SYMPOSIUM F
Materials and Technologies for Direct Thermal-to-Electric Energy Conversion
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* Invited paper
SESSION F1: Thermoelectrics Research Directions & Oxides I
Chairs: Terry Trifit and Jihui Yang
Monday Morning, November 28, 2005
Room 313 (Hynes)

8:00 AM OPENING REMARKS

8:15 AM *F1.1
New Directions for Nanoscale Thermoelectric Materials Research
Mildred S. Dresselhaus 1,2, Gang Chen 2 and Zhifeng Ren 2
1Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; 2MIT, Cambridge, Massachusetts

Many of the recent advances in enhancing the thermoelectric figure of merit are linked to nanoscale phenomena or through the new thermoelectric materials which are explicitly prepared as nanostructured materials. From a fundamental standpoint, theoretical and experimental proof of principles studies on isolated quantum well and quantum wire samples have demonstrated the factors that are most important for enhancing the thermoelectric figure of merit ZT. Having shown that reducing the thermal conductivity while maintaining the electric conductivity is a key strategy, research efforts have now moved into studies on bulk samples containing nanostructured constituents. In this talk a strategy is presented for the self-assembly of such structures for thermoelectric applications and a review of some of the results obtained to date are presented.

8:45 AM *F1.2
Recent Development of Thermoelectric Materials in China.
Lidong Chen, Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China.

In recent years, we have viewed the quickly growth of the number of people working on thermoelectric materials and devices in China. This talk mainly covers part of research works that is going on in my group in Shanghai Institute of Ceramics, CAS for improving the performance of thermoelectric materials by different approaches. 1) Defects of different size are introduced into the skutterudite materials to reduce the lattice thermal conductivity and to improve the thermoelectric performance of the CoSb3-based materials (ZT=1.2). 2) By introducing iso-electronic alloying for ZnSb-based alloys, the thermal conductivity of the materials are depressed significantly. The obtained value of ZT can be as high as 0.7 at 800K. 3) Bi2Te3-based materials with preferred grain orientation have been prepared by Spark Plasma Sintering technique to get materials with good thermoelectric performance as well as excellent mechanical properties for industrial processing. Bending strength as high as 80MPa can be obtained in our laboratory. 4) A novel structure of polydiacetylene/Bi2Te3 nano-wire in Alumina template is fabricated by means of chemical as well as electrochemical deposition from aqueous solution. Thermoelectric properties of the composite system will be studied. 5) Camphorsulfonic acid doped conducting polyaniline with a special sub-micron-fibril structure has been fabricated, which has higher power factor than the polyaniline of general grain structures. 6) We are searching for new filled skutterudites with potential better thermoelectric performance by combining experimental and theoretical approaches. Some new results will be discussed in the talk.

9:15 AM *F1.3

The Department of Energy initiated a competitive program this year to provide a 10 percent improvement in diesel engine efficiency by waste heat utilization. This Program was developed to move the advances made in the laboratories over the past 10 years, which were primarily funded by DARPA and ONR, to commercially viable sizes. The proposed program will involve the installation of a device to recover electrical energy from engine waste heat. Four teams were selected. The BSST Team includes Vistron, BMW, NASA’s Jet Propulsion Lab, Teledyne, Purdue University, and the University of California-Santa Cruz. General Motors teamed with General Electric, MIT’s Lincoln Lab, RTI International, Oak Ridge National Lab, University of Michigan and University of South Florida. Michigan State University organized a team which includes the Cummins Engine Company, NASA’s Jet Propulsion Lab, Tellurex, and Iowa State University. The United Technologies Research Center’s Team includes Pratt & Whitney, Hi-Z Technologies, Pacific Northwest National Lab, and Caterpillar. Results from the program with the single thermoelectric generator will be the basis for the decision to proceed with follow-on Programs. The thermoelectric generators developed in this program will provide a good benchmark for the road map to commercial feasibility of 60 percent efficient diesel engines. Consider the energy in diesel fuel used in a heavy duty class 7 & 8 truck diesel engine. About 40 percent of this energy winds up as engine output shaft work. The remaining 55 percent is lost as waste heat including the cooling losses. The primary approach to gain useful work from this waste energy is using high efficiency thermoelectric generators (TEG’s). Thermoelectric applications include the engine’s radiator, lube oil cooler, exhaust gas path, exhaust gas recirculation (EGR) loop, compressor discharge air (engine intake air) and braking. These TEG’s provides electrical power which is readily mated with either the fuel cell engine concept, wherein all accessories are electric motor driven, or the integrated alternator/motor/starter/damper (ISMD) to reduce engine drag. In the process of generating electricity, the thermoelectric generators also reduce the cooling load on the water pump, lube oil cooler, EGR loop, and compressor discharge air. The same thermoelectric devices can be connected with DC power to provide air conditioning or heating, depending on the polarity of the DC current. This technology would be competitive with the conventional gas-fired heat pumps when a Coefficient of Performance (COP) of 2.5 is obtained at a lower cost. Then thermoelectric air conditioning systems could replace compressed gas refrigerant systems. The refrigerant gas used in all air conditioning cars since 1996 is R-134a which has 1390 times the greenhouse gas effect as CO2. Cars leak 10 to 70 g per year of R-134a and 90 percent of the cars sold on North America and Asia are air conditioned while the European percentage is 87 percent.

10:15 AM *F1.4
Commercialization of Thermoelectric Technology.
Francis R Stabler, Powertain, General Motors Corp, Pontiac, Michigan.

Thermoelectric technology capable of solid state electric power generation and cooling has been known for almost 170 years. Over the past 50 years has this technology found its way out of the laboratory and into niche military, space, and commercial products. Most of the profitable commercial products have made their appearance in the past decade. Many of you are working hard to advance the state of the art in thermoelectric materials, and I am sure that you do not want to wait another 180 years, 50 years, or even another decade to commercialize your results. There are many potential ways to commercialize this technology, but the area that I think represents the biggest market is the internal combustion engine. There are over 17 million automobiles sold in the US each year and over 60 million worldwide. With the possible exception of the electric power industry, I know of no other market segment that is even close to the potential of the automotive industry for using a high volume of thermoelectric materials. Every vehicle produced has an electrical system supplied by a one to two kilowatt generator with increasing power demand as electrical features are added. A high percentage of vehicles have air conditioning systems with 3 to 5 kilowatts of cooling. Sufficiently advanced thermoelectric materials can be the heart of systems that supplement or replace the mechanical or electro-mechanical devices performing these functions today. This paper addresses the boundary conditions for the function, technology and value needed to commercialize thermoelectric technology. Timing to introduce subsystems with this technology is also addressed. Thermoelectric technology has to compete with the existing technologies and other emerging technologies to be successfully commercialized. While it seems out of reach today, there is even the potential that sufficiently advanced thermoelectric materials and device construction could one day replace the internal combustion engine and even rival fuel cells in energy conversion efficiency.

10:45 AM *F1.5
Layered Cobaltites with High Thermoelectric Power.
Qiang Li, Brookhaven National Lab, Upton, New York.

There is a growing interest in exploiting charges and spins in cobaltates (A2Co3O7) for potential thermoelectric (TE) applications. Cobaltates are oxides in which Co ions define a layer, on a body centered lattice. At 0 K, the spins remain in a disordered quantum state with no discernible pattern (often called “spin liquid”). The electron correlation in cobaltates, coupled with their layered structure, offers new ways to tailor the TE functionality. Here we provide an overview of recent developments at Brookhaven National Laboratory in the field through a discussion of a series of experiments from synthesis to characterization designed for investigating the mechanism and optimizing the thermoelectric power in cobaltates. We found a crossover in the number of effective dimensions, from three to two, with increasing temperature using the angle-resolved photoemission spectroscopy (ARPES) and electronic transport measurements. The correlation between the TE properties of an interacting electron system and its effective dimensionality is explored. We demonstrate a successfully growth of c-axis oriented Ca2Co3O7 thin films with high thermoelectric power at substrate temperatures above 200°C. Furthermore, the cobaltates are promising candidates for low temperature amorphous silicon wafer and glass, which offers the promise of using available state-of-the-art silicon fabrication technology for potential
electronic applications. We describe a few approaches we use to synthesis bulk aligned cobaltates, as well as other oxides for TE applications. Furthermore, we discuss the need of a model, which may have to step beyond the conventional Fermi-liquid theory, in order to explain many exotic behaviors of cobaltates. In collaboration with Y. F. Hu, T. Valla, W. D. Si, P. Johnson, A. Moolenaar, and E. Sutter 1) T. Valla, E. Sutter, Appl. Phys. Lett. 86 082103 (2005). 2) Y. F. Hu, W. D. Si, E. Sutter, and Q. Li, Appl. Phys. Lett. 86 082103 (2005).

11:35 AM E1.6
First Principles Study on Sodium Ordering and its Relation to the Electronic Properties of P2-NaxCoO2 Thermoelctrics. Ying Shirley Meng 1, Maria K. Y. Chan 1, Anton Van der Ven 2, and Gerbrand Ceder 1; 1) Massachusetts Institute of Technology, Cambridge, Massachusetts; 2) University of Michigan, Ann Arbor, Michigan.

The unusual electronic properties of NaxCoO2 make it a material of considerable interest. Over a large range of sodium compositions, the system displays an unusual combination of high Seebeck coefficient and low thermal resistance [1]. For low sodium content the layered form of the material is superconducting [2]. NaxCoO2 is also an interesting material on which to test our basic understanding of mixed valence transition metals. NaxCoO2 is a mixed valence system with a fraction x CoIV and (1 - x) CoIII ions. Because of the high mobility of Na and large vacancy concentration, Na-vacancy ordering is likely in NaxCoO2. This ordering breaks the symmetry on the Co sublattice and may affect in charge ordering of CoIII and CoIV [3, 4]. Mixed CoIV/CoIII system and disorder in the electronic structure, it is important to accurately establish the structure of this material. In this study, we use both standard Density Functional Theory (DFT) in the Generalized Gradient Approximation (GGA) as well as GGA U calculations to investigate the possible Na-vacancy and cation ordered structure of Na0.75CoO2. We also discuss the electronic/magnetic behavior of the system, which is crucial for understanding the thermoelectric properties of this material and similar mixed valence oxides. Reference: 1) Chiang, Y. and Ceder, G. Phys. Rev. B 72, 104414 (2005). 2) Y. F. Hu, W. D. Si, and Q. Li, Appl. Phys. Lett. B 56, 12085 (1990). 3) W. Takahashi, H. Kojima, E. Takayama-Murata, et al., Nature 422, 53 (2003). 3) C. A. Marianetti, G. Kotliar, and G. Ceder, Nature Materials 3, 627 (2004). 4) M. M. Bish, J. I. Lee, E. Sutter, and E. Kaldis, Journal of Materials Chemistry 9, 1135 (1999).

11:40 AM E1.7
Cobaltates as perspective thermoelectrics. Jiří Hejtmánek 1, Zdeněk Jiráš 2, Karel Knížek 3, Hirooyuki Fujishiro 3, Bertrand Lenoir 2, and Christine Belloir 3; 1) Department of Magnetics and Superconductors, Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic; 2) Dept. of Materials Science and Technology, Faculty of Engineering, Iwate University,Morioka, Morikawa, Japan; 3) LPM, Ecole Nationale Superieure des Mines de Nancy, Nancy, France.

The recent material research of mixed cobalt oxides is strongly motivated by the potential of some of them to be used as chemically stable high temperature thermoelectric materials. This fact together with both the theoretical and experimental ambitions to fulfill the desire of efficient thermoelectric conversion motivated both their theoretical and experimental research. Nonetheless, despite the intensive investigations of the prototype materials represented by 3D perovskites Ln1-xAxCoO3 (La = La, Y, rare-earth, A = alkaline-earth) and 2D cobaltates of NaCoO2 type, the precise physical background of their transport and magnetic properties remain still a matter of debate. This is likely due to a fact that cobalt ions can be stabilized either in low-spin state (diamagnetic for “pure” CoIV) or in high-spin state (magnetic), with filled eg states. As the energy difference between respective states is due to comparable strength of crystal field and Hund’s energies rather small, the thermodynamically most stable ground-state, with energy differences of hundreds meV per carriers, can be critically influenced by an interplay of additional degrees of freedom - orbital and charge. The challenge for unequivocal theoretical model represents e.g. the thermoelectric power of mixed cobaltates where, up to now, somewhat ambiguous models based either on “classical” approach, associated with diffusion of itinerant charge carriers, or more exotic - based on configurational entropy of quasi-itinerant carriers - are often used for similar materials. Simultaneously, the open question is a complete assessment of phonon scattering in 2D cobaltates which can "confirm" or "rule-out" the theoretically postulated "phonon-glass electron -crystal" behaviour insinuated for NaxCoO2 bronzes. Consequently, in a present paper, we report on the comparative study of highly conducting 3D and 2D cobaltates. Using a complex structural, magnetic, transport and thermal characterization in a wide range of temperatures we analyze and discuss the thermoelectric power, specific heat, magnetic and magnetotransport data. While a concurrence of a small negative thermopower, positive Hall coefficient and huge electronic contribution to the specific heat characterized layered NaxCoO2 bronzes. This fact point to a complex character of the Fermi surface while further experiments insinuates that the large positive thermopower can be linked with strong electron correlations.

