effect will be discussed.

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Thermoelectric figure-of-merit enhancement in Te-coated Bi composites

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Keywords: *thermoelectric figure-of-merit; thermal conductivity; bismuth; hydrothermal tellurium coating*

Abstract not presented

Prospects of nanostructures $Bi_{1-x}Sb_x$ for thermoelectricity

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Keywords: *thermoelectricity; nanostructure, semiconductor*

Abstract:
There is renewed focus on the thermoelectric properties of BiSb. Reduced dimensionality samples of these alloys, such as nanowires, may exhibit exotic behavior that relate to the properties of the surfaces of topological insulators. It has been predicted that surface states of topological insultors have large thermopower and also ultrahigh mobilities.[1,2] The authors report results of magneto-thermoelectric investigation of single crystal $Bi_{1-x}Sb_x$ nanowires in a glass cover with diameters ranging from 90 nm to 5 μm. The wide- ranging antimony concentration ($0.01 < x < 0.2$) enabled us to study the effect of nanowire dimensionality the (bulk) semimetal ($x < 0.05$), semi-conductor $0.08 < x < 0.2$ and gapless ($x = 0.04$-0.06) regimes.

Bi-2at%Sn nanowires are particularly interesting. Quantum size effect, shown in temperature dependences of resistance R (T) and thermopower α(T) at the diameters significantly higher than the critical diameter for pure Bi- wires, are observed. The thermopower is very large; in weak magnetic fields (to 1 T), reaches values as high as + 400 μV/K at T= 20 - 40 K. We will show that this effect in not related to phonon drag effect but, rather, is associated with the large hole band partial thermopower. Power factor $\alpha^2 \sigma$ depending on diameter of wires, structure, temperature and a magnetic field is calculated. In connection with topological insulators, we will discuss the effect of the surface in the thermoelectric properties that we observe.

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Enhancement of thermopower anisotropy in Bi and Bi-Sn wires at elastic deformation in magnetic field

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Keywords: *nanowire, anisotropic thermoelement*

Abstract:
In this work we have studied the possibility to enhancement the thermopower anisotropy in Bi and Bi-Sn nanowires under the influence of elastic tension and low magnetic field. Glass coated single-crystal Bi and Bi-Sn wires with diameters 100 nm – 2 μm were manufacturing by the liquid phase casting method [1]. The wires with trigonal orientation were obtained by the method of zone recrystalliyation of wires with standard orientation (1011), which made it possible to study the thermopower anisotropy (without magnetic field).

It is shown that low magnetic field (H || ΔT), Sn doping and elastic tension leads to a significant increase of thermopower in absolute value and significant grows of its anisotropy at 250-300 K. That is important for design of transverse anisotropic thermoelements with low useful current. The stable thermoelectric properties, high flexural strength, the long wire length (up to 1 m and much more) allow designing thermoelectric devices of various configurations.

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Layered materials for thermoelectricity

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Keywords: *oxides ; sulfides ; selenides*

Abstract not presented

Thermal diffusivity measurement system applied to polymers

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Keywords: *thermal, diffusivity, polyaniline*

Abstract:
Nowadays one of the main society challenges is to obtain cleaner sources of energy. Thermoelectric materials, which are able to convert heat into electricity and vice-versa, are one of the candidates. Cost-Effective energy harvesting from temperature gradients requires thermoelectric materials with high electrical conductivities and Seebeck coefficient, but low thermal conductivity. Conducting polymer can fulfill these conditions if doped appropriately.

One of the most promising polymers is Polyaniline. In this work the thermal diffusivity of the polyaniline and polyaniline with nanoclays has been studied, using a new experimental set-up at IMM developed under NANOTERMA project. The novel system is based on the steady-state method and it is used in order to obtain the thermal diffusivity of the polymers and their nanocomposites, see figure 1.

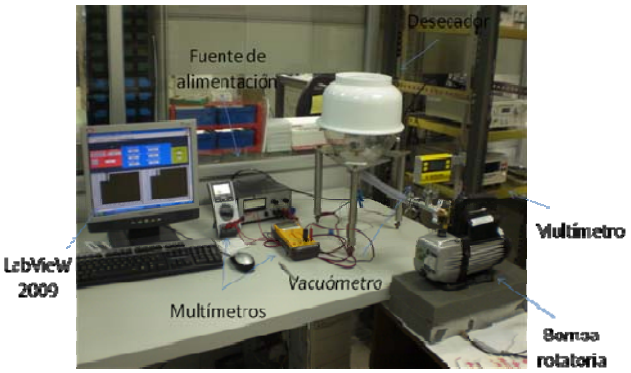

Fig. 1 Experimental system built under the NANOTHERMA project

The thermal diffusivity is directly related with the thermal conductivity by this expression $\alpha = \kappa/\rho C_p$. With the new experimental set-up, we are able to measure thermal diffusivity, but we need to measure the specific heat to obtain the thermal conductivity. It is already made in collaboration with technological center LEITAT by Differential Scanning Calorimetry (DSC).

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Thermoelectric properties of SnO_2-based ceramics doped with Nd, Hf or Bi

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Keywords: *Oxide material, SnO_2, multiple impurity doping*

Abstract:

The influence of multiple impurity doping on the thermoelectric properties of SnO_2-based matrix with the nominal composition of $Sn_{0.98}Sb_{0.01}Zn_{0.01}O_2$ was investigated. Polycrystalline SnO_2-based samples ($Sn_{0.97}Sb_{0.01}Zn_{0.01}M_{0.01}O_2$, M= Nd, Hf or Bi) were prepared by solid state reactions. X-ray diffraction analysis revealed that single-phase with a rutile structure was obtained for the Hf-doped sample, but the Nd- or Bi-doped samples contained secondary phases along with the main SnO_2 phase. Microstructure analysis by scanning electron microscopy showed that Hf- or Nd-doping increased the grain size of the sample. The values of power factor for the Nd- or Hf-doped samples were smaller than those for the matrix material ($Sn_{0.98}Sb_{0.01}Zn_{0.01}O_2$). On the other hand, we confirmed that Bi-doping increased the power factor due to both the enhanced electrical conductivity and Seebeck coefficient over the measured temperature range. The maximum power factor of 5.2×10^{-4} $Wm^{-1}K^{-2}$ was obtained for the Bi-doped sample at 1100 K. This study suggests that n-type SnO_2-based materials have potential to be one of candidate oxide materials for thermoelectric applications.

In-situ PXRD Investigation of the hydrothermal synthesis of ZnO and presentation of OTE power project

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Keywords: *ZnO, Oxide Thermoelectrics, In-situ PXRD, Sub and supercritical synthesis*

Abstract:
ZnO is recognized as one of the most promising oxide n-type thermoelectric materials, when doped with Al and Ga. In this study synchrotron powder x-ray diffraction has been utilized as a means to investigate the influence on several synthesis parameters on the nucleation and growth of ZnO nanoparticles during subcritical hydrothermal synthesis. It has been found that synthesis temperature, pH and choice of base used for synthesis will influence the growth habits of ZnO in different ways.

The research presented here is a part of a new project (OTE power) between several academic and industrial partners. The participants in the group are: from Denmark, Denmarks Technical University, Aarhus University, Aalborg University and the companies Dantherm Air Handling, FL Smidth A/S, ALPCON A/S, RAIS A/S og HWAM A/S, from the United states California Institute of Technology and from Japan Kyushu University. It is financed by the Danish Strategical Research council.