11:45 AM E1.8
Thermoelectric Properties and Microstructure of c-axis Oriented Ca3Co4O9 Thin Films: Yufeng Hu 1, Qiang Li 2, Weidong Si 3, and Eli Sutter 2; 1) Materials Science Department, Brookhaven National Laboratory, Upton, New York; 2) Physics Department, Brookhaven National Laboratory, Upton, New York; 3) Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York.

c-axis oriented Ca3Co4O9 thin films have been grown on various substrates, such as Si(100), glass and Al2O3, by pulsed laser deposition. Detailed microstructure analysis showed stacking faults abundant throughout the films grown on glass and Al2O3 substrates. However, the Seebeck coefficient (100 ~ 130 μV/K) and resistivity (1 ~ 4.3 mΩcm) of these films on glass and Al2O3 substrates at room temperature were found comparable to the single crystal samples. The presence of these structural defects could reduce thermal conductivity, and thus enhance the overall performance of cobaltate films to be potentially used in the thermoelectric devices. This work was supported by the U. S. Dept. of Energy, Office of Basic Energy Science, under contract No. DE-AC-02-98CH10886.

SESSION F2: Oxides II and New Directions

Monday Afternoon, November 28, 2005
Room 315 (Hynes)

1:30 PM F2.1
New Directions in Bulk Thermoelectric Materials Research. Terry M. Tritt 1, J. He 2, B. Zhang 2, N. Gorthard 1, D. Thompson 1, E. Weeks 1, T. Xiaoeng 1, R. Aaron 2, X. J. 1 and J. W. Kolls 2; 1) Physics and Astronomy, Clemson University, Clemson, South Carolina; 2) Chemistry, Clemson University, Clemson, South Carolina.

The focus in this talk will be on some new directions in bulk thermoelectric materials research that we have recently been pursuing. The requirements for a potential thermoelectric material will be discussed and how these relate into giving a favorable figure of merit, ZT, defined as $ZT = a^2T/κ$, where $a$ is the Seebeck coefficient, $κ$ electrical resistivity, and $T$ thermal conductivity and $T$ is the temperature in Kelvin. Thermoelectric materials are inherently difficult to characterize and a short discussion of these difficulties will be part of the presentation. These difficulties are magnified by high temperatures and many challenges remain. Specific materials will be discussed, and especially those results in bulk materials that exhibit favorable properties for potential high temperature power generation capabilities. A brief discussion of the synthesis techniques and highlights of several systems of materials will be presented. For example, a system of ceramic oxide thermoelectric materials based on NaCo2O4, has been generating a lot of recent interest. This material is a two dimensional layered compound which exhibits strong electron correlation within the layers. Other two-dimensional materials, such as TiS2, will also be discussed as well as why this type of structure may well be critical to the development of the next generation high efficiency thermoelectric systems. Several cubic systems will also be part of this presentation. Small grain sizes and their effect on thermal conductivity have been known for several years. This effect will be reviewed and used in relation to some of our recent results. A discussion of the future directions in our materials research will be highlighted, including some bulk materials, which are based on nano-scaled composites.

2:00 PM F2.2

Layered cobaltate NaxCoO2 has attracted much attention recently due to its exceptional properties, one of which is its unusually high
thermoelectric power with low resistivity, and high carrier density. We have studied structural and transport properties of epitaxial Na$_2$Co$_2$O$_7$ thin films on (001) sapphire substrate prepared by topotaxially converting an epitaxial Co$_2$O$_4$ film to Na$_2$Co$_2$O$_7$ with annealing in Na vapor generated from annealing either with sodium bicarbonate (NaHCO$_3$) or sodium acetate (NaOOCCH$_3$). The films are c-axis oriented and plane-aligned with [10-10] Na$_2$Co$_2$O$_7$ rotated by 30° from [10-10] sapphire. Different Na vapor pressures during the annealing resulted in films with Na concentrations of x < 0.68 and x>0.75, which showed distinct temperature dependent resistivity. The thermal power factor of the best cut SrTiO$_3$ is ~70 mW K$^{-2}$ cm$^{-1}$ which is similar to the single crystal samples of the same composition.

2:15 PM F2.3 Sr$_6$-doped LaRuO$_3$ as a Potential Thermoelectric Material. J. He, B. Edwards, H. Zhang, D. Thompson and T. M. Tritt; Physics & Astronomy, Clemson University, Clemson, South Carolina.

The perovskite La$_{1-x}$Sr$_x$RuO$_3$ (0.1 < x < 0.5) polycrystalline samples have been prepared using solid state chemistry reaction. The phase constituent, compositional homogeneity and micro-morphology have been checked by Rietveld powder diffraction, Energy Dispersive X-ray spectroscopy and scanning electron microscopy before being characterized with respect to the electrical resistivity, thermal conductivity and Seebeck coefficient between 10 and 300 K. Particularly, the resistivity, thermal power factor and Seebeck coefficient of present compounds was studied in line of the comparison with the strongly correlated system Na$_2$Co$_2$O$_7$ and the relevant model proposed by W. Koshiba. Finally, the potential of using La$_{1-x}$Sr$_x$RuO$_3$ as a practical thermoelectric material is discussed.

3:30 PM F2.4 Synthesis and Thermoelectric Properties of Na$_2$Co$_2$O$_7$ Oxide Materials. Xiaofeng Tang$^1$, Ed Abbott$^2$, Joe K. Kolis$^3$, Kelvin Aaron$^1$ and Timothy R. Tritt$^1$; 1Chemistry, Clemson University, Clemson, South Carolina; 2Chemistry, Clemson University, Clemson, South Carolina; 3Physics & Astronomy, Clemson University, Clemson, South Carolina.

In 1997 Terasaki reported that Na$_2$Co$_2$O$_7$ possesses unexpected intriguing electric and thermal transport properties. This oxide material has attracted much attention since that time, due to its high chemical and thermal stability and the potential to be a promising p-type thermoelectric material with its high ZT for high temperature application. The Na-content dependence of electric, thermal transport and magnetic properties, such as resistivity, thermal conductivity, heat capacity and magnetic susceptibility and moment of composition precisely controlled Na$_2$Co$_2$O$_7$ polycrystalline samples, which were prepared by a rapid-heat-up technique, were systematically studied and will be reported here. The anomalous decrease in resistivity and increase in thermal stability and the potential to be a promising additional control over phase transition, although the thermopower continues to increase with increasing Na-content. The thermal conductivity of single crystals Na$_2$Co$_2$O$_7$ grown via typical NaCl flux method was measured by our designed steady state and parallel thermal conductance (PTC) system and was found to be ~5W/m.K. Along with the high in-plane resistivity ~0.30 m-cm and high thermopower ~100 mV/K, the power factor a$^2$/$\rho$ and ZT of Na$_2$Co$_2$O$_7$ crystal have high values of ~10$^{-4}$ W/m$^2$ K$^2$ and 0.2 at 300K, respectively. We have developed a novel low temperature flux method using NaOH/NaCl as the flux and metallic Co powders as the Co source. We successfully synthesized plate-like Na$_2$Co$_2$O$_7$ single crystals with sizes up to 6mm at low temperature of 550°C. The as grown crystals were found to be Na-deficient and resistivity measurements revealed there exist two different types of crystals, one is metallic and another is semiconducting. Measurements on the compact pellet of crystals via hot press also revealed the semiconducting resistivity behavior, where energy gap E$_g$ was found to be between 0.1 and 0.3eV.

3:45 PM F2.5 Fabrication of Na$_x$CoO$_2$ Thin Films for Thermoelectric Applications. Hans-Ulrich Habermann, Yoshiru Kroenerberger and Lan Yu; MPI-FKF, Stuttgart, Germany.

Terasaki et al. discovered 1999 unusual thermoelectric properties of Na$_x$CoO$_2$. Their uniqueness is based on the large Seebeck coefficients combined with low resistivity. The physics behind these properties might stem from the crystallographic anisotropy and the strong correlations of the electronic system. The application of this material, however, requires the availability of a reliable thin film technology able to controllably produce single phase epitaxial thin films. Kroenerberger et al. have recently accomplished the preparation of such films using pulsed laser deposition techniques combined with in-situ annealing procedures for the Na-concentration x ~ 0.7. In this contribution we describe the further development of this technique in a two-stage process to expand the Na-concentration range for epitaxial single crystal-like thin films to 0.3 < x < 1. The films are characterized by X-ray diffraction techniques, transport and magnetization measurements, and electron microscopic techniques. Thermoelectric experiments have been performed using nanosecond pulsed laser irradiation as source for the temperature gradient and measuring the generated voltage in analogy to previous experiments yielding giant laser-induced voltages in YBCO deposited onto vitreous substrates. The results for the thermoelectric signals for Na$_x$CoO$_2$ films are compared with those of YBCO and doped manganites and other relevant device aspects will be discussed.

4:00 PM F2.6 Giant Seebeck Effect Originating from 2DEG at the TiO$_2$/SrTiO$_3$ Heterointerface. Hiroichi Ohba$^1$, SungWang Kim$^1$, Kenji Nomura$^2$, Shingo Ohita$^2$, Takashi Nomura$^2$, Masahito Hirano$^3$, Hideo Hosono$^4$, and Kunihito Kouno$^{1,2}$; 1Graduate School of Engineering, Nagoya University, Nagoya, Japan; 2CREST, JST, Kawaguchi, Japan; 3ERATO-SORST, JST, Yokohama, Japan; 4Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, Japan.

A high-density (~10$^{21}$ cm$^{-3}$) two-dimensional electron gas (2DEG) that is confined within several atomic layers at the interface between two dielectric oxides, TiO$_2$/SrTiO$_3$ was found to be over a trade-off between the two material-based parameters, —S— and $\sigma$ in ZT. According to an idea which was proposed by Hicks and Dresselhaus in 1993, confined carriers electrons within several atomic layer spaces should dramatically enhance —S— due to an increase in the density-of-states for conduction and/or valence band edge, while keeping the $\sigma$ value almost unchanged. In order to realize several atomically confined 2DEG, C-V measurements of the TiO$_2$/SrTiO$_3$ were performed. The 2DEG at the interface should be confined to an extent by means of the Debye shielding effect, since the dielectric constants of both TiO$_2$ (~100) and SrTiO$_3$ (~300) are very large. Epitaxial layers of TiO$_2$ was deposited on (100)-oriented SrTiO$_3$ single-crystal plates by pulsed laser deposition with the fourth harmonic of a Nd:YAG laser with a polycrystalline TiO$_2$ target at 700°C in an oxygen atmosphere. Optical absorption measurements of the TiO$_2$/SrTiO$_3$ indicated that the carrier electrons are produced in SrTiO$_3$ due to the O$^2$ - vacancy formation during the TiO$_2$ deposition, and the electrons are confined at the interface in terms of band bending to form a high-density 2DEG. C-V measurements of the TiO$_2$/SrTiO$_3$ confirmed that a high-density 2DEG (~1.4 x 10$^{21}$ cm$^{-3}$) was successfully fabricated, which is localized in several molecular layers of TiO at the interface of TiO$_2$/SrTiO$_3$. The —S— values are as large as ~1 mV/K, ~7 times larger than that of the bulk, whereas the electron system maintains the rather high $\sigma$ value of 1.4 x 10$^3$ S$^{-1}$ m$^{-1}$, leading to a ZT value of ~5 at room temperature, which is substantially larger that of TE materials developed thus far. This finding provides a novel route in the materials design and expands broadly the range of possible choices for TE materials.

4:30 PM F2.7 Thermoelectric Refrigerators. Gerald D. Mahan and Julian D. Maynard; Physics, Penn State University, University Park, Pennsylvania.