The goal of the joint effort is to produce a working oxide thermoelectric module for high temperature applications.

Spark Plasma Sintering (SPS) synthesis and thermoelectric properties of Ti_2O_3

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Nowadays, research is entrust with the task of finding energy-efficient synthetic routes for a producing a bulk quantities of the new and industrially applicable materials with specified shape. Spark plasma sintering (SPS) is a one of the advanced consolidation techniques developed in the last few decades, what is conforming to all these standards. The significant features of the SPS method include a high heating rate, an application of pressure, and effect of *dc* current [1]. Recent trends demand from researches a synthesis of novel materials, which are highly durable at high temperature in air, non-toxic, low cost and minimal in environment impact. Binary and multicomponent oxides waked an attention of researchers as promising thermoelectric materials.

Numerous studies are occupied by an investigation of Titanium (III) oxide Ti_2O_3 due to its unusual properties [2]. It undergoes a semiconductor-metal transition during the heating and becomes apparent on the specific heat accompanied by second-order phase transition without change of its crystal structure [3]. The aim of our work is synthesis of scale amounts of Ti_2O_3 dense material by using SPS technique. This oxide was synthesized in one-step reaction starting from the mixture of rutile/anatase with metallic titanium powders. At initial stages of the synthesis the components of reactive mixture are mutually diffused and several phases with the compositions slightly deviated from those of starting materials are formed. After longer annealing and increasing of the temperature these phases are deeply developed to formation of the Ti_2O_3 compound and their neighboring phases. Finally, the Ti_2O_3 as a single phase is obtained at 1200 °C after 180 min treatment. The obtained products are characterized by chemical analysis, X-ray diffraction, metallographie. The thermoelectrical properties are investigated.

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Thermoelectric power studies of misfit-layered NiO-added $Ca_3Co_4O_9$ oxides

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Keywords: *Oxides; Electrical conductivity; Seebeck coefficient; Microstructure*

Abstract:

In recent years, great attention has been giving to the misfit-layered oxide $Ca_3Co_4O_9$ due to its high value of figure-of-merit and excellent thermal and chemical stabilities at high temperature in air. $Ca_3Co_{4-x}Ni_xO_9$ (x=0, 0.1, 0.15, 0.2, 0.25, and 0.3) thermoelectric samples were fabricated by solid-state reaction method, using solution combustion processed $Ca_3Co_{4-x}Ni_xO_9$ nano-sized powders. To synthesize nano-sized $Ca_3Co_{4-x}Ni_xO_9$ powders, aspartic acid ($C_4H_7NO_4$) was employed as fuel and $Ca(NO_3)_2 \cdot xH_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $Ni(NO_3)_2 \cdot 6H_2O$ nitrates as oxidizers. The obtained powders were calcined at 800 ℃ for 12h. Subsequently, the calcined powders were cold-pressed under 98 MPa to prepare green pellets. The pellets were heated at 850 ℃ for 24h in air and then furnace cooled. The synthesized $Ca_3Co_{4-x}Ni_xO_9$ ($0 \le x \le 0.3$) powders showed spherical and ultra-fine, and showed a smooth surface. In the present study, we investigated the thermoelectric properties of $Ca_3Co_{4-x}Ni_xO_9$ samples as a function of Ni^{2+} contents. The incorporation of Ni^{2+} reduced the grain size and density, thereby decreasing electrical conductivity. The Seebeck coefficient of the $Ca_3Co_{4-x}Ni_xO_9$ samples increased with an increase in Ni^{2+} content up to 0.2 and then decreased for higher Ni^{2+} content.

Electrical conductivity and thermoelectric power of $Na(Co_{1-x}Ni_x)_2O_4$ thermoelectric oxides

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Keywords: *Oxides; Electrical conductivity; Seebeck coefficient; Microstructure*

Abstract:
The $Na(Co_{1-x}Ni_x)_2O_4$ powders were synthesized by solution combustion method. The synthesized powders were calcined at 800 ℃ for 12 h. The calcined powders were cold-pressed under 135 MPa to prepare green pellets. The pellets were sintered twice at 900 ℃ for 12 h with intermediate grinding to obtain homogeneous compositions. The microstructure, electrical conductivity, and Seebeck coefficient of once- and twice-sintered $Na(Co_{1-x}Ni_x)_2O_4$ samples were investigated. The synthesized $Na(Co_{1-x}Ni_x)_2O_4$ powders showed a homogeneous distribution of size and shape as well as a nanocrystalline nature. The amount of impurity phases, such as Na_2CO_3 and $NaNiO_2$, present in twice-sintered $Na(Co_{1-x}Ni_x)_2O_4$ samples was much lower than that in once-sintered $Na(Co_{1-x}Ni_x)_2O_4$ samples. Twice-sintered $Na(Co_{1-x}Ni_x)_2O_4$ samples showed lower porosity compared to once-sintered $Na(Co_{1-x}Ni_x)_2O_4$ samples. In addition, the electrical conductivity and Seebeck coefficient of twice-sintered $Na(Co_{1-x}Ni_x)_2O_4$ samples were higher than those of once-sintered $Na(Co_{1-x}Ni_x)_2O_4$ samples, giving rise to enhanced thermoelectric power factor.

Microstructure and thermoelectric properties of Sm_2O_3-added $CaMnO_3$

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Keywords: *Oxides; Electrical conductivity; Seebeck coefficient; Microstructure*

Abstract not presented

$Zn_{1-x}Dy_xO$ ($0 \leq x \leq 0.04$) thermoelectric oxides for power generation

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Keywords: *Oxides; Electrical conductivity; Seebeck coefficient; Microstructure*

Abstract:

Oxide-based materials are regarded as a potential candidate for power generation because they are chemically and thermally stable as well as highly oxidation resistant in air at high temperatures. In this work, we selected an n-type zinc oxide (ZnO) as a candidate material for power generation and investigated the influence of the addition of Dy_2O_3 on the thermoelectric properties of the ZnO. $Zn_{1-x}Dy_xO$ ($0 \leq x \leq 0.04$) thermoelectric oxides were prepared by solid state reaction method. For low Dy_2O_3 contents ($0 \leq x \leq 0.01$), samples had a wurtzite structure with a $P6_3mc$ (186) space group. On the other hand, for high Dy_2O_3 contents ($0.02 \leq x \leq 0.04$), samples consisted of the majority ZnO and a secondary phase Dy_2O_3. The addition of Dy_2O_3 to ZnO showed a significant effect on the thermoelectric properties. The sign of the Seebeck coefficient for all samples was negative over the entire temperature range (600-800℃), i.e., n-type conduction. The microstructure and thermoelectric properties of $Zn_{1-x}Dy_xO$ samples as a function of Dy_2O_3 content were investigated.

Spark plasma sintering of Al-doped ZnO nanoparticles and its thermoelectric properties

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Keywords: *Al-doped ZnO nanoparticles, Spark plasma sintering, Thermoelectric*

Abstract:
ZnO has attracted considerable attention as n-type thermoelectric materials for high temperature range. To improve thermoelectric conversion efficiency, materials have to possess a high Seebeck coefficient, high electrical conductivity, and low thermal conductivity. In this respect, doping of ZnO with impurities such as Al, Ga and Ni is demanded for increasing an electrical conductivity. Among them, Al is known to be a suitable dopant for thermoelectric application of ZnO because of a significant reduction of electrical resistivity. Furthermore, nanocrystalline in bulk material can lead to a low thermal conductivity due to enhanced boundary scattering of phonon. Therefore, it is important to fabricate bulk materials with Al-doped ZnO nanocrystalline for the thermoelectric application.