We discuss the theory and experiment of solid state energy conversion devices based upon the thermoelectric effect. It is a multilayer device with alternate layers having different thermoelectric properties. When the small device is forced to oscillate, dc heat will flow because of the nonlinear thermoelectric coupling of the different layers of material. The device can be used as a refrigerator, or as an energy conversion device. The model of this device is described, as well as the performance characteristics of several bench top models.
Thermoelectric (TE) materials with high figure-of-merit (ZT) are of fundamental and practical interest for energy conversion. Low-dimensional nanomaterials provide new possibilities to improve ZT based on quantum effects. The use of quantum dots, wires and wells as TE materials is an active area of study. However, most investigations focus on TE nanomaterials (e.g., Bi$_2$Te$_3$, Bi) for refrigerator (cooling) applications. We propose to study a new class of boron-based TE nanomaterials that will operate at high temperature, and be used for energy generation. In this presentation, recent experimental results on synthesis of n-type boron-based TE one-dimensional nanostructures (i.e., CaB$_6$, SrB$_6$ and BaB$_6$ nanowires) will be reported. The nanostructures were synthesized by pyrolysis of diboron (B$_2$H$_6$) over certain metal oxide powders (e.g., calcium oxide (CaO) for synthesis of CaB$_6$) at elevated temperature and low pressure. The experiments were performed in a home-built low-pressure chemical vapor deposition (LPCVD) system. Nickel (Ni), PbSe, BiSe$_2$, and PbTe nanostructures are effective catalytic growth materials for the formation of aforementioned borohydride TE nanostructures. The as-synthesized nanostructures were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy. Possible mechanisms for the growth of these novel boron-based TE nanostructures will be presented. Combined with other properties of boron-based materials (e.g., low-density, superior mechanical properties, excellent thermal and chemical stability), these new TE nanostructures may find applications in the automotive industry and in high temperature micro- and nanoelectromechanical systems (MEMS and NEMS), electronics, and others.

F3.3 Nanoscale SiGe Thermoelectric Modules. David T. Mays, Physics, Illinois State University, Normal, Illinois.

Nanoscale structures are expected to yield higher figure of merit values than presently available bulk thermoelectrics because the Seebeck coefficient and electrical conductivity may be improved through quantum confinement of charge carriers and an increased density of states. In addition, the thermal conductivity of these materials is expected to be reduced through an increase in boundary scattering. Researchers have already reported figures of merit exceeding 2.4. However, it is expected that these values will continue to rise with further research. In our facilities, we have begun examining several semiconducting nanoscale thermoelectric structures and materials; and our progress will be reported. The work is guided by our unique nanoscale model of phonon properties in semiconductors nanocrystals. Our method for measurement of thermal conductivity and the Seebeck coefficient will also be discussed.


Here we present the synthesis and characterization of individual nanocrystals as model assemblies. Specifically, we describe the synthesis, and structural and optical characterization of, monodisperse PbX (X = Se, S, Te) nanocrystals. We will also report electronic and thermal measurements of densely packed films of PbX nanocrystals which are coupled to exhibit either p-type or n-type behavior. Additionally, we will discuss efforts toward the assembly of multifunctional materials by rationally assembling nanocrystals with a variety of electronic, optical, magnetic, and thermoelectric properties into AB and AB$_3$ superlattices. This will also serve to highlight recent work on the synthesis and thermoelectric properties of GeTe nanocrystals.

F3.5 (W$\text{I}_x$(WSe$_2$)$_y$) Superlattices - Materials Designed for Low Thermal Conductivity. Ngoc Thanh Nguyen$^1$, David C. Johnson$^1$, Catalin Chiritescu$^1$ and David G. Cahill$^2$; 1Chemistry, University of Oregon, Eugene, Oregon; 2Materials Science, University of Illinois at Urbana-Champaign, Urbana-Champaign, Illinois.

One concept for producing extremely low thermal conductivity superlattices is by combining naturally occurring materials with different vibrational characteristics. We have prepared superlattices consisting of a variable number of layers of WSe$_2$ and a 1.5 nanometer layer of W as building blocks. The superlattices were synthesized using modulated electron beam deposition. Altering the number of layers of W and Se were deposited with a 1 to 2 ratio of W to Se and an appropriate thickness to yield an integral number of Se-W-Se layers of WSe$_2$ followed by a layer of W to form the repeating unit of the superlattice. The structure as a function of annealing temperature will be discussed using data obtained from x-ray reflectivity, x-ray diffraction, electron backscattering diffraction and transmission electron microscopy data.

F3.6 Electrochemically-Deposited Bi$_2$S$_3$ and Pb$_{3-x}$Bi$_2$Bi$_{1-x}$S$_3$ Nanowires. Jana Sommerlatte, Woo Lee, Roland Scholz, Ulrich Goswale, Korns Bente$^2$, Cornelia Niehls$^1$, Max Planck Institute of Microstructure Physics, Halle, Germany; 2Institute of Mineralogy, University of Leipzig, Leipzig, Germany.

Thermoelectric nanowires have been predicted to have superior thermoelectric properties over bulk materials. Sulfosalts in general and especially bismuth sulfide and the Bi$_2$S$_3$-PbS compounds are semiconductors with a direct band gap transition. The band gap of the bulk Bi$_2$S$_3$-PbS alloys can be adjusted over a wide range from 0.5 to 1.6 eV and exhibit a large variety of crystal structures. Due to the modular crystal structure Pb$_3$Bi$_2$X$_3$ (X = S, Se) tends to grow in a needle-like shape. Therefore these compound semiconductors are very suitable for the synthesis of crystallographically-oriented 1D nanowires. In this paper we report on the synthesis of Bi$_2$S$_3$ and Pb$_3$X$_2$Bi$_2$X$_3$ nanowires by electrodeposition in highly ordered alumina membranes with a monodisperse pore diameter of 50 nm. According to Baranaski et al. [J. Electrochem. Soc. 127, 766 (1980)] we have chosen DMSO as a nongaseous solvent for the electrolyte. The deposition of Bi$_2$S$_3$ and Pb$_3$X$_2$Bi$_2$X$_3$ took place under inert gas atmosphere at elevated temperatures (110°C). For the Bi$_2$S$_3$ deposition we have obtained nearly single-crystalline nanowires and a homogeneous porous filling up to mesoporous thicknesses of 1500 nm. The Bi$_2$S$_3$ nanowires exhibit the bismuthinite phase with a preferential orientation of the c axis parallel to the nanowire axis. In case of Bi$_2$S$_3$-PbS compounds we obtained polycrystalline phase mixtures with an extended amount of lead dissolved in the crystal structure. In comparison to the corresponding crystal phase of the bulk material. By varying the bismuth concentration from x = 0.2 to 0.5 we have obtained Pb$_3$X$_2$Bi$_2$X$_3$ nanowires which exhibit the cosalite Pb$_2$Bi$_2$S$_4$ or illinitite Pb$_2$Bi$_2$Se$_4$ phase as the dominating crystal structure. We thank the German Ministry for Education and Research (BMBF, project number 05N8701) for financial support.

F3.7 Thermal Conductivity of (Bi$_2$Te$_3$)(TiTe$_2$)$_x$ Superlattices. Mary Smalley$^1$, David Johnson$^1$, David Cahill$^2$ and Catalin Chiritescu$^1$; 1Department of Chemistry, University of Oregon, Eugene, Oregon; 2Department of Materials Science and Engineering, University of Illinois, Urbana Champaign, Urbana, Illinois.

A series of (Bi$_2$Te$_3$)(TiTe$_2$)$_x$ superlattice films were deposited using modulated elemental reactants (MER). Rietveld analysis was performed on x-ray diffraction scans to confirm the structures of the compounds. Thermal conductivity values were measured using time domain thermoreflectance (TDTR). A thermal conductivity of 0.39 W/mK was measured for a (Bi$_2$Te$_3$)(TiTe$_2$)$_3$ superlattice, half as low as a similar value reported by Venugopalam et al. (J. Appl. Phys. 2001) for (SB2Te3)(Bi2Te3) superlattices of the same superlattice period. The improvement is thought to be due to 30% structural mismatch between the layers and the mass mismatch between Ti and Bi.

F3.8 Thermal characterization of sub-micron, free-standing Bi wires. Thein-Andra Borca-Tasright$^1$, Gang Chen$^2$ and Andi Grozav$^3$; 1Rensselaer Polytechnic Institute, Troy, New York; 2Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 3Institute of Applied Physics, Moldovan Academy of Sciences, Chisinau, Moldova.

Simultaneous characterization of thermal conductivity, heat capacity and thermal diffusivity of individual Bi nanowires is carried out employing the 3w method on free-standing wires. The specimens under investigation are fabricated through the electron beam induced deposition method. The fiber composites fabricated through this method consist of a Bi core, with a diameter that may range in different samples from a few hundreds of micrometers to tens of microns, surrounded by a Pyrex shell tens of microns thick. These fibers are millimeter to meter long and may be easily manipulated to make electrical contacts with the Bi core. In order to carry out thermal characterization, the glass shell is removed by a HF vapor etching technique. Calibration is carried out on a 6 µm diameter, free-standing Bi wire. Temperature dependent thermal conductivity and specific heat agree well with published data for bulk Bi. Preliminary results are presented for Bi wires of sub-micrometer diameter.

F3.9 Effects of Nanoporosity on Thermoelectric Properties: A One-Dimensional Model. Rohyun Lee and Gang Chen; MFT, Cambridge, Massachusetts.
Thermoelectrics is direct energy conversion between heat and electricity within a material. Its efficiency is denoted by the thermoelectric figure of merit, $ZT$, which is proportional to electric conductivity, square of the Seebeck coefficient, and inverse of thermal conductivity. Previous experimental studies suggest that porosity and pore size change thermoelectric properties. In this study, we present a one-dimensional approach on the effect of porosity on the thermoelectric properties. The model considers a periodic structure of thermoelectric slabs separated by vacuum gaps. Thermal conductivity, electrical conductivity, and the Seebeck coefficient through the structure are modeled.

**F3.10** Synthesis and Analysis of (Sb$_2$Te$_3$)$_x$(TlTe)$_{2y}$ Superlattices. Benjamin Schmid, Clay Mortensen, Raimar Rostek and David C. Johnson; University of Chemistry, University of Oregon, Eugene, Oregon.

A series of (Sb$_2$Te$_3$)$_x$(TlTe)$_{2y}$ superlattices with varying ratios of $x$ and $y$ was synthesized using the technique of modulated elemental reactants. This system parallels (Bi$_2$Te$_3$)$_x$(Sb$_2$Te$_3$)$_y$ and PbTe/PbSeTe nanostructured materials, which have both been found to have enhanced figures of merit as a result of a reduced thermal conductivity. Superlattice structure and composition were determined by x-ray reflectivity, x-ray diffraction, electron probe microanalysis and Rietveld analysis. Thermal conductivity measurements were conducted to correlate superlattice period with properties.

**F3.11** Thermoelectric Properties of Bi$_2$Te$_3$-Based Nanocomposites. Qing Hua,1 Bed Poulet$^2$, Yi Ma$^2$, Dezhi Wang$^2$, Wenzhong Wang$^2$, Zhifeng Ren$^2$, Mildred S. Dresselhaus$^2$ and Gang Chen$^1$.

1Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Department of Physics, Boston College, Chestnut Hill, Massachusetts; 3Department of Physics, Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.

As the best thermoelectric materials available near room temperature, tremendous efforts have been devoted to bismuth telluride during the decades. Recently, the idea of using nanotechnology to further improve its ZT value has attracted considerable attention and triggered active research in Bi$_2$Te$_3$ nanostructures. Compared with other attempts, nanoparticle composites have shown potentials to improve the ZT value with one or more merits. The interesting factors in the composite is expected to significantly reduce its thermal conductivity without affecting the electrical conductivity. Moreover, the Seebeck coefficient can also benefit from both quantum and classical effects, resulting in a higher ZT value. In this paper, we present experimental studies on the thermoelectric properties of Bi$_2$Te$_3$-based nanocomposites. These nanocomposites are made from nanoparticles synthesized by chemical methods and compacted by hot-pressing. Thermal conductivity, electrical conductivity, and Seebeck coefficient of the nanocomposites are reported as a function of temperature.

**F3.12** Bulk (Bi$_2$Te)$_3$(TlTe)$_2$ Nanoparticle Hot Pressed from Thin Films. Sising Li$^2$,1 Mary M. Smeller$^1$, Maisha K. Kamundu$^1$, Clay D. Mortensen$^1$, Benjamin A. Schmid$^1$, David C. Johnson$^1$, Terry M. Tritt$^2$, Brad Edwards$^2$, Nobuyoshi Imaoka$^2$ and Isao Morimoto$^1$.

1Chemistry, University of Oregon, Eugene, Oregon; 2Cl spun, University, Clemson, South Carolina; 3Asahi Kasei, Fuji-City, Japan.

Using the modulated elemental reactant method, thin films of (Bi$_2$Te)$_3$(TlTe)$_2$ were prepared, removed from the silicon substrate, and annealed to form superlattices. To confirm the structure of these superlattice films, x-ray diffraction scans were refined using rietveld. A 0.3092g bulk pellet was prepared by hot-pressing the thin films at 520°C and 7000kgf/cm² for 24 hours. The thermal and electrical properties of this bulk pellet are presented.


Bulk Bi$_2$Te$_3$ is one of the best known thermoelectric materials with a $ZT \sim$ 1 at room temperature. Theoretical studies have suggested that low-dimensional materials may exhibit ZT values that exceed 1. In this study, we used the pulsed laser deposition method to prepare Bi$_2$Te$_3$ nanostructures by ablating a rotating Bi$_2$Te$_3$ target in an inert atmosphere. Si substrates are pretreated with poly-L-lysine to form an adhesion layer for 10 nm colloidal Au particles which serve as catalyst seed particles for the growth of the nanostructures. Alternatively, we also prepared Bi$_2$Te$_3$ nanostructures by subliming Bi$_2$Te$_3$ powder in the presence of gold coated substrates. Results from electron microscopy and vibrational spectroscopic studies will be presented.

**F3.14** Preparation and Characterization of (TlTe)$_2$(Bi$_2$Te)$_3$(TlTe)$_2$(Sb$_2$Te$_3$) Superlattices. Clay Mortensen, Benjamin Schmid, Raimar Rostek and David C. Johnson; Department of Chemistry, University of Oregon, Eugene, Oregon.

We explored TlTe$_2$ as a diffusion barrier between Bi$_2$Te$_3$ and Sb$_2$Te$_3$ to limit interdiffusion of Sb and Bi. A series of (TlTe)$_2$(Bi$_2$Te)$_3$(TlTe)$_2$(Sb$_2$Te$_3$)$_z$ superlattices has been synthesized using modulated elemental reactants. Interdiffusion of Bi and Sb as a function of TlTe$_2$ thickness was studied. X-ray diffraction, transmission electron microscopy and time of flight-secondary ion mass spectrometry were utilized to characterize the superlattices. Thermal conductivity of the target superlattices will be compared to (Bi$_2$Te)$_3$(Sb$_2$Te$_3$)$_z$ layered structures.

**SESSION F4: Low Dimensional Structures I (Films & Particles)**


The development of nanostructured thermoelectric materials that exhibit both p-type and n-type conductivity, while maintaining high thermoelectric figures of merit, is an important step towards the demonstration of highly efficient electrical generators based on such materials. In this presentation, we will review the remarkable progress that has been in the development of Na-doped, p-type Pb$_{1-x}$Bi$_x$Te quantum-dot superlattice (QDSS) materials grown by molecular beam epitaxy, where we have now achieved ZT values of up to ~1.1 at 300 K (Ref.1). While these values are not yet as high as the best values that were previously obtained for more optimized n-type Pb$_{1-x}$Bi$_x$Te QDSS materials (~1.5 at 300K), the rapid rate of progress confirms the favorable mirror-image band structure of the Pb$_3$chalcogenides and validates our expectation that comparable p- and n-type figures of merit will be obtained for high-quality QDSS materials. In addition to the QDSS material science developments, we will also report on some contact resistance and related device studies. We have been evaluating unipolar devices that consist of a substrate-free, bulk-like thermoelement of nanostructured Pb$_{1-x}$Sb$_x$Te$_2$/PbTe as the n-type or p-type leg (typically 0.1 mm in length with a cross-sectional area of 2 mm by 2 mm) and a metal wire as the opposing leg. With such unipole devices, we have obtained a power density of ~2 W/cm² for both n- and p-type QDSS materials, with a temperature difference across the devices of approximately 220 K at 310K. We will discuss these unipolar device measurements as well as the on-going development of fabrication techniques suitable for producing multiple arrays in QDSS materials. 1. T. C. Harman, M. P. Webb, B. E. LaForge, and G. W. Turner, J. Electron. Mater. Lett. 34, L19 (2005).

**8:30 AM F4.2** III-V Semiconductors Containing Epitaxially Embedded Semimetallic Nanoparticles for Efficient Thermoelectric Materials. Joshua M. Zieg, Ge Hong Zeng, Je-Hyeong Bahk, John E. Bowers, Woosul Kim, Arum Majumdar, Ali Shakouri and C. Gossard; 1Materials, University of California, Santa Barbara, Santa Barbara, California; 2Electrical and Computer Engineering, University of California, Santa Barbara, Santa Barbara, California; 3Chemical Engineering, University of California, Berkeley, Berkeley, California; 4Electrical Engineering, University of California, Santa Cruz, Santa Cruz, California.

We present the molecular beam epitaxy (MBE) growth of III-V semiconductors containing epitaxially embedded semimetallic nanoparticles for use in efficient thermoelectric power generation. A nanoparticle made by incorporating semimetallic nanoparticles into semiconductors can have drastically different properties than the semiconductor itself, and these properties allow the material to be tailored for a wide range of applications, including thermoelectric power generation. The efficiency of a thermoelectric material is strongly dependent on a rare dimensionless figure of merit, $ZT=\sigma^2S^2/T\kappa$, where $S$ is Seebeck coefficient, $\sigma$ is electrical conductivity, and $\kappa$ is thermal conductivity. ErAs is a rocksalt semiconductor which forms an epitaxial nanometer-sized particles on a III-V semiconductor surface. Overgrowth is nucleated on the exposed semiconductor surface between the particles and is essentially defect-free. The properties of the resulting nanoparticle are dependent on the composition of the host semiconductor and on particle morphology, which can be
controlled during growth. We present experimental results on the incorporation of ErAs into various compositions of InGaAlAs (lattice matched to InP). We observe ErAs nanoparticles to reduce the Fermi level in the InP matrix by 50 meV, which is dependent on particle size and the composition of the semiconductor. For example, the Fermi level in InGaAs is pinned within the conduction band, increasing the free electron concentration and thus the electrical conductivity. In InAs, the Fermi level is pinned ~400meV below the conduction band edge, and so the particles serve as a buried Schottky barrier. By carefully choosing the composition of the InGaAlAs, we can use the particles to increase the electron concentration (and the electrical conductivity) of the material while providing Schottky barriers around the particles to create a non-planar electron filtering (solid-state thermionic) system to improve the Seebeck coefficient. The thermoelectric power factor $S^2\rho$ can be optimized at a given temperature by changing this barrier height. We also demonstrate further improvement in ZT by reducing the thermal conductivity of InGaAs by a factor of two to three through the incorporation of ErAs. This reduction is due to increased scattering of acoustic phonons and makes the system one of the only materials in which thermal conductivity is reduced below the so-called “allloy limit” without creating defects. This absence of defects allows us to reduce thermal conductivity without reducing electrical conductivity.

8:45 AM F4.3

Cross-plane Seebeck Coefficient of InGaAs/InGaAlAs Superlattices with Embedded ErAs Nanoparticles in a Wide Temperature Range. Yan Zhang1, Ali Shakouri1, Gehong Zeng2, Zhiyi Bian3, Josh Zide3, Art Gossard4, Woohul Kim5, Suzaan Sanger6, Arun Majumdar6, Rajveer Singh7 and John Bowers2; 1EE, UC Santa Barbara, California; 2UCSB, Santa Barbara, California; 3Materials Sci. & Eng., UCSB, Santa Barbara, California; 4Mechanical Engineering, UC, Berkeley, California.

Seebeck coefficient is one of the key parameters to evaluate the performance of thermoelectric coolers and power generators. However, it is very difficult to directly measure Seebeck coefficient perpendicular to thin film devices because of the difficulty of creating a temperature gradient and measuring accurately temperature and electrical potential on both sides of the thin film simultaneously. It has been shown that embedded ErAs nanoparticles reduce the thermal conductivity of the bulk InGaAs substantially with a modest increased electrical power factor (Seebeck coefficient to square times electrical conductivity). In InGaAs/InGaAlAs superlattices with embedded ErAs nanoparticles, it is anticipated that the additional electron filtering can improve the thermoelectric power factor. A series of superlattice structures with various silicon co-dopings ranging from 2e18 to 1e19 cm-3 were grown using molecular beam epitaxy (MBE). Cross-plane Seebeck coefficient was characterized utilizing thin film resistive heaters on top of the superlattice structure. This resistive heater acts both as a heat source and also as a thermometer once its resistance versus temperature was characterized. Since the superlattice is grown on InP substrate, the measured thermoelectric voltage has contributions from both the substrate and the superlattice. In order to extract the superlattice contribution, similar measurements were done on samples where the superlattice layer was etched off and only the substrate contribution was measured. The thermal conductivity of the 0.5 microns thin Si02/SiN layer used to insulate the thermometer resistor from the semiconductor surface has a non-negligible contribution compared to the total thermal resistance of the device. Thus independent 3W technique was used to measure the Si02/SiN thermal conductivity in the whole temperature range.

In this paper, we will describe in detail the test device and methodology we used to characterize the cross-plane Seebeck coefficient of in a temperature range of 100-600K.

9:00 AM F4.4

Transient Harman Measurement of the Cross-Plane ZT of InGaAs/InGaAlAs Superlattices with Embedded ErAs Nanoparticles. Rajeel Singh1,2,3,4, Biam Zhide5,6, Daryoosh Vashish7, Ali Shakouri1,2,3,4, Josh Zide5,6, Yih-Peng Chuang2, Art Gossard2 and John Bowers2; 1Electrical Engineering, University of California, Santa Cruz, Santa Cruz, California; 2Electric and Computer Engineering, University of California, Santa Barbara, California; 3Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Transient Harman technique is used to characterize cross-plane ZT in InGaAs/InGaAlAs superlattices with embedded ErAs nanoparticles to study various compositions of Si co-doping in the well regions. It has been shown that ErAs nanoparticles reduce the thermal conductivity of bulk InGaAs substantially and slightly increase the thermoelectric power factor Seebeck coefficient square times electrical conductivity. The InGaAs/InGaAlAs superlattice structure was designed to have a barrier height of ~250meV.

Calculations estimate that the power factor can be improved substantially in the cross-plane direction. ErAs nanoparticles provide free carriers inside the semiconductor matrix. Additional doping with Si increased the Fermi energy to just below the barrier height. Hall mobility and Seebeck measurements in the plane of the superlattice give a power factor similar to bulk ErAs/InGaAs. Due to measurements of the cross-plane thermoelectric properties (specifically the electrical conductivity) are challenging for thin-film superlattices. Transient Harman technique can directly measure cross-plane thermoelectric power factor in superlattice structures, reducing signal ringing due to parasitics and achieve short time resolution (<1 micro seconds) in transient Seebeck voltage measurement. Direct ZT measurements are compared with independent measurements of cross-plane thermal conductivity and Seebeck coefficient.

9:15 AM F4.5

A Band Structure Phase Diagram Calculation of 2D Bi8Sb Films. Ming Y. Tang1 and Mildred S. Dresselhaus1,2; 1Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; 2Physics, MIT, Cambridge, Massachusetts.

Ever since the birth of thermoelectrics, it has been well known that semiconductors (materials with a relative small bandgap) give the best thermoelectric performance. From quantum mechanics, it is also well known that low dimensional quantum confinement leads to changes in the band alignment of a material. Thus, a semimetallic material can be made semiconducting through low dimensionality quantum confinement effects. Bi8Sb alloys have been of particular interest for thermoelectric application in the temperature range of 70K to 100K. In bulk form, a Bi5Sb alloy can either be either a semimetal or a semiconductor, depending on the alloy composition. Moreover, semimetallic Bi8Sb alloys can be made semiconducting by using the low dimensionality quantum confinement concept. With the previous concept and alloy composition of Bi8Sb nanowires by Rabin, Lin, and Dresselhaus (Appl. Phys. Lett., 79, v.1, p.81-83), we now examine the corresponding effect of the Sb concentration and the wire diameter on the semimetallic or semiconducting properties of Bi8Sb alloys nanowires. Following the study of the effect of the Sb concentration and the wire diameter on the semimetallic or semiconducting properties of Bi8Sb alloy films, we now examine the corresponding effect of the Sb concentration and the film thickness on the properties of Bi8Sb alloy films. A band structure phase diagram is constructed, giving the details on the dependence of the relative band edge position on the film thickness and the Sb concentration. This phase diagram gives a first hand guideline for choosing the film thickness and the Sb concentration to better improve the thermoelectric performance of Bi8Sb alloy films.

9:30 AM F4.6

Thermoelectric Transport Properties of Bi2Te3: Novel Nanostructures. Seong Yul Kim1, Erin Dunbar2, Daniel Tsang2, Abhishek Jain1, Arup Purkayastha1, Ganapathiraman Ramanath1 and Theodorios Boreas Tzeng1; 1Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York; 2Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Engineering the electric and thermal transport in nanostuctures has emerged as a candidate for factorial enhancements in the thermoelectric figure of merit. This work explores thermoelectric transport in films of self-assembly Bi2Te3: Nanostructures. The particles are grown with control over size and size distribution using a novel room temperature synthesis method from microemulsions. Nanostructures are functionalized with desired termini for re-dispersion and controlled assembly. Films are obtained by spin coating or drop-casting and drying the dispersed nanostructures solutions on glass substrates instrumented with micro-heaters and microelectronics for Seebeck and electrical conductivity characterization. For Seebeck characterization a temperature gradient is established along the specimen. The junctions of two fine (25 μm diameter) thermocouples are brought in contact with the thermoelectric film to monitor the Seebeck voltage drop. The dependence of the Seebeck voltage as a function of the temperature similar to bulk ErAs/InGaAs. Seebeck coefficient of the film can be extracted from the slope as $S = -\frac{\Delta V}{\Delta T}$. Electrical conductivity is determined using a two probe technique. A linear I-V characteristic is obtained for the films indicating ohmic behavior. Temperature dependent electrical measurements are performed in the 80-300K temperature range. Thermoelectric measurements on films with particles sizes ranging from 3nm and 13nm are reported. The presentation will discuss the dependence of the power factor of the films on the nanoparticle size and film structure.