Until now, many research groups have reported Al-doping in ZnO by using solid state reaction between powders of ZnO and Al_2O_3. However, in this case, secondary phase, such as $ZnAl_2O_4$, can be easily generated during the reaction, and it has a detrimental effect on the thermoelectric properties. Thus, we carried out direct doping of Al in ZnO nanoparticles through solution method.

In this work, Al-doped ZnO nanoparticles were prepared via solution method using zinc nitrate hexahydrate, hexamethylenetetramine, and aluminum nitrate nonahydrate as dopant material. In order to maintain nano-size of the particles, bulk materials consisting of the nanocrystalline ZnO were obtained by spark plasma sintering process. Thermoelectric and structural characterizations were conducted, and the doping effect of Al in nanocrystalline ZnO on the thermoelectric properties was also discussed.

Acknowledgments: This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials (K0006007) funded by the Ministry of Knowledge Economy, Republic of Korea.

Titanium suboxides – obtained from an organo-metallic precursor - as thermoelectrics

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Keywords: *thermoelectric, precursor, titanium suboxide, TiO_x*

Abstract:

An industrial application requires cheap and sustainable thermoelectric materials and preferably a high efficiency at a broad and high temperature range. An alternative material to commercially available thermoelectric materials (Bi_2Te_3, PbTe) could be titanium suboxide (TiO_x) because these oxide ceramics can be used at temperature above 700 °C [1].

The synthesis of titanium suboxide was realized using a precursor route. Compared to the conventional solid state reaction the advantage of this synthesis method is the possibility to control the stoichiometry of titanium and oxide with a preset molecular design to create a special coordination in the organo-metallic complex. Additionally, using precursors allows a disperse homogenous doping of the titanium suboxide and therefore yielding in an increase of electrical conductivity which could cause a positive change in the thermoelectric properties.

The precursor route allows the tailoring of the microstructure in the range of µm to nm with the probability to scale up the synthesis and to produce nanostructured thermoelectric like thin film and core shell composites.

The precursors have been synthesized via a ligand exchange reaction and afterwards thermally transformed to a ceramic material by removing the organic groups during pyrolysis. Subsequently, a compacting treatment was implemented using spark plasma sintering (SPS) technique at a temperature up to 1500 °C.

We present here the investigations on the influence of the pyrolysis temperature on the bulk properties such as density, microstructure, phase composition, and thermoelectric properties. The density has been determined using Archimedes and geometric methods. The investigation on the microstructure was performed using FESEM. The crystal structure has been studied using XRD. The thermoelectric measurements were carried out using the simultaneous measurement system ULVAC ZEM 3 and the laser flash method.

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Optimization of Thermoelectric Efficiency of $LaCoO_3$ by Double Substitution with Nickel and Iron

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Keywords: *perovskites, structure, thermoelectric efficiency*

Abstract:
Lantanum cobaltate, $LaCoO_3$, with a perovskite type structure is recently considered as a material with potential application in thermoelectricity. The state-of-the-art research is mainly devoted to the improvement of the thermoelectric efficiency of $LaCoO_3$ by lanthanum or cobalt substitution.

The aim of this contribution is to study the effect of nickel and iron double substitution for Co on the thermoelectric efficiency of $LaCoO_3$. Perovskites are obtained from freeze-dried citrate precursors at 900 ^oC. Structural and morphological characterizations are carried out by powder XRD and SEM analysis. The thermoelectric efficiency of the perovskites is determined by the dimensionless figure of merit, calculated from the independently measured Seebeck coefficient (S), electrical resistivity (ρ) and thermal conductivity (κ).

The replacement of cobalt with nickel and iron in $LaCo_{1-x}(Ni,Fe)_xO_3$ for the concentration range $0 \le x \le 0.5$ yields oxides with a rhombohedrally distorted perovskite structure. The single substitution in $LaCoO_3$ affects its thermoelectric parameters (S, ρ and κ) differently for Ni and Fe. The electrical resistivity decreases substantially during the progressive replacement of cobalt by nickel. In the same order, there is a decrease in the values of the Seebeck coefficient and the thermal conductivity. As a result, slightly doped $LaCo_{1-x}Ni_xO_3$ oxides ($0.05 \le x \le 0.10$) display a higher thermoelectric efficiency as compared to $LaCoO_3$: ZT=0.072. The substitution for cobalt with iron leads to an increase in ρ, while κ decreases and S tends to increase. As a result, slightly doped $LaCo_{1-x}Fe_xO_3$ (x=0.05) exhibits a dimensionless figure of merit ZT=0.044 which is comparable with that of $LaCoO_3$. Using the specific effect of Ni and Fe doping on S, ρ and κ, new perovskite-type thermoelectric materials with double substitution ($LaCo_{1-x}Ni_{x/2}Fe_{x/2}O_3$) are prepared. The perovskite $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$ exhibits best thermoelectric efficiency with ZT=0.158, which is an order of magnitude higher than that of $LaCoO_3$ at room temperature.

Transition-metal-based perovskite oxides for enhanced thermopower

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Keywords: *thermopower; perovskites, oxides*

Abstract not presented

Thermoelectric properties and microstructure of modified novel complex cobalt oxides $Sr_3RECo_4O_{10.5}$ (RE = Y and Gd)

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Keywords: *Complex cobalt oxides; Perovskites; Electrical conductivity; Thermopower*

Abstract:

Thermoelectric properties from 300 to 1200 K and microstructure of novel complex cobalt oxides $Sr_3RECo_4O_{10.5}$ (RE = Y and Gd) have been investigated in terms of Ca and Ga doping at the Sr- and Co-sites, respectively. We found that the sample with RE = Gd shows a significant higher electrical conductivity (σ) than the RE = Y sample in the high temperature region above 500 K, while the Seebeck coefficient (S) of these samples remains almost the same over the whole measured temperature range. With Ga substituting for Co, S at temperatures above 700 K increases, and its values tend to increase with increasing Ga concentration. The power factor (σS^2) of the $Sr_3GdCo_{4-x}Ga_xO_{10.5}$ system is significantly enhanced and further improved by the substitution of Ca on the Sr-site due to a simultaneously increase in both σ and S. At 1150 K, the highest σS^2 value of $Sr_2CaGdCo_{3.9}Ga_{0.1}O_{10.5}$ sample attains about 60 $\mu Wm^{-1}K^{-2}$, which is 8 times larger than the $Sr_3GdCo_4O_{10.5}$ counterpart. Interestingly, microstructure shows a clear evolution of crystalline grains for the Ga and Ca dually doped-sample resulting in a substantial decrease of its porosity.

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Experiments with semiconducting p-type misfit compound

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Keywords: *thermoelectric oxide, p-type, misfit compound*

Abstract:

$Ca_3Co_4O_9$ is a p-type semiconductor and a promising thermoelectric material. Cobalt based layered structure materials have been studied as thermoelectric material candidates because their non-toxicity, light weight, high thermal and chemical stability and oxidation resistance at high temperatures. Cobalt oxide nanostructures and calcium cobalt oxide misfit layer structures enable to control the thermoelectric properties of $Ca_3Co_4O_9$. The operating area of $Ca_3Co_4O_9$ in thermoelectric applications is roughly from 800K to 1000K.