9:45 AM F4.7

Bi2Te3: Structural Modulations in Epitaxially Grown Superlattices and Bulk Materials. Nicola Porin1, Oliver Ebi1 and Joachim Nunn1; 1University of Tuebingen, Institute for Applied Physics, Tuebingen, Germany; 2Fraunhofer Institut Physikalische Messtechnik, Freiburg, Germany.

Multiquantum well structures of Bi2Te3 are predicted to show an
enancement of the thermoelectric figure of merit of ZT [1].

Bi2Te3/Bi2Te(0.85Sb0.15)3 superlattices (SL) with a layer thickness of 12 nm were grown on Si(111) substrates by molecular beam epitaxial techniques (MBE) [2]. The microstructure was investigated by transmission electron microscopy (TEM) [3]. By high resolution the SL could be imaged with strong contrast due to the intersublattice interference, which is related to the reflections of the superstructure. The period length of the SL is 13.1±0.4 nm. The SL is slightly bent with an amplitude of 30 nm and a wavelength of 400 nm. Threading dislocations were found with a density of 102 cm−2. The superstructure interfaces are strongly bent by several degrees in the region of the threading dislocations, undisturbed regions have a maximum lattice size of 300 nm. A structural modulation (nns) parallel to the (1,0,10)-planes with a wave length of 130 nm was also found. This modulation in n-type Bi2Te2Se3 and p-type (Bi,Sb)2Te3 bulk material and turn out to be of great importance for Bi2Te3 materials. The (nns) did not show bending due to the superlattice and vice versa. Therefore, the structure is a combination of the optical and structural superlattices (nns) and the structural modulations (nns). The structural modulation was analysed in n-type bulk material in detail. The (nns) consists of parallel dislocations lying on (1,0,10)-planes only a few nanometers apart with a high dislocation density of 1012 cm−2. The Burgers vectors and the dislocation line directions were determined by stereomicroscopy. The investigations showed the presence of none, one or two (nns). Particularly the heat conductivity should be significantly decreased due to phonon scattering on the (nns) with its high dislocation density. Therefore, the heat conductivity (nns) could yield a reduced dimensionality and localization and anisotropic behaviour in the basal plane. Cubic AgPmStTe2+4 bulk materials also showed a similar (nns) and an enhancement of the thermoelectric figure of merit [4].


Lamprecht A. et al., Proc. 20th Int. Conf. on Thermoelectrics, Beijing, P.R.China (2001), pp. 325-328 [6].

Farman N. et al., Proc. 23rd Int. Conf. on Thermoelectrics, Atlanta, Georgia (2004), in press [7].


Recent development in thermoelectric conversion, especially in the area of quantum well (QW) thin film materials, has demonstrated the potential to achieve the high efficiency and power density to fabricate future power supplies, self powered appliances and power devices for both space and exoterritorial applications. Both theory and experiment have indicated that improvements in the thermoelectric figure of merit of QW multilayer film materials can enhance the electrical conductivity, Seebeck coefficient, and thermal conductivity resulting in much higher figures of merit. In our study, we demonstrated the development of multilayer films consisting of 40 period QW films of N-type SiC/SiC doped p-type B5C/C5B, which can be used in practical devices for waste heat recovery. The approach is to fabricate thick large area film stacks (up to 11 mm) deposited by photolithography process on p-type (100) silicon substrates. This deposition approach might be prove to be the most suitable for potentially manufacturing large area thermoelectric devices in a cost effective manner. These more basic studies are being carried out to better understand variables such as film thickness, deposition rate and other important parameters of these ~10 nm films. The resulting multilayer stacks are being examined in terms of film uniformity, thickness, growth rate, composition, resistivity, and thermoelectric performance through ellipsometric quantification, Focused Ion Beam (FIB), Secondary Ion Mass Spectroscopy (SIMS), cross section Transmission Electron Microscopy (TEM), and electrical measurements. Issues, which could cause film stack degradation, such as interface layer formation, film contamination, and crack formation, are expected to influence device performance and are presented and correlated to device efficiency.

10:45 AM E4.10 Fabrication and Characterization of Si-Ge Nanocomposite for Thermoelectric Applications. Dezhui Wang1, Wenzhong Wang1, Shuo Chen1, Zhifeng Ren1, Huhyun Lee2, Gang Chen3, Ming Tang3, Mildred Dresselhaus1,2, Pawan Gogna1, Jean-pierre Fleural1 and Bradley Klots1,2,3. Physics, Boston College, Chestnut Hill, Massachusetts; 1 Mechanical Engineering, MIT, Cambridge, Massachusetts; 2 Electrical Engineering, MIT, Cambridge, Massachusetts; 3 Physics, MIT, Cambridge, Massachusetts; 4 Dynamic Science, In, Aberdeen Providing Ground, Maryland.

Low dimension is one of the most promising directions to search for high-ZT thermoelectric materials. It has been predicted by theory and proved by experiments that structures such as quantum well and superlattice can increase ZT by several times vs the corresponding bulk materials. However, it is very difficult to manufacture those low dimensional structures in large scale for bulk applications. To realize those principles, we have designed a new structure so called Si-Ge nanoplatelets, nano Si-Ge alloy. The Si-Ge nanoplatelets were made of nano silicon and germanium particles by hot-press. A unique hot-press procedure was developed in order to make the nanoplate composite structure. The samples are characterized by TEM, SEM, and XRD. The thermoelectric properties of the samples will be reported.

11:00 AM E4.10 Thermoelectric and thermomagnetic transport in PbTe with nanoscale structures. Joseph P. Heremans, Delphi Research Labs, Shelby Township, Michigan.

The development of bulk materials with nanoscale inclusions would be very useful for many large-scale applications. Nanometer-scale inclusions in lead chalcogenides are known to improve the thermoelectric figure of merit through a combination of two factors, a strong decrease in lattice thermal conductivity and an increase in the Seebeck coefficient over that of bulk PbTe for a given carrier concentration. This talk is focused on experimental results obtained on two types of PbTe nanocomposites, namely samples prepared by sintering powders with nanometer-sized grains, and samples prepared with nanoprecipitates of metallic Pb. The results are analyzed using the method of four coefficients. At each measurement temperature there are four unknowns, the carrier concentration, the mobility, the Seebeck coefficient and the thermal conductivity of the sample. This time, which is modeled by a power law αT γ F α. In order to determine these four unknowns uniquely at each temperature, four measurements are taken: the electrical conductivity, and the Hall, Seebeck and transverse Nernst-Ettinghausen coefficients. The analysis concludes that the increased Seebeck coefficient in samples with nanoscale inclusions is due to an increase in the scattering parameter α. The mobility of the sintered samples is much lower than that of the PbTe samples. In the first group of PbTe samples the mobility is also an issue that could be added to the situation in samples containing nanoprecipitates is more favorable. No decrease in lattice thermal conductivity is measured in binary PbTe with nanoprecipitates.


A novel class of quaternary compounds AgPmStTe2+4, denoted as LAST-m have attracted considerable attention during last two years because of their large thermoelectric figure of merit ZT at high temperatures[1]. Ab initio electronic structure calculations have shown that these compounds can be described as a sequence of Pb0.5Sb0.5Te2+4 compounds which rise to dramatic modification of the density of states (DOS) near the band gap of the parent compound PbTe[2]. These modifications can have significant effect on the Seebeck coefficient (n-type in LAST-m) and hence on ZT. Recently, Na0.5Pb0.5Sb0.5Te2+2, a maximum figure of merit ZT ~1.7 has been obtained around 650 K[3]. In order to explore the generality of this defect induced modifications of the DOS concept we have carried out extensive studies in a large class of systems characterized as MPb1−xSb1+2xTe2 (n=10), where M is a defect which can be a Pb vacancy, a monovalent atom (alkali atoms, Cu), a divalent atom (type Hf, Zn, Cd, Hg and type IVA S, Ge) and a trivalent atom (Ga, In, Ti). We find that valence and conduction band DOS are strongly perturbed, particularly near the band gap region by these defects. Na is found to be an ideal acceptor, it does not perturb the DOS of PbTe near the band gap region. Other monovalent impurities and vacancy increase the DOS near the top of the valence band (good for p-type thermoelectric). Zn, Cd, and Hg give rise to strong resonance states near the bottom of the conduction band and have an opposite effect to DOS near the top of the valence band (good for n-type thermoelectric). Sn and Ge behave like Pb and do not modify the DOS near the band gap region. The trivalent atoms Ga, In, and Ti behave differently than Sb because their valence configuration is (n+1)6p5 for Sb, whereas Na gives rise to states in the gap region, for Ga and Ti the impurity induced states are resonant with the valence band. * Work supported by ONR-MURI. References [1] K. F. Hsu et al., Science 303, 818 (2004). [2] Daniel Bile et al., Phys. Rev. Lett. 93, 146403 (2004). [3] Pierre F. P. Poudeu and Mercouri G. Kanatzidis (private communication).

11:45 AM F4.12 Thermoelectric Properties of Hot-pressed core-shell
Nanoparticles Having the Shell of InSb. Seiji Take\textsuperscript{1}, Kikuo Okuyama\textsuperscript{2} and Yukio Yamauchi\textsuperscript{2}; 1Japan Chemical Innovation Institute, Tokyo, Japan; 2Department of Chemical Engineering, Hiroshima University, Hiroshima, Japan; 3Department of Chemical System Engineering, The University of Tokyo, Tokyo, Japan.

Many studies have been reported about various particles which are dispersed in thermoelectric materials in order to improve the thermoelectric properties. But significant improvement has not been reported because dispersed particles cause reduction of electric conductivity as well as increasing of phonon scattering. Here, we propose hot-pressed core-shell nanoparticles. The core is well dispersed in sintered shell in nano-scale, which is expected quantum confinement of the carriers. We fabricated the hot-pressed Pt/Au core-shell nanoparticles. The Pt/Au nanoparticles used had following sizes: the core (Pt) was about 2nm diameter, and the shell (Au) thickness was an average of 1nm. The value of figure-of-merit ZT measured was 2.6E-3 at 300K, which was bigger than both 1.1E-3 of bulk Pt and 1.5E-3 of bulk Au. It was confirmed that the hot-pressed Pt/Au was not alloying means of XRD investigation. Seebeck coefficient (S) of Pt/Au, bulk Pt and bulk Au were 8.3, 1.9, 5.1µV/K, respectively. So, it was considered that significant improvement of S mainly increases the property of ZT in the case of Pt/Au. We have established the method of synthesizing core-shell nanoparticles having the shell of InSb. And their thermoelectric properties will be discussed. This work is supported by the NEW Energy and Industrial Technology Development Organization (NEDO)’s Nanotechnology Materials Program - Nanotechnology Particle Project\textsuperscript{3}.

SESSION F5: Low Dimensional Structures II (Bulk: Pressed and Self Assembled)
Chair: Ryoji Funahashi and Joseph Poon
Tuesday afternoon, November 29, 2005
Room 315 (Hynes)

1:30 PM F5.1 Size-selective High-yield Growth of PbTe Nanocrystals Using a Chemical Vapor Deposition Technique. B. Zhang, N. Gothard, J. He, D. Thompson and T. M. Trit; Physics & Astronomy, Clemson University, Clemson, South Carolina.

PbTe nanocrystals have been synthesized using a chemical vapor transport (CVT) technique. The size-selective precipitation mechanism enables good control of particle size distribution by variation of heating temperature, Ar gas flow rate and admixture with Au particles. As the result, a yield of hundreds milligrams nanocrystals with narrow size distributions at 100, 200 and 600 nm have been obtained. It is found that the lattice constant monotonically increases with diminishing particle size. XRD patterns taken on the three samples show sharp Bragg reflections, which indicate good crystallinity of samples. The relevant growth mechanism is discussed.

1:45 PM F5.2 Nanostructured Bulk Thermoelectric materials. Savankaar Sengupta, Bao R. B., Troc Phipps J. R. Schorr, Jennifer Nelson, Julie Anderson, James H. Adair and Norbert Elsner; 1MetaMateria Partners, Columbus, Ohio; 2Penn State University, University Park, Pennsylvania; 2Hi-Z, San Diego, California.

Significant improvement in thermoelectric performance has been realized in low-dimension semiconductor systems. However, these gains have only been demonstrated in thin film systems. To become commercially viable, new lower cost processing routes are needed for preparing bulk materials that contain nanostructured, thermoelectrically active components. In this paper, an approach that maintains nanoscale features in a bulk material, which may lead to improvement in thermoelectric properties will be reviewed. In this approach, nanoparticles of PbTe were first synthesized. These PbTe nanoparticles were then coated with a thin film of PbSe. The resulting coated particles, as well as uncoted PbTe particles, were then consolidated into pellets and the thermoelectric properties of the dense samples were measured. Our investigation reveals an enhancement in thermoelectric power, a decrease in thermal conductivity and an increase in electrical resistivity compared to conventionally processed PbTe.

2:00 PM F5.3 PbTe-based Nanomaterials for Thermoelectric Application. Bed Poujol; 1W. Z. Wang; D. Z. Wang; Y. Ma; Z. F. Ren; Q. Hao; H. Lee; G. Chen and M. S. Dresselhaus; 1Physics, Boston College, Chestnut Hill, Massachusetts; 2Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 3Department of Physics and Department of Electrical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

PbTe nanocrystals having sizes in the range of 5-50 nm have been synthesized using a hydrothermal method. As-prepared nanopowder was pressed using P9C die and samples, with almost 100% density, having small grain sizes were achieved. The thermoelectric properties of such samples have been investigated. For further enhancement of the thermoelectric properties, the PbTe nanocrystals are doped with different elements, for example Ag, Sn, Cu, Eu etc, and their thermoelectric properties have been studied.

2:15 PM F5.4 Thermoelectric Properties of PbTe-based Nanostructures. N. Gothard, B. Zhang, H. Zhang, B. Edwards, D. Thompson, J. He and Terry M. Trit; Physics & Astronomy, Clemson University, Clemson, South Carolina.

Research into thermoelectric materials has been advanced for many years by doping studies, but many of these materials seem to have reached a plateau of improved performance with the last several years. Recent investigations of bulk materials have resulted in the synthesis and characterization of more and more complex structures. Theoretical work has lately suggested that the path to improved thermoelectric materials may be opened up by synthesizing them on the nanometer scale. Certainly, this prediction was proven correct with the recent results on superlattice and quantum dot materials constituted based on good bulk thermoelectric materials. The challenge has been to achieve higher performance levels in a bulk material that may be easily transitioned into a device. Recently, we have accomplished high yield synthesis of PbTe-based nanostructures by a thermally driven vapor transport method. We have performed compaction techniques in order to yield a bulk electrically composed of these nanostructured materials. Measurements of the thermoelectric parameters of a material are problematic in general, and the nanostructured samples present several measurement difficulties. We briefly discuss measurement techniques for these nanoscale compacted samples and present thermopower, resistivity, and thermal conductivity data for these materials.

2:30 PM F5.5 The Nanostructured Thermoelectric Materials AgPbmSnSeTe\textsubscript{2+2m} (LAST-m). Mercouri G. Kanatzidis, Michigan State University, East Lansing, Michigan.

The family of chalcogenide lead-based compounds, AgPbmSnSeTe\textsubscript{2} or LAST-m materials (LAST for Lead Antimony Silver Tellurium), comprises of several members which exhibit large ZT values up to \textasciitilde 1.8 (LAST-18) at 700 K. Thermal transport in these systems is a key factor for achieving a high figure of merit. Electron diffraction and high resolution transmission electron microscopy studies indicate the LAST phases to be inhomogeneous at the nanoscale with at least two different set well defined phases. Electrochemical examination revealed endotaxially dispersed quantum nanotubes (i.e., regions 2 to 4 nm in size that are rich in Ag-Sb and are surrounded by a PbTe matrix) similar to those found in the PbSe/PbTe thin films. The impact of these nanostructural features on the thermoelectric properties of these materials is strong. We will discuss the dependence of charge and thermal transport properties of these materials on the composition and preparation conditions.

4:00 PM F5.6 Electronic Structure of Ag$_{2}$Sn$_{1-x}$Sb$_{x}$Te$_{2}$ (M=Pb, Sn) Compounds - Implications of Thermoelectric properties*. Kha Huang and S. D. Mahanti; Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan.

Thermoelectric properties of a material depend sensitively on the nature of electronic states near the chemical potential $\mu$. It has been suggested that resonant structures in the neighborhood of $\mu$ can indeed give rise to enhanced thermoelectric figure of merit [1]. Abinitio electronic structure calculations can shed some light on the possibility of finding such resonant structures [2]. Recently, chalcogen compounds Ag$_{2}$Sn$_{1-x}$Sb$_{x}$Te$_{2}$ (M=Pb, Sn) have emerged as materials for potential use in efficient thermoelectric power generation at high temperature [3,4]. These systems possess simple cubic NaCl structure at room temperature, however, detailed information about the ordering of Ag and Sb ions is not available. Monte Carlo (MC) simulations on the systems using an ionic model show a variety of nanostructures associated with the ordering of Ag and Sb ions [5]. In order to investigate the relationship between the nanostructures of these quaternary compounds observed in MC simulations [5] and their electronic structure, we have carried out detailed calculations in several compounds: M=Pb (m=2,14) and M=Sn (m=1,2). These calculations were carried out in density-functional theory (generalized-gradient approximation for exchange-correlation) using
P AW method[6]. Results for a monolayer structure of M=Pb and M=Sb (one layer of AgSbTe2 sandwiched between 7 layers of Pb2Te4) show the disappearance of the SnI and SnII doublets at high temperatures as the layer thickness increases to a value of 12 Å. This behavior persists for a bilayer structure of the same M and m. For M=Sb and m=2, this effect is absent in AgSbTe2 and Pb2Te4, this peak persists but its shape in the high energy end is changed due to 3-dimensional coupling perpendicular to the layers. In addition, the band gap region fills up and only a pseudo gap appears. In AgSbSnTe2 we find extremely high density of states in the low-lying bands in the near-gap energy (2.5 eV). There are 3 peaks (positions -0.25 eV, 0.25 eV, and 0.90 eV) and the FE lies at the minimum between the 1st and the 2nd peak and the system is metallic (DOS at FE is ~2 states/fu, 1.8~4 states/fu for AgSbTe2). A small amount of hole doping (decrease in electron concentration) shifts the chemical potential to a lower energy where the DOS decreases rapidly with increasing energy. These observations are consistent with the recent experiments (large carrier concentration and high positive thermoelectric power in AgSbTe2) [4] described by ONR-MURI. References [1] G. D. Mahan and J. O. Sofo, Proc. Natl. Acad. Sci. USA 93, 7436 [1996], [2] D. B. Bie et at., Phys. Rev. Lett. 93, 146603 (2004). [3] K.-F. Ha et at., Science 303, 708 (2004). [4] J. Androulakis et at.(to be published) [5] K. Hoang, K. Desai and S. D. Mahanti, Phys. Rev. B (to be published 01 July 2005). [6] P. E. Böckl, Phys. Rev. B 50, 17956 (1994).

4:15 PM F5.7
Thermoelectric Materials AgPb0.8Sb0.2Te2+m (LAST-m) with High Figure of Merit. Structural Evidences Breaking the Myth of Solids Solutions, Eric Quarez1, N. Francis2, E. K. Polychronakos3, Kuei-Fung Hsu1, Robert Pcionek1, Jonathan D’Angelo3, Adam Downey4, Joseph Sootsman5, Robert J. Pcionek5, Zhenhua Zhou5, Oleg Palchik2, Timothy P. Hogan2, Citrad Uher2 and Mercouri G. Kanatzidis1. 1Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan; 2Department of Electrical and Computer Engineering, Physics, University of Michigan, Ann Arbor, Michigan; 3Solid State Science Program, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 4Department of Chemistry, and Center for Fundamental Materials Research, University of Illinois at Urbana-Champaign, Urbana, Illinois; 5Department of Physics, Chemistry, and Biochemistry, Ball State University, Muncie, Indiana.

Recently, we described the family of chalcogenide lead-based compounds, AgPb0.8Sb0.2Te2+m, or LAST-m materials (LAST for Lead Antimony Silver Tellurium), several members of which exhibit large thermoelectric power factor values from +1.2 (LAST-10) to +2.2 (LAST-18) at 800 K. Preliminary electron microscopy studies of these samples revealed endothermally formed quantum dots (i.e., regions 2-4 nm in size that are rich in Ag-Sb and are surrounded by a PbTe matrix). This is a significant observation and raises important new questions as to the possible impact of these nanostructured features on the thermoelectric properties. We present here structural studies to fully characterize the LAST materials on the atomic scale and probe the extent and nature of nanostructuring, AgPb0.8Sb0.2Te2+m, samples with different m values were prepared and characterized by powder/single crystal X-ray diffraction, electron diffraction and high resolution transmission electron microscopy. Powder diffraction patterns of different members (m = 0, 6, 12, 18, 26, 34, 42, 50) are consistent with pure phases crystallizing in the NaCl-type structure (Fm-3m space group) and the proposition that the LAST family behaves as solid solutions between the PbTe and AgSbTe2 compounds. However, electron diffraction and high resolution transmission electron microscopy studies suggest the LAST phases are inhomogeneous at the nanoscale with at least two coexisting sets of well-defined phases. Moreover, within each nanoscale domain we observe extensive long-range ordering of Ag, Pb and Sb, which can be formed by single crystal X-ray diffraction studies. Indeed, data collections of five different single crystals were successfully refined in space groups of lower symmetry than Fm-3m including P4/2/mnm and R-3m. The results reported here dispel the decades long belief that the systems (AgSbTe2)1−m(PbTe)m are solid solutions.

4:30 PM F5.8
Nanostructuring and its Influence on the Thermoelectric Properties of the AgSbTe2-SnTe Quaternary System, Ioannis Androulakis1, Robert Pcionek2, Eric Quarez2, Oleg Palchik2, Citrad Uher2, Jonathan Dangello2, Tim Hogan3 and Mercouri G. Kanatzidis1. 1Department of Chemistry, and Center for Fundamental Materials Research, University of Illinois at Urbana-Champaign, Urbana, Illinois; 2Department of Electrical and Computer Engineering and Materials Science and Mechanics, Michigan State University, East Lansing, Michigan; 3Physics, University of Michigan, Ann Arbor, Michigan.

The structural and thermoelectric properties of the AgSbTe2-SnTe quaternary system have been studied. Powder x-ray diffraction indicates a cubic NaCl-type structure in contrast with the single crystal refinements, which point towards a CdI2-type crystallization scheme. The apparent discrepancy was lifted by high-resolution electron microscopy imaging which revealed the system to be a nano-composite formed by thermodynamically driven compositional fluctuations rather than a solid solution as it was viewed in the past. As a result the thermal conductivity is retained at very low values, which is in accord with recent theories on thermal transport in heterogeneous systems. The charge transport properties of the system exhibit a rich physical behavior. This is highlighted in the Ag0.8Sb0.2Sn0.1Te3 composition where a very high almost metallic carrier concentration (~5×1024 cm-3) was found to coexist with a large thermoelectric power response of the order of ~100 μV/K, which is consistent with the experimental data of a recent hole effective mass that is almost six times that of the electron rest mass. Financial support from the Office of Naval Research (Contract No. N00014-02-1-0867 MURI program) is gratefully acknowledged.

4:45 PM F5.9
Effects of Antimony on the Thermoelectric Properties of the Cubic Pb0.8Sb0.2Te1−m−Sb, Materials.

Piere Ferdinand Poudel1, Jonathan D’Angelo2, Adam Downey3, Joseph Sootsman4, Robert J. Pcionek5, Zhenhua Zhou5, Oleg Palchik2, Timothy P. Hogan2, Citrad Uher2 and Mercouri G. Kanatzidis1. 1Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan; 2Department of Electrical and Computer Engineering, Physics, University of Michigan, Ann Arbor, Michigan.

The effects of the variation of Sb and Se contents on the thermoelectric properties of Pb0.8Sb0.2Te1−m−Sb, in the intermediate temperature range were investigated. The Pb0.8Sb0.2Te1−m−Se family was derived from Pb0.8Sb0.2Te1−m by isoelectronic substitution in analogy with the Te vacancy annihilation in PbTe. Single crystals samples from a polycrystalline PbTe matrix. Increasing the Sb content to y = 0.4 results in a dramatic drop of the thermoelectric with only modest improvement of the electrical conductivity.

SESSION F6: Low Dimensional Structures III (Nanowires) and New Materials

Chairs: Lidong Chen and Hiroimichi Ohta

Wednesday Morning, November 30, 2005

Room 313 (Hynes)

8:00 AM F6.1
Energy-Specific Equilibrium in Heterostructured Nanowires for High-Efficiency Thermoelectric Energy Conversion.

Heiner Linke1 and Tammy E. Humphrey2. 1Physics Department and Materials Science Institute, University of Oregon, Eugene, Oregon; 2Department of Electrical Engineering, University of California Santa Cruz, Santa Cruz, California.