$Ca_3Co_4O_9$ powders were synthesized by sol-gel method which enables fabricating of high purity and small diameter particles. Calcium and cobalt nitrate hydrates were used as feedstock and citric acid as complexing agent in the sol-gel procedure. Powders were calcinated at 850°C. Further processing included ball milling. Pure $Ca_3Co_4O_9$ powders were sintered by utilizing SPS as well as more conventional methods. Samples were characterized by Scanning Electron Microscopy, X-ray diffraction and Termogravimetry – Differential Scanning Calorimetry before and after sintering procedure. Thermoelectric properties of the samples are presented as well.

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Nb-doped SrTiO3 glass-ceramics as high-temperature stable n-type oxide thermoelectrics

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Keywords: *Thermoelectric materials, oxides*

Abstract:
Niobium doped SrTiO3 is known for its high potential as an oxide thermoelectric material and is one of the possible candidates for the n-type site in an oxidic thermoelectric module. The high thermal conductivity [2] and the lack of high-temperature stability of the oxygen vacancies [1] limit its properties in the ceramic systems. Glass-ceramics are intrinsic nanostructured systems and provide crystal phases densly embedded in a glass matrix which prevents the material from detoriation at high temperatures. In particular, the glass matrix prevents an uncontrolled reoxidization as well as an uncontrolled grain growth therefore retaining the nano-structure even at high temperatures. Here, measurements and results of first glass-ceramic systems are presented, which show a low thermal conductivity due to the residue glass phase. Furthermore a stable thermal cycling up to 650°C is demonstrated.

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Influence of electrodeposition parameters in the thermoelectric properties of ZnO films

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Keywords: *oxide; thermoelectric power, film*

Abstract:

In recent years, Zinc Oxide (ZnO) has been of great interest because it is a material with remarkable and varied properties. Due to its wide band gap (3.36 eV) it is transparent in the visible range. It has large exciton energy (60 meV). Those characteristics provide an efficient emission in the ultraviolet and visible ranges, even at room temperature. Moreover, when doped with Al, it presents a large thermopower factor at high temperatures when compared to other metal oxides [1].

In this study, ZnO films have been grown by constant and pulsed electrochemical deposition. Electrodeposition of ZnO was performed using a standard three-electrode cell. ZnO films at constant potential were grown using two different OH- sources: nitrate and peroxide in order to obtain a comparative study between those films. While, ZnO films at pulsed potential were grown in 0.1 M zinc nitrate aqueous solutions, the oxidation potential was maintained at + 0.9 V and the reduction potential was changed from – 1.5 V to - 0.5 V versus Ag/AgCl decreasing in 0.2 V from film to film.

The morphology and structural characterization of the films were investigated depending on the solution used and the applied potential. Scanning Electron Microscopy pictures show different morphologies in each case. X-Ray Diffraction confirms that the films are pure ZnO oriented along the (0002) direction.

Seebeck coefficient and electrical resistivity of the best films deposited under the different conditions (different solutions, pulses and the applied potential). It can be concluded that the Seebeck increases with temperature for all films except for the film grown at pulsed potential. And, the resistivity increases with the temperature in all cases. The resistivity of the films grown at pulsed potential is higher that the resistivity of the films grown at constant potential. The resistivity of the films grown in peroxide solution is higher that the resistivity of the films grown in nitrate solution.

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Seebeck coefficient and electrical conduction changes of Si nanowire arrays filled with polymers.

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Keywords: *silicon nanowire arrays, polymer, thermoelectricity*

Abstract:

Nanowires are considered to be promising structures for boosting the thermoelectric performance of semiconducting materials. In this work, we present the fabrication and characterisation of arrays of vertically upstanding Si nanowires filled with polymers. The purposes of the polymer are: thermal and electrical insulation of the Si nanowires, improvement of the robustness of the composite material, use of the polymer to boost the conductivity of the nanowires in the array without the use of doping. The nanowire arrays (NWAs) were etched from lowly n-doped Si wafers using metal-assisted electroless etching. Three different polymers were used: poly-acrylic acid, poly-acrylamide and poly-allylamine. These polymers were chosen because they can be easily dissolved in H_2O and the last two contain a primary amine group in each of their monomers that can act as electron donors for hydrophilic Si nanowires. After etching of the NWAs, each sample was treated in H_2O_2 or HF to make them hydrophilic or hydrophobic. The H_2O_2 treatment terminates the nanowire surfaces with –OH groups while HF with –H. The arrays were immediately immersed into beakers with different polymers. The arrays are left in the polymer bath to allow the polymer to fill the gaps between the wires via diffusion. The NWAs are dried at room temperature in air (fig.1). Reactive ion etching using an oxygen plasma is used to remove the polymer from the top of the wires before ohmic contact evaporation. The Seebeck coefficient and the current voltage characteristics are measured for the different samples with different surface treatment and polymer filling. It was found that the hydrophilic surfaces allowed a more homogeneous filling of the arrays. The Seebeck coefficient tends to be higher for HF treated samples while the current is highest in most cases of H_2O_2 treatment. This might point towards a carrier enhancement of the surface of the H_2O_2 treated polymer filled samples. However, the polymer filling decreases the overall electrical conductivity of the NWAs, possibly due to the incomplete removal of the polymer at the tops of the nanowires before metallisation. The largest temperature drop can be maintained across the HF treated samples and the poly-acrylamide sample followed closely by the bare NWA. This implies the lowest thermal conductivity of the HF treated samples.

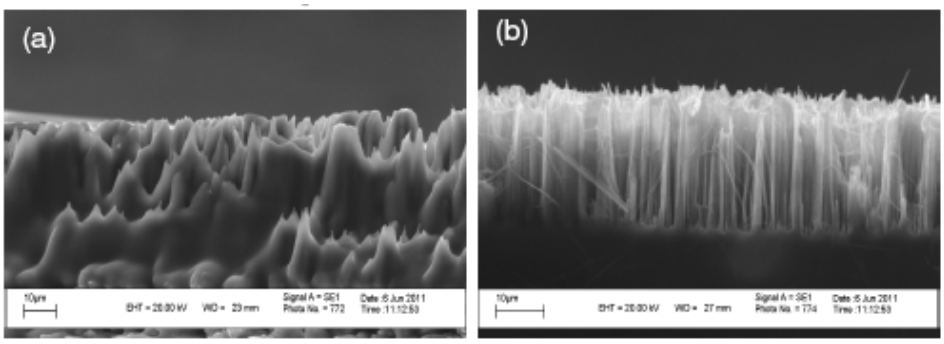

Figure 1: SEM picture of NWAs filled with poly-acrylic acid. (a) NWA is H2O2 treated. (b) HF treated.

The effect of substrate on the thermoelectric properties of rf sputtered Bi_2Te_3 film

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Keywords: *substrate, rf magnetron sputtering, bismuth telluride thin film, thermoelectric*

Abstract:

The fine control of composition in Bi-Te based thin film by changing the deposition parameters such as substrate temperature and flux of reactants has been an issue for optimizing the thermoelectric properties of the film deposited by sputtering. Especially, the effects of substrate on the properties Bi_2Te_3 film is one of the most essential matters for fabricating thin-film based thermoelectric device. Even though Ferhat et al.[1] suggested the Bi_2Te_3 film deposited on SiO_2 shows better electrical properties than that of the film deposited on Si substrate, further study on the substrate effects on thermoelectric properties of bismuth telluride thin films are needed. In this study, Bi_2Te_3 films were deposited on various substrates which include SiO_2, GaAs, and sapphire, and the differences in structural and electrical characteristics of the films are discussed.

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The thermoelectric properties of Bi_2Te_3 and In_2O_3 nanowires

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Keywords: *thermoelectric; thermal conductivity, power factor*

Abstract:

With the perpetuating increase in green house gases and the gradual shortage of conventional energy sources, new and more efficient energy substitute is unceasingly being developed and sought after. Below room temperature, the thermoelectric material Bi_2Te_3 is one such candidate widely studied. In this investigation, the fabrication and the TE properties (Seebeck coefficient, resistance, and thermal conductivity) of a single Bi_2Te_3 nanowires were studied. Rhombohedral structured Bi_2Te_3 nanowires grown along (110) direction were prepared. The typical resistivity of the nanowires (150 nm in diameter) was around 5.16 μΩ-m, half of that of its bulk counterpart[1]. However, the absolute value of the Seebeck coefficient of the nanowires (S= -68.49μV/K) is lower than the bulk value (S= 214 μV/K). This is attributed to the sensitivity of the Seebeck coefficient to the atomic composition of Bi and Te. From our results, ZT values in the range of 0.49~0.51 were obtained. The thermal properties of In_2O_3 nanowire were also studied in this article. The ZT value improvement was observed in In_2O_3 nanowire at 380 K (ZT = 0.018) compare with its bulk counterpart (ZT = 0.011)[2]. This is due to the thermal conductivity reduction and the oxygen deficiency in the nanowire. The In_2O_3 nanowires with lengths of 10~30 μm and diameters of 100~200 nm were revealed by SEM images. The power factor of single In_2O_3 nanowire was $2.07x10^{-4}$ W/m-K^2 at room temperature, slightly smaller than that of the bulk material, $2.56\ x10^{-4}$. As temperature rises from 300K to 570K, the power factor shows a descending trend. The thermal conductivity of In_2O_3 nanowire was measured by self-heating 3ω method. A sagging structure of In_2O_3 nanowire was prepared by E-beam lithographic and reactive ion etching techniques. The thermal conductivity of In_2O_3 nanowire decreases from 9.8 W/m-K to 2.5 W/m-K from 300 to 380 K. In this study, the thermal conductivity of In_2O_3 nanowire is reduced by a factor of three in compare with In_2O_3 bulk material (9.7 W/m-K to 7.7 W/m-K).

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Correlation of local and global thermoelectric properties in laterally structured thermoelectric materials

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Keywords: T*hermoelectricity, photolithography, ZnS, ZnO*

Abstract:
Interfaces are a promising way to perturb or even block the propagation of phonons through a solid to reduce its thermal conductivity. Therefore a better understanding of the influence of the structure of the interface on the thermoelectric transport parameters is essential for improving the figure of merit Z of nanostructured thermoelectric materials.

With photolithography and various etching methods we have produced ZnO/ZnS bar structures of different interface design. Measurements of the Seebeck coefficient and the electrical conductivity perpendicular to these interfaces have been carried out locally and globally.

The results have been compared to simulations within a simple network model that allows the calculation of the thermal and electric conductivity and the Seebeck coefficient.

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Comparison of different methods for measuring thermal conductivities

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Keywords: *ZnS, 3ω method*

Abstract:

Two different methods for the measurement of the thermal conductivity of bulk and thin-films have been applied to glass (borosilicate) bulk samples and ZnS thin-films. The first method was in the steady state using an arrangement of gold wires on the sample to create a thermal gradient and to measure the temperatures locally. The same wire arrangements were also used for 3ω measurements which are based on periodical heating and a frequency dependent analysis of the temperature response. The results of both methods are in good agreement with each other for isotropic materials. The thermal conductivity in in-plane direction can be determined with the steady state method, whereas the results of the 3ω method are in cross-plane direction for thin-films and a mix of the two directions for bulk materials. To understand the heat flow in the steady state method, especially in the case of thin-film measurements, finite element analysis has been applied. The results can be used to optimize the wire positions and therefore minimize the measurement error due to inhomogeneities in the heat flow.

New measuring techniques for the investigation of thermoelectric properties of nanowires

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Keywords: *nanowires; thermoelectric properties; measuring techniques*

Abstract:

The poster focuses on the determination of thermal and electrical transport properties of individual nanowires, preferably thermoelectric bismuth and bismuth compound nanowires, prepared by ion-track-technology [1,2]. Also the thermoelectric parameters S, σ, λ, z (with S: Seebeck coefficient; σ: electrical conductivity; λ: thermal conductivity; z: thermoelectric efficiency) of template-embedded nanowire arrays have been investigated. For measurements of S, σ, λ and z, specially designed microchips have been developed and employed [3,4]. The microfabricated z-chip is designed and optimized to determine all thermoelectric parameters on one and the same individual nanowire. The Seebeck microchip can also be applied for measurements on nanostructures, prepared by electron beam induced deposition (EBID) [5].

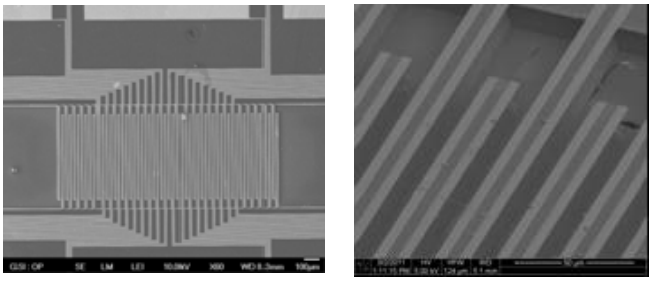

Fig. 1: z-chip for the measurement of all thermoelectric parameters S, σ, λ, z on one and the same individual nanowire

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Cross-plane Seebeck coefficient measurement of highly crystalline $CuFeSe_2$ thin film

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Keywords: *cross plane; Seebeck coefficient, 3 omega*

Abstract:

Type I-III-VI_2 chalcopyrite semiconductor, i.e. $CuInSe_2$, has been extensively studied because of its middle range band gap can be applied to optoelectronic devices. Although the $CuFeSe_2$ belong to the I-III-VI_2 family, it shows very different physical properties, which include the tetragonal structure, the small band gap (0.16 eV) and the weaker magnetic behavior. Only a few articles focused on this material in the recent years. The wide temperature range Seebeck coefficient measurement and thermal conductivity measurement of high quality $CuFeSe_2$ sample could provide useful information in this system.

In this report, the highly preferred orientated $CuFeSe_2$ thin film sample was prepared by excimer laser deposition on SiO_2/Si substrate. The thickness of this thin film sample is 200 nm, and shows the (h 0 0) preferred orientation normal to the substrate, which is confirmed by X-ray diffraction pattern. The differential 3ω method with additional two voltage probes was applied to study the cross plane thermal conductivity and thermoelectric behavior. The heater/sensor for differential 3ω method was deposited by thermal evaporation, one located on the thin film and the other located on substrate. The cross plane thermal conductivity is 1.2 W/m-K at 300 K. The voltage probes for Seebeck coefficient measurement was located above and below the thin film. When the AC current applied to the heater/sensor, the temperature gradient will be generated across thin film at frequency 2ω and the cross plane EMF can be measured. The cross plane Seebeck coefficient is -56 μV/K at 300 K. The cross plane thermal conductivity and Seebeck coefficient were measured in large temperature range from 50 to 300 K.