We recently showed theoretically how the bandstructure in thermionic (1) or thermoelectric (2) devices can be tuned to minimize irreversible electronic effects which limit the efficiency of thermoelectric energy conversion. Specifically, the bandstructure in heterostructured nanowires can, in principle, be designed such that all mobile electrons are in energy-specific equilibrium in the presence of a temperature gradient and a bias voltage, eliminating irreversibilities, and increasing the efficiency. While in the absence of phononic heat conduction it is possible in principle to reach Carnot efficiency, the gains that can be made in real materials will depend on the magnitude of lattice heat conduction. In this presentation we will discuss the underlying physics of these insights conceptually, and will quantitatively discuss the gains that can be made. We will then discuss the specific implications of our theoretical predictions using high-quality, heterostructured III-V nanowires, which will be used for proof-of-concept experiments. (1) T. E. Humphrey, R. Newbury, R. P. Taylor and H. Linke, Phys. Rev. Lett. 89, 116801 (2002). (2) T. E. Humphrey and H. Linke, Phys. Rev. Lett. 94, 096601 (2005).

8:30 AM F6.2
Thermoelectric Modeling of Si-Si1-xGe x Ordered Nanowire Composites. Ming Y. Tang1, Mildred S. Dresselhaus2,3, Roman Yang2 and Gang Chen3. 1Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; 2Mechanical Engineering, MIT, Cambridge, Massachusetts; 3Physics, MIT, Cambridge, Massachusetts.

Nanowires have always been attractive for power generation and cooling because of power reliability and environmentally friendly issues. However, this concept remains non-competitive due to the
limitation in the efficiency of available thermoelectric materials and device design. In the 1990s, Hicks and Dresselhaus predicted the possibility of a dramatic enhancement in thermoelectric performance based on the special behavior of low dimensional materials. This enhancement is mainly due to the increase in quantum confinement effects, the increase in carrier density of states at specified energies, and the presence of phonon pathways for low dimensional structures. Nanowires and core-shell nanowires are 1D systems that exemplify low dimensional materials. It is expected that a system made out of nanowires or core-shell nanowires would have a higher thermoelectric performance than its bulk counterpart due to an increase in the number of interfaces. The interfaces introduced must be such that phonons are readily scattered but not the electrons. Theoretical studies have been carried out to better understand the transport properties of the Si-SiGe ordered nanowire composite. The composite can be viewed as having the Si wires inside the Si1-xGe host matrix. Thus, core-shell Si/SiGe nanowires can be considered as the building block of the composite. The effect of the wire diameter and the shell alloy composition on ZT will be presented. Experimental realization of this model will also be discussed.

8:45 AM F6.3 Synthesis of Bi2Se3 Nanowires Using a Hydrothermal Method. Yi Ma, Wenzhang Wang, Dezhi Wang and Zhifeng Ren; Physics, Boston College, Chestnut Hill, Massachusetts.

Bi2Se3 nanowires of a few micrometers long and 100 nm in diameter have been successfully synthesized via a hydrothermal route for the first time. The as-prepared nanowires were characterized by an X-ray diffraction meter, a focused ion beam microscope (Ka, Bruker AXS), a field emission transmission electron microscope (SEM, JEOL-6340F), and a field emission scanning electron microscope (TEM/HREM, JEOL-2010F) equipped with an energy-dispersive X-ray spectrometer (EDS). XRD pattern clearly indicates that the majority of the as-prepared powders are of pure Bi2Se3 phase. The SAED and HRTEM studies indicate that the as-prepared Bi2Se3 nanowires are highly crystallized single crystals. Based on our experimental results, a possible growth mechanism is discussed.

9:00 AM F6.4 Thermoelectric performance of pulse-deposited bismuth telluride nanowire arrays. Lynn Trahey1, Jeff Sharp1 and Angelica Stacy1,1 Chemistry, University of CA, Berkeley, Berkeley, California; 2Marlow Industries, Inc., Dallas, Texas.

Nanowire arrays of a good room temperature thermoelectric material, bismuth telluride, have been electrodeposited into porous alumina templates using pulsed-potentiostatic methods. The pulse-deposition parameters, including reduction potential, rest potential, time at set potentials, and scan rate can dramatically affect the rate of electrodeposition. Reduction rates influence the morphology of the nanowires, the filling percentage of the templates, and the nanowires' primary crystallographic orientation, all of which impact the thermoelectric performance that the arrays exhibit. Template and nanowire morphology can be controlled by using scanning electron microscopy (SEM) and the orientation of the nanowires inside the templates has been determined using powder x-ray diffraction (XRD), AC resistance, DC resistance, ΔT and Seebeck coefficients have been measured, and the linear electrical conductivity of the nanowires that are roughly 35 nm in diameter and 50 μm in length. Although not yet at small enough diameters for predicted quantum confinement, the bismuth telluride arrays have shown enhanced figures of merit compared to their bulk counterparts.

9:15 AM F6.5 Incorporation of Bismuth Antimony Nanowire Arrays into Thermoelectric Couples. Jennifer Keynan1, J. W. Sharp1 and Angelica M. Stacy1,1 Chemistry, University of California, Berkeley, Berkeley, California; 2Research and Development Division, Marlow Industries, Inc., Dallas, Texas.

Thermoelectric (TE) nanowires are predicted to show an enhanced figure of merit (ZT) over bulk materials due to quantum confinement effects. Dresselhaus et al. predict that bismuth antimony (Bi1-xSb_x), the best n-type, low temperature bulk TE material, will show enhanced ZT at nanowire diameters less than 50 nm. We have fabricated Bi1-xSb_x nanowire arrays in porous alumina templates and assembled them into hybrid nanowire-bulk TE couples to extract data about the nanowire array. For the most efficient nanowire TE device performance, each wire of an array should be in electrical contact within the circuit. To achieve this goal, the TE nanowires have been electrochemically deposited with a very narrow length distribution over a 10 to 20 μm length scale. This has been accomplished within 40 nm diameter pores for alloy compositions of 0.07 < x < 0.30. Metal contacts were electrodeposited on top of the nanowires, and the nanowire/alumina composite was then incorporated as one leg of a TE couple. The ZT of the device was extrapolated from ΔT, AC resistance, and DC voltage measurements.

9:30 AM F6.6 Thermoelectric Properties of Bi and Bi1-xSb_x Nanowires. M. V. Vodenikov, O. N. Uryupin and Yu. V. Ivanov; A. F. Ioffe Physical-Technical Institute, St. Petersburg, Russian Federation.

Natural asbestos was used for a preparation of Bi and Bi1-xSb_x nanowires. This mineral consists of thin tubes with internal diameter of about 5 nm and length up to 1 cm. The asbestos nanotubes were filled with melted Bi or Bi-Sb-In melt at high pressure. The samples prepared by this method were bundles of the 5 nm wires with length of about 1 mm. We have measured the temperature dependences of the thermoelectric power and resistivity and the voltage-current characteristics of these samples. It has been shown that the thermoelectric power of the Bi0.75Sb0.25 nanowires is comparable with that of Bi nanowires. The possible explanation of unusual thermoelectric properties of these nanowires is presented.

10:15 AM F6.7 Electronic States of TiS2, MoS2, and (Ti,Mo)S2 in Bulk, Single Layer, and Nanotube Forms. Lingyun Xu and Murray S. Daw; Department of Physics and Astronomy, Clemson University, Clemson, South Carolina.

Recent experiments have investigated the thermoelectric properties of bulk TiS2, MoS2, and Mo-doped TiS2. Also, nanotubes have been grown of both TiS2 and MoS2, and their properties measured. To understand the properties of these materials, we have calculated the electronic states of TiS2 and MoS2 in various geometries, as well as Mo-doped TiS2. The calculations are performed within the framework of density functional theory. We have investigated bulk structures as well as single layers, and also some nanotube structures. These represent the first calculations of the electronic structure of nanotubes formed from these materials.

10:30 AM F6.8 Rhenium Silicide as a New Class of Thermoelectric Material. Haruyuki Inui; Department of Materials Science and Engineering, Kyoto University, Kyoto, Kyoto, Japan.

Silicide formed with rhenium is of interest owing to potentials as a promising candidate material for thermoelectric generators. We report that the silicide is a defect disilicide with the stoichiometry of ReSi1.75 instead of ReSi2. We have recently determined the crystal structure belongs to the monoclinic system with an ordered arrangement of Si vacancies in the parent C115 lattice. Binary ReSi1.75 exhibits significantly anisotropic thermoelectric properties such that the value of Seebeck coefficient along [100]C115 is positive (230μV/K at 330K) while it is negative (−300μV/K at 600K) along [001]C115. This may result from the highly anisotropic electronic structure of ReSi1.75. The dimensionless figure of merit (ZT) for binary ReSi1.75 is as high as 0.7 at 1073 K when measured along [001] while the ZT value along [100] is moderate. We have made two attempts to improve the thermoelectric properties of ReSi1.75 by adding some elements such as In, Al, and Ge. The Si vacancy concentration changes when ternary elements with a valence electron number different from that of Re are alloyed, accompanied by the appearance of shear structures. When the valence electron number is larger, the Si vacancy concentration decreases with the appearance of shear structure on (107). When the valence electron number is smaller, the Si vacancy concentration increases with the appearance of shear structure on (−109). In general, no significant improvement in thermoelectric properties is observed when the shear structures appear upon alloying. When Mo is alloyed, however, the adaptive (incommensurate) structure is formed as a result of simultaneous and random occurrence of (−109) and (107) shear in every unit cell. No significant increase in electrical resistivity occurs with this defect structure and significant improvement in thermoelectric properties is observed in Mo-bearing alloys, as exemplified by the high value of dimensionless figure of merit (ZT) of 0.95 at 800 °C when measured along [001]. On the other hand, when Al is added, thin defect layers containing a kind of shear structure are locally and sporadically formed at some of twin boundaries. In the defect layer, shear occurs mostly on (109); the microstructure containing these thin defect layers is very effective in reducing thermal conductivity and thus increasing the ZT value to the level of 0.95 is achieved at 150 °C. Structure-property relationships of rhenium silicide will be fully discussed, in particular in the light of nano-scale defect structures.

11:00 AM F6.9 Highly Anisotropic Thermoelectric Properties of ReSi1.75 Single Crystal. Min Wook Oh1, Katsushi Tanaka2, Haruyuki Inui3, Myung-Hoon Oh1 and Dang-Moon Wee1; 1Dept. of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejon, South Korea; 2Dept. of Materials Science and Engineering, Kyoto University, Kyoto, Japan; 3Dept. of Materials
Currently, ReSi$_{1.75}$ is gaining attention because of its potential as an advanced thermoelectric material. Its crystal structure belongs to the monoclinic system with an ordered arrangement of Si vacancies in the parent tetragonal lattice. Although the electrical transport properties of the silicides have been reported by several researchers, they are controversial with each other. Our recent measurements on the electrical transport properties of single crystals of ReSi$_{1.75}$ indicated that the activation energy of electrical resistance of ReSi$_{1.75}$ (the $c$-axis of the parent C11$_2$ structure) is higher than that along [100] (the $a$-axis of the parent C11$_2$ structure). Also, our findings reveal a semiconducting behavior in the temperature dependence of the electrical resistance for both orientations. It is noteworthy that the thermoelectric power showed highly anisotropic behaviors. The value of the thermoelectric power along [100] is positive (+150 $\mu$V/K at 600 K) while it is negative along [001] (−300 $\mu$V/K at 600 K). These peculiar orientation dependences of the thermoelectric power (positive or negative) are unique, to the best of our knowledge. Of course, the anisotropic thermoelectric power mechanism is not yet well understood. The transport properties of electrons in semiconductors can be conveniently derived by solving the Boltzmann equation. Most theoretical works derive the coefficients related to electrical transport properties, such as the drift mobility and thermoelectric power under the assumption of parabolic and isotropic band structures. However, non-parabolic and anisotropic band structures are important for narrow band gap semiconductors such as ReSi$_{1.75}$. We have made some effort to calculate the electrical conductivity and thermoelectric power of ReSi$_{1.75}$ for various temperatures with the assumption of the non-parabolic and anisotropic band structures and to clarify the origin of the anisotropic thermoelectric power with the derived values. We found that the contribution of holes to the whole energy transportation along [001] induced by the Seebeck effect is negligible due to the large effective mass of holes along [001], which is mainly derived from the characteristic flat band feature of the band structures. In this picture, the negative thermoelectric power along [001] at high temperatures is well understood within the two-band conduction.

11:15 AM 5F6.10
Thermoelectric Properties of Icosahedral Cluster Solids, Kaoru Kimura$^{1,2}$, Junpei Tanuma Okada$^3$, Hongo Kimi$^1$, Takehito Hamamatsu$^1$, Tomohiro Nagata$^4$ and Kazuhiro Kirihara$^4$.

12 Department of Advanced Materials Science, The University of Tokyo, Chiba, Japan; 13 Department of Applied Physics, The University of Tokyo, Tokyo, Japan; 14 Department of Materials Science, The University of Tokyo, Tokyo, Japan; 15 Nanochantronics Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan.