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Acknowledgments: We would like to thank the technical support from NanoCore, the Core Facilities from Nanoscience and Nanotechnology at Academia Sinica in Taiwan and the micro optics electrical laboratory (National Central University, Taiwan). We also like to thank Z. W. Zhong for the help in the X-ray diffraction measurement. The work was supported by Academia Sinica and National Science Council, Republic of China, under Grant No. NSC 99-2120-M-001-001.

Metrology for Energy Harvesting

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Keywords: *figure of merit, reference material, Seebeck coefficient*

Abstract:
End of 2009 EURAMET, the European metrology organization opened a call to advance measurement science and technology in the field of Energy [1] by providing funding for Joint Research Projects. The present project "Metrology for Energy Harvesting" started in September 2010 with scheduled project duration of three years. It addresses the grand challenge energy in aiming to develop new technologies, devices, and appropriate metrological measurement means to exploit new sources of reliable and sustainable energy. This paper discusses general aspects and objectives of the project but is mainly focused on the traceable measurement of the Seebeck coefficient of thermoelectric materials.

The energy sources of interest are the largely untapped sources of ambient energy resulting from human activity and environmental energy flows in the form of waste heat, movement and vibration. If only a fraction of the energy wasted in heat and vibration can be recovered, this would have a significant impact on CO_2 reduction.

Thermoelectric materials convert wasted heat directly into electrical energy. The performance of the energy conversion scales with the thermoelectric figure of merit (ZT) of the active material, which is defined as $ZT = S^2\sigma T/\kappa$, with S, σ, κ and T are the Seebeck coefficient, the electrical conductivity, the thermal conductivity, and the absolute temperature, respectively. The traceable determination of the efficiency of thermoelectric converters is crucial to enable a fair international competition for improving the figure of merit. The evaluation of ZT on basis of undisputed reference materials with known thermoelectric properties is indispensable to validate testing methods and to allow a reliable benchmarking of thermoelectric materials.

Thermoelectric reference materials with measurable Seebeck coefficients in the temperature range from 300 K to 900 K are missing at present. The paper describes the methods to reach one important stopover of the project: the development of traceable and robust metrology to provide reliable property specifications for thermoelectric materials; in particular for Seebeck coefficients.

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Modified Harman's method

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Keywords: *measurement, thermoelectric parameters, Harman's method, errors*

Abstract:
Precise determination of thermoelectric material parameters becomes an increasingly relevant task. Particularly attractive among the well-known methods is Harman's method which allows determining material characteristics on small-size samples, with high response speed and over a wide temperature range. However, the accuracy of this method needs to be improved.

This paper describes new approaches to determination of material parameters based on Harman's method. New measurement methods are proposed, analysis of errors is made and their instrumental determination methods are elaborated. Examples of exact measurement of thermoelectric material properties are given.

Study Harman response of different parts of one-cascade and multi-cascade modules along the thermoelectric contour

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Keywords: t*hermoelectric modules, cascading, Harman method, thermoelectric contour*

Abstract not presented

Construction of Seebeck-coefficient measurement by Kelvin-probe force microscopy

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Keywords: *Seebeck coefficient, nanostructure, Kelvin-probe force microscopy*

Abstract:
The introduction of nanometer-scale structures into thermoelectric materials has been expected to lead to breakthroughs for enhancing the thermoelectric figure-of-merit. However, it is difficult to evaluate the thermoelectric characteristics of these materials because of the very small dimensions. In order to characterize the nanostructured thermoelectric materials, therefore, we have constructed a new method for measuring Seebeck coefficient on a nanometer scale [1]. By Kelvin-probe force microscopy (KFM), surface potential or Fermi energy is locally measured on a semiconductor sample with a temperature gradient in a plane parallel to the sample surface, which gives us the Seebeck coefficient.

We measured time evolution of the surface potential, simultaneous with the temperature measurement at the high- and low-temperature regions on a Si wafer (N_D=1x10^{13}cm^{-3}). Then, the surface potentials at the high- and low-temperature regions were plotted as a function of temperature difference. From this graph, the Seebeck coefficient of Si was evaluated to be -1.25mV/K, which is close to the value measured by a conventional method, -1.27mV/K. This result indicates that the KFM technique has the ability to evaluate the local Seebeck coefficient.

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Influence of the Thermal Aging Phenomena on the Al-Substituted ZnO Thermoelectric Properties

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Keywords: *Thermoelectric properties, Al-substituted ZnO, TEM, SEM, XRD*

Abstract:
Al-substituted ZnO is a well-studied material and recently a lot of interest arose in its thermoelectric properties. Its non-toxicity and low-cost production together with a high power factor of up to 1 mW/K^2m at 1275 K make it a promising oxide n-type material. However, the results vary considerably between different studies in literature and there is a dependence of the transport properties on the synthesis and the processing methods and on the atmosphere. In this work $Zn_{1-x}Al_xO$ (x = 0.02, 0.06) was prepared by soft chemistry and solid state reaction synthesis methods. The thermoelectric properties and the thermal stability were studied in air and in oxygen. Crystal and microstructure were studied by X-ray diffraction (XRD), scanning (SEM) and transmission electron microscopy (TEM). Soft chemistry leads to a lower electrical resistivity of less than 0.01 Ωcm from room temperature to 1275 K compared to around 0.02 Ωcm for the sample prepared by solid state reaction for 2% Al-substitution. Both samples have a similar Seebeck coefficient with -100 to -250 µV/K in the same temperature range. The difference in the electrical resistivity results from a dissimilar grain connectivity and structural defect concentration. Substituting ZnO with 6% Al halves both the electrical resistivity and the absolute value of the Seebeck coefficient compared to the 2% Al-substituted sample prepared by soft chemistry. Cycling during the thermoelectric measurement leads to an increase of the electrical resistivity and the absolute value of the Seebeck coefficient. The reason for this ageing phenomenon can be assigned to a change in the stoichiometry by an uptake of oxygen with a change in the defect concentrations. The ageing is enhanced if the cycling is performed in oxygen atmosphere. The highest ZT value of 0.21 is reached at 1275 K for the sample with 2% Al-substitution prepared by soft chemistry synthesis.

Thermoelectric Standardisation – Reference Materials and Characterisation methods

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Keywords: Thermoelectric *Standardisation, Reference Materials, Traceable Characterisation*

Abstract:
Thermoelectric materials for working temperatures between 300 K and 1000 K become continuously more important for energy recuperation applications. The efficiency is determined by the transport properties (electrical and thermal conductivity and Seebeck coefficienct), which form the known thermoelectric figure of merit ZT. The thorough determination of ZT represents the basis for the assessment of thermoelectric materials research. Due to different continuing difficulties measurement errors distinctly higher than 15 % can be observed repeatedly, which is still too high for an industrial benchmark and deficient for many scientific investigations and technological developments. Against this background a project was launched this year together with the Fraunhofer Institute of Physical Measurement Techniques (IPM, Freiburg), the Department Temperature of the Physikalisch-Technische Bundesanstalt (PTB, Berlin) and the company Netzsch Gerätebau GbmH (Selb, Germany). The aim of the project "Thermoelectric Standardisation" (TESt) is to minimise the measurement uncertainties and to develop traceable, high-accurate thermoelectric characterisation techniques and thermoelectric reference materials for the mentioned temperature range. Here we initially present the project to the thermoelectric society and want to give a survey on the planned activities and the current status of the contributions of the German Aerospace Center (DLR, Cologne).

Acknowledgments: The authors would like to thank the German Federal Ministry of Education and Research for funding this project at the Institute of Materials Research of the German Aerospace Center (Grant number: 03X3550B).

Simultaneous Measurement of Thermoelectric Properties with the new IPM ZT-Meter

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Keywords: thermoelectric, scientific instrument, figure of merit

Abstract:
The dimensionless figure of merit ZT ranks good thermoelectric materials. The higher the ZT-value the better is the efficiency of thermoelectric conversion from heat into electricity. It is therefore important to measure it accurately. The best is to measure all the properties on one sample simultaneously at the temperatures of operation, e.g. for wasted heat harvesting. This was hardly possible for most researchers since no ZT-Meter was available on the market for temperature above 400 K. Recently, Fraunhofer-IPM developed a ZT-Meter for measurements up to 900K. Measurement of the figure of merit of known thermoelectric materials like $Bi_2(Te,Se)_3$, PbTe, PbSnTe, Mg_2Si and SiGe are presented. A verification of the measurement accuracy has also been performed with two samples of Macor™ (technical ceramic) with known thermal properties. This material was also measured using a Netzch LFA 457. But the IPM ZT-Meter can more than just measure the ZT-values, with all the transport properties measured in the same direction. It can be used also to determine the figure of merit of module components (legs) with or without build-in electrode(s). Change in electrical and thermal contact resistance in real time and on a broad temperature range can be investigated by comparison. Also thermal stability, cycling and annealing experiments can be made with an online monitoring of Z, power-factor, Seebeck-coefficient, thermal and electrical conductivity, Lorenz-Number, bringing new insight into materials science and engineering.

Investigation of the thermoelectric property of polyaniline nanorods doped with inorganic dopant

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Keywords: Conducting Polymers, Thermoelectric

Abstract not presented

Micro thermoelectric devices using Bi-Te and Sb-Te thin films deposited by co-evaporating

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Keywords: *micro thermoelectric device, Bi-Te thin films, Sb-Te thin films, co-evaporating*

Abstract not presented

Design and construction of a thermoelectric module based on natural pyrite

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Keywords: *Pyrite; Seebeck coefficient; resistivity; device*

Abstract:
During the last decade, thermoelectric phenomena are gaining importance in a wide range of applications using the residual heat of different process. At present, among the compounds that exhibit nice thermoelectric properties (high Seebeck coefficient (S) and low thermal (κ) and electrical resistivity (ρ)), metal chalcogenides are very attractive to built thermoelectric based-devices. For instance, Bi_2Te_3 is widely used in commercial thermoelectric devices [1] because their thermoelectric properties are reasonable adequated and the synthesis methods are well established. Particularly, among different chalcogenides, iron disulfide (FeS_2) is an attractive compound [2]: it is an abundant semiconductor that is found in the nature exhibiting n and p conductivity, presents a moderately high Seebeck coefficient (hundreds of μV/K) and low resistivity (0.1 ~ Ωcm). Moreover, its low cost turns FeS_2 into a very promising material to built simple and cheap thermoelectric generators.

In this work, a thermoelectric module based on natural pyrite was made. Pyrite crystals (n and p type) were obtained–from ores of Logroño (Spain) and Konstanz (Germany), respectively. A structural (XRD), morphological (SEM), compositional (EDX) and transport characterization of different FeS_2 crystals was carried out. The module was done with 12 couples of n and p legs linked with Cu wires. I-V curves of the module carried out at different temperature gradients obtaining output powers of ~0.1 μW. Finally, the thermoelectric viability of iron disulfide will be compared to well known chalcogenides, from an economic point of view as well as considering non-bulk pyrite (films, nanoparticles).

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A new method to improve the efficiency of the heat flow path of a micro thermoelectric generator

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Keywords: *thermoelectric generator, energy harvesting, heat flow path, heat concentrator*

Abstract:
This work proposes a new method to improve the efficiency of the heat flow path of a micro thermoelectric generator (TEG) realized in our laboratory. A Silicon heat concentrator is placed on a planar TEG built of polySilicon/metals thermocouples patterned into a ribbon shape on a low stressed SiO_2/Si_xN_y thin film. This concentrator has a contact with every hot junction (under which SiO_2/Si_xN_y membranes are released) and can form a 150 µm thick air cavity over every cold junction (under which the substrate is not etched as a heat spreader). This enables to thermally isolate heat source from the cold junctions and to link it to the heat sink.

A 10 µm thick polyimide layer is deposited between the thermocouples and the heat concentrator as an electrical isolation layer. Four silicon legs at the edges of the concentrator are mechanical support to prevent the breaking of the TEG's membranes. In such a configuration, the heat flow is firstly guided to the hot junctions by the concentrator, and then it passes through the thermocouples and is evacuated at each cold junction through the substrate which is placed on a heat sink. A gradient of temperature ΔT is hence periodically created between each hot/cold couple of junctions leading to the building of a thermoelectric voltage.

Several TEGs were characterized by injecting power to a heating resistance printed on the upper surface of the concentrator and by studying the output voltage. The results show that each thermocouple is able to stand for a high generated ΔT; we could characterize some of the TEGs up to $\Delta T = 114\,°C$). For a 5.7 x 6 mm² size thermoelectric generator with 560 thermocouples, when a 4W/cm² power is injected to the heat concentrator, a 68°C temperature difference is created. This ΔT builds an output voltage of 9.9V (29V/cm²) which can supply an output power of 14µW to a matched load resistance (41µW/cm²).

A 3D modeling via Comsol has been developed to predict and optimize the TEGs. We have compared the generated ΔT deduced from the experimental output voltage with the modeled. Both of them were found very close (error <5%).

Influence of heat exchange system on thermoelectric equipment efficiency

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Keywords: *heat exchange, thermoelectricity, computer simulation, efficiency*

Efforts aimed at improving the efficiency of thermoelectric generators and cooling devices are mainly related to quality enhancement of thermoelectric materials. However, under real conditions of their use the possibilities of thermoelectric conversion are essentially reduced due to losses in heat-exchange systems.

This paper studies generalized models of energy conversion under generation and cooling modes with regard to the effect of heat-exchange systems on the energy characteristics of devices. It is shown that heat-exchange devices of inadequate quality and not specialized reduce the energy characteristics by 30-50%, or, in many cases, even more. Possibilities of improving this situation are analyzed. Computer technologies for design of specialized heat-exchange systems are considered. Examples that confirm the efficiency of such approaches are given.

Energy possibilities of permeable generator thermoelements based on segmented legs

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Keywords: *thermoelement, segmented, permeable, electric power generation, design, optimization, energy efficiency, efficiency*

This paper presents the results of research on permeable segmented generator thermoelement based on materials Bi2Te3, PbTe, SiGe, FeSi2 for n-type and Bi2Te3, PbTeGe, PbTe, SiGe, FeSi2 for p-type leg. Methods for theoretical calculation and optimization of energy characteristics of thermoelement based on the mathematical theory of optimal control and computer design methods are described.

Optimal parameter values – heat carrier flow rate, electric current density coordinated with temperature operating modes of leg segments whereby energy conversion process has maximum thermodynamic efficiency are determined. Results of calculation of thermoelement energy characteristics for different temperature differences indicate the presence of rational number of leg segments whereby the efficiency is maximal. Comparison to traditional thermoelements has shown the possibility of efficiency increase by 30 – 40% and generated power by 20-30%.

Fabrication of thermoelectric modules with Mg_2Si and $SrRuO_3$ by the spark plasma sintering method.

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Keywords: *Mg_2Si, $SrRuO_3$, SPS method, module*

Abstract:
Thermoelectric (TE) modules with a π structure were fabricated by the spark plasma sintering method. The modules were composed of $SrRuO_3$ for the p-type semiconductor, Mg_2Si for the n-type semiconductor, and Ni for the electrodes. The $SrRuO_3$ powder was synthesized using the metal-citric-acid complex decomposition method. Mg_2Si bulk prepared by melt-quenching was ground into powder and sieved to a particle size of 75 μm or less. To obtain the sintered body of $SrRuO_3$, the powder was sintered using spark plasma sintering (SPS). For SPS, the precursor powder was placed in a graphite die and kept at that temperature under a uni-axial pressure of 50 MPa and in vacuum conditions (less than 7 Pa). After sintering by SPS, the ceramic sample was annealed at 1573K in air because the $SrRuO_3$ was slightly reduced during the SPS process in the graphite die. These TE sintered bodies were cut and polished. The dimensions of the samples used for fabrication of the p-type parts of the TE modules were 4.50x9.50x7.45 mm^3 and those for the n-type parts were 5.50x11.45x7.45 mm^3. Pressed Ni powder was put between these TE materials and the Ni electrodes in order to connect them together, and electrical power was passed through the electrodes from the SPS equipment.

The output power under temperature differences ΔT ranging from 100 to 500 K was measured. The open-circuit voltage, maximum output current and maximum output power increased with increasing temperature difference ΔT. The open-circuit voltage of the single module was 91.0 mV, and the maximum output current and maximum output power were 500 mA and 110 mW at ΔT= 500 K, respectively.

Automobile Exhaust Pipe Thermoelectric Generator (TEG) - Saving or Waste of Fuel the Car

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Keywords: *Automobile thermoelectric generators (ТЭГ), mass factor TEG, conflict TEG to an internal combustion engine (ICE), saving of fuel*

Abstract not presented

Experimental study of waste heat recovery in off-road vehicles

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Abstract:
The paper presents the preliminary results of the waste heat recovery investigations for an agricultural tractor engine (7.1 dm^3) and excavator engine (6.4 dm^3) in real operating conditions. The temperature of exhaust gases and exhaust mass flow rate has been measured by precise portable exhaust emissions analyzer SEMTECH DS (SENSORS Inc.). The heat exchanger of the prototype thermoelectric generator TEG was used as a tool for benchmark studies of heat recovery from exhaust gases of both type of vehicles.

The analysis shows that engines of tested vehicles operates approximately at constant speed and load. The average temperature of exhaust gases in TEG exchanger is in narrow range from 300 to 400 °C for maximum gas flows 650 kg/h and 500 kg/h for tractor and excavator engine respectively. Preliminary tests show that application of TEGs in tested off-road vehicles offers much more beneficial conditions for waste heat recovery than in case of road automotive engines [1,2].

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Thermoelectric equipment for treatment of radiculitis and spinal massage

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Keywords: Thermoelectric devices, treatment of radiculitis

Abstract:
This paper deals with the results and technical specifications of device for treatment of radiculitis and spine massage the operating principle of which is based on thermoelectric Peltier effect. The device consists of two units – control unit that allows setting temperature on the operating plate and keeping it during the required time interval, as well as treatment unit for making immediate therapeutic manipulations. Treatment unit, in turn, is composed of operating plate, thermoelectric module, heat sink, fan and handle. This device can produce thermal effect on the damaged areas of human body in the temperature range of 0ºC ÷ +50ºC. Medical-clinical investigations of the elaborated device were made. It was established that this device is an efficient means for therapy of hernias of interverterbral disks with pronounced radiculitis and membranous syndromes, at meningitis, other spine diseases and back traumas.

Thermoelectric converters for etalons of alternating current

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Keywords: thermoelectric measuring converter, design, measurement, simulation, standard.

Abstract:
Thermoelectric alternating current converters remain priority devices when creating standard equipment. The present paper gives the results of design and manufacture of alternating current converter for the national standard of alternating current of Ukraine. The results of computer simulation of thermal and electrical processes in converters, ways for optimization with a view to achieve both high volt-watt sensitivity and improved accuracy of alternating current signal representation are given. Device construction and results of metrological tests are described. The quality of specially created thermoelectric material for alternating current metrology is confirmed. The converter was used in alternating current standard for the frequency range from 10 Hz to 30 MHz. The efficiency of using thermoelectric signal converters in measuring instruments is confirmed.

Experimenting with Hot Isostatically Pressed (HIP) Nano Grained Bismuth-Telluride-based alloys

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Keywords: *Hot Isostatic Pressing, Bismuth-Telluride, Properties*

Abstract:
Nano grained bismuth-telluride samples were hot isostatically pressed (HIP) to study the effect of process parameters on their properties. The powders were essentially the same as presented by Vasilevskiy[1] et al, 2010. The $(Bi_xSb_{1-x})_2(Te_ySe_{1-y})_3$ thermoelectric alloys studied in this article were produced by mechanical alloying under an inert atmosphere. The p-type alloy composition corresponds to x = 0.2, y = 1 and for the n-type material x = 0.95, y = 0.95.

For HIP treatment the n- and p-type powders were encapsulated in copper cylinders of Ø38mm x 180mm under protective argon atmosphere. The weight of the n-type powder filled in was 648g and p-type 561g. The filled capsules were evacuated at room temperature to vacuum level of 3 10-5mbar. After evacuation and sealing the capsules were charged in QUINTUS Hot Isostatic Press type QIH-9 with useable charge room of Ø130mm x 280mm.

The HIP parameters used were: Heating up to 200°C with the initial argon pressure of 65 bar, pressurizing of the HIP chamber to 400 bar, heating and pressurizing to 300°C / 1000bar in 120 minutes, dwell for 30 minutes, and free cooling to room temperature with the HIP. The selected HIP temperature was kept low to avoid excess grain growth of the materials. After HIP the capsules were cross cut for evaluation of the density, electric conductivity and thermoelectric properties of the consolidated materials.

References:

[1] Vasilevskiy, D., Dawood, M.S., Masse, J.-P., Turenne, S., Masuti, R.A., *Journal of Electronic Materials* 39 (2010) 1890.

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Efficiency of thermoelectric energy recuperators of internal combustion engines exhaust gas

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Keywords: heat recovery, thermoelectricity, computer simulation, waste heat

Abstract:
Results of computer simulation of thermoelectric generators utilizing the waste heat of internal combustion engines are presented. Sectional generator schemes are considered whereby maximum efficiency is attained for the case of and cases of real temperature dependences of the most suitable thermoelectric materials.

Besides, a model optimized for minimum cost is also considered.

The results of experimental research on generator utilizing from stationary electric power plant with a diesel engine are presented. Computer simulation is confirmed by the test results.

The prospects of using such heat recuperators in stationary working plants are considered.

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