Boron- or Aluminum-rich icosahedral cluster solids (ICS) consist mainly of Bi$_2$ or Al$_2$I icosahedral clusters. In the ICS, a slight change of the structure of icosahedral cluster can be expected by metalloid-cova lent bonding conversion, which can cause that the electrical conductivity $\sigma$ and the Seebeck coefficient $S$ can be as high as those of metals and semiconductors, respectively. Five-fold symmetry of icosahedral clusters does not match with the translational symmetry of a crystal, consequently makes lower thermal conductivity $\kappa$ with complex structure. For these reasons, ICS are promising candidates for thermoelectric materials. Using MEM/MRFV method, we successfully obtained the clear image of the electron density distribution for $\alpha$-AlReSi at approximant crystal structure. The bond strength distributes widely from weak metallic to strong covalent bond, and the intra-cluster bonds are stronger than the inter-cluster ones. This means that $\alpha$-AlReSi is located at the intermediate state of molecular, metallic- and covalent-bonded solids. Composition dependences of atomic density and quasi-lattice constant for AlPdRe icosahedral quasicrystals show the above situation is the same in the quasicrystalline. The thermoelectric figure of merit Z and the effective mass $m^*$ of AlPdRe quasicrystals can be increased by strengthening the intra- and weakening the inter-cluster bonds. According to this scenario, $Z$ was improved by a factor of 1.5 by substitution on Al site. In $\alpha$-AlPdRe, several interstitial sites, which have space large enough to accommodate foreign atoms, are known. For the V doped sample, in which V atoms mainly occupy A1 site, the metallic-covalent bonding conversion may occur, $\sigma$ is increased very much, $S$ is decreased even to negative value and $\kappa$ is decreased. The maximum and n-type ZT value is obtained and is approaching to that of Bi$_2$, which is considered to have the largest and p-type ZT value in boron-rich ICS.

11:45 AM 6F6.11
Improving Thermoelectric Figure of Merit: Investigation of Zn-doped Yb$_{14}$Mn$_{1-x}$Zn$_x$Sb$_{11}$, Shawana R. Brown$^1$, Susan M. Kazuchar$^1$, G. Jeff Riedy$^2$ and Frank Gasior$^2$.

1 Chemistry, University of California, Davis, Davis, California; 2 Materials and Device Technology, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

Thermoelectric research has seen a renewed interest in the past decade which has been spurred by the increased environmental, energy and aerospace challenges facing today's society. The drive for the discovery of a thermoelectric material that can withstand high-temperatures and also produce the greatest figure of merit has prompted an in-depth investigation in the thermoelectric properties of Zintl phase compounds. Preliminary measurements of the transition metal Zintl phase material, Yb$_{14}$Mn$_{1-x}$Zn$_x$Sb$_{11}$ with $x = 0.17$, 0.33, 0.50, 0.67 and 0.83, has been synthesized with aims of evaluating the doping influence on the physical properties of the material, and also improvements of the figure of merit beyond that of Yb$_{14}$Mn$_{1-x}$Sb$_{11}$ by adding disorder and lowering the thermal conductivity. Recent microprobe, single crystal diffraction, DSC/TG, electrical resistivity, Seebeck and PMPS measurements on these doped crystals will be presented. The results obtained from these compounds will be compared to other promising thermoelectric materials.

SESSION F7: Thermionics and Photovoltaics

Chairs: Gerald Mahan and Ali Shakouri
Wednesday Afternoon, November 30, 2005
Room 313 (Hynes)

1:30 PM F7.1 Thermal Energy Conversion, Ali Shakouri, Electrical Engineering, Univ. of California Santa Cruz, Santa Cruz, California.

A brief overview of the research activities at the ONR MURI center on Thermionic Energy Conversion will be presented. The goal is to achieve direct thermal to electric energy conversion with >20% efficiency and >1W/cm$^2$ power density at a hot side temperature of 300-650$^\circ$C. The core of the solution we are investigating is an integrated approach to engineer electrical and thermal properties of nanostructured materials. Thermionic emission in both vacuum and solid-state devices are integrated with cooling, emission, and thermal transport at both device and nanostructure level are used to verify model predictions and thereby lay the foundation for improved material and system design.

2:00 PM F7.2 Design of Heterostructures for High Efficiency Thermionic Emission, Zhaoli Biao and Ali Shakouri, Electrical Engineering Department, University of California Santa Cruz, Santa Cruz, California.

The performance of a thermoelectric material is determined by the figure of merit ZT, which is a function of the Seebeck coefficient, and the electrical and thermal conductivities. Heterostructure integrated thermionic energy converters are expected to offer larger thermoelectric power factor than bulk counterparts. When the quantum confinement effect is taken into account, the planar superlattices or multilayers, it has been shown that the improvement in efficiency due to enhanced electronic transport properties is limited. The important advantage is in the reduction of phonon transport and the parasitic heat loss. As an example, in AlSb/GaSb superlattices, the thermal conductivity of the planar barriers is lower than the material due to the larger barrier height. Many other hot electrons with large in-plane momentum are blocked by the potential barrier resulting in low electrical conductivity. In this paper we propose and analyze two heterostructure designs to improve the thermionic emission efficiency of energy conversion. The first method is to use planar heterostructure interface with roughness in order of electron mean free path. This is expected to have some combined benefits of increased effective interface area, and reduced total internal reflection for the electron trajectories arriving at the interface. Monte Carlo simulations of various geometries show that the carrier emission can be improved by 70% for nonplanar barrier compared to the planar counterpart. The second method is to use planar high barrier heterostructures with different effective masses for charge carriers in well and barrier regions. When an electron passes from a lower effective mass emitter and arrives at a barrier with higher effective mass, since both the lateral momentum and total energy are conserved, part of the lateral energy is coupled to the vertical direction and the electron gains momentum in the direction perpendicular to the interface to enter the barrier region. For high potential barriers, the improvement is about the same as the ratio of the effective masses of the two materials, which can be a factor of 5-10 for typical heterostructure material systems.

2:15 PM F7.3 Transport Formalism for Multibarrier Thermionic Devices, Tammy Eilen Humphrey and Ali Shakouri, Electrical Engineering,
University of California Santa Cruz, Santa Cruz, California.

Solid-state power generators and refrigerators in which electron transport is primarily ballistic and those in which it is primarily diffusive both achieve reversibility in the same limit; when the transport of electrons is restricted to the energy where the occupation of states is thermal. From a purely thermodynamic perspective there is therefore no particular reason to favor one or the other of these two types of devices. Even the materials parameter for solid-state refrigeration is independent of whether transport is ballistic or diffusive. However, we expect that there may indeed be an optimum design for solid-state refrigerators and power generators which incorporates elements of both ballistic and diffusive transport. This expectation is based on the fact that devices offering to optimize the distribution of the energy spectrum of transmitted electrons; in a thermoelectric device energy selectivity in electron transport is provided by the conduction/valence band edge where the density of states is always zero, whereas in a solid-state thermal energy source energy selectivity is provided by the conduction band-edge of a barrier material, but the density of states for transmitted electrons is determined primarily by the reservoir material. Maximizing the number of electrons flowing at the band-edge is very important, as it is these electrons which do work with an electronic efficiency close to the Carnot limit. An important question is whether the benefits of thermoelectric devices can be maintained in multibarrier devices designed to have a length longer than the electron mean-free path in order to reduce heat flow through the lattice. In a material with a periodicity on the order of the electron mean-free path, it is expected that most electrons move ballistically through the barrier, but the probability that an electron will be transmitted increases with longer mean-free path and the relaxation time is long, but diffusively through intermediate reservoirs. The difficulty in studying and optimizing such a system is that important features of the problem may potentially be lost if electron transport is treated as either purely ballistic or purely diffusive transport formalisms. We are approaching this problem by adapting techniques developed in mesoscopic physics to describe transport through conductors connected to a multiplicity of reservoirs with different temperatures and chemical potentials.

3:30 PM F7.4
Metal-Semiconductor Nitride Multilayers for Solid-state Thermionic Energy Conversion. Vijay Rastogi1, 2; He Young Kim2 and Timothy Sands1, 2. 1Materials Engineering, Purdue University, West Lafayette, Indiana; 2Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana;

Solid-state thermionic direct energy conversion devices based on metal/solid-state multilayers are predicted to exhibit optimal thermoelectric figures of merit (ZT) for Schottky barrier heights in the range of 0.5 to 1.5 kBT (ref. 1). At high barrier height, the thermoelectric performance of these multilayered structures depends on the cross-plane thermal conductivity of the multilayer, thus alloying and a high interface density are desirable. For application in moderate to high temperature applications (T~300-700°C), the multilayers must be stable under corrosion, composition, and interdiffusion. The nitrides meet these criteria, and offer potential materials combinations for metal-semiconductor multilayers with tunable electronic and thermal transport properties. Nitrides such as TiN, ZrN, VN, and TaN are metals whereas GaN, InN, ScN and their alloys are semiconductors. In this presentation, we describe our efforts to evaluate the potential of metal/semiconductor nitride multilayers for direct thermal energy conversion. Prototype multilayers have been synthesized by reactive pulsed laser deposition in ammonia at substrate temperatures from 550-700 °C. (TIN)0.5(ZrN)0.5 multilayers with periods from 5 to 15 nm and individual layer thicknesses down to 0.5 nm have been grown on MgO and sapphire substrates. Analysis by transmission electron microscopy and x-ray diffraction shows that the interfaces are stable and pinning-free, and are well detectable in cross-sectional. Examination of the case of the very thinnest GaN layers (~1 nm or thinner), the GaN adopts the wurtzite structure while the TIN or VN exhibits the rocksalt structure. These multilayers are crystallographically textured, with the (111) GaN basal planes parallel to the basal planes of the TIN or VN Schottky barrier height measurements by the I-V method yield barrier heights in the range of 400 to 500 meV, suggesting that replacement of GaN with (In,Ga)N alloys will permit tuning of the barrier height in the range of 150 to 500 meV. Preliminary thermal transport measurements at room temperature show a transition from semiconducting to metallic behavior as the TIN layer thickness increases from the sub-nm range to a few nm. For multilayers with 10 nm GaN layers, the TIN layer thickness at a fixed T of 500°C was measured as 1 nm, with a value of 0.5 m.K/W. Analysis of the cross-plane thermal conductivity of these multilayers is in progress and will be presented at the meeting. Reference: [1] Improved Thermoelectric Power Factors in Metal–Benzene Superlattices, D. Vashae and A. Shakoory, Phys. Rev. Lett. 92, 106103 (2004).

3:45 PM F7.5

Improving the performance of a vacuum thermionic energy conversion device (TEC) involves increasing the output current from the emitter and mitigating the negative space charge effect. Adding nanostructures to the surface of the emitter and/or collector addresses these issues in the following three ways: the increased surface area of the electrode corresponds to an increased current, high electric fields at the tips of the nanostructures locally increase the output current due to Schottky barrier lowering (SBL), and higher electric fields in the interelectrode space accelerate electrons and mitigate space charge. We have developed a model to calculate the effect that field enhancing nanostructures have on the output current. This model uses the finite element method to approximate the solution to Laplace's equation which is used to calculate the electric field normal to the surface of the emitter. The value of the normal electric field is used to modify Richardson's equation for thermionic emission in an effective local lowering of the work function. We have used the model to compute the output current and output power characteristics of a vacuum TEC with planar collector and emitter and ultra-nanocrystalline diamond tip structures. The results show that the field enhancement at the very tips of the structure are large, but only modestly increase the output current. The model can be expanded to approximate the space charge effects in a single species of electrons; namely those with energy kT, where k is Boltzmann's constant and T is the emitter temperature. Time of flight calculations of single electrons emitted from field enhancing structures indicate that nanostructures will allow for larger interelectrode spacings.

4:00 PM F7.6

Carbon dimer, C2, a nucleation and growth species in hydrogen-poor plasmas leads to high secondary nucleation rates (1019 cm−2 sec−1) and results in ultrananocrystalline diamond (UNCD) films composed of 3-5 nm crystallites. (I) Such films can be made n- or p-type conducting (up to 500 S/cm) by the addition of nitrogen or boron to the synthesis gas. (2) Although single crystal diamond is highly thermally conducting, UNCD has a thermal conductivity of 0.02w/Kcm because of effective phonon scattering at the disordered grain boundaries. (3) Tight-binding density functional calculations show that UNCD has a similar electronic structure to that of crystalline diamond. (4) The band gap of diamond with a pronounced narrow peak in the DOS at the Fermi level. (5) Grain boundary conduction is enhanced by the presence of nitrogen which results in an increased fraction of p-type bonded carbon atoms which are known to lower the grain boundary resistivity. Enhancement of thermoelectric properties in low dimensional materials has been extensively discussed. (6) Preliminary measurements on UNCD indicate ZT values near unity can be reached. Work currently under way is aimed at optimizing ZT values by using nanotube/UNCD composites. Such composites have already been synthesized but not characterized. (7) The presence of “graphitic” nanowires covalently bonded to thermally insulating UNCD crystallites can be expected to result in improved electrical transport mobility. Measurements on simultaneously synthesized and self-assembled nanotube/UNCD composites will be presented. (8) This work was supported by the U.S. Department of Energy, DE-FG02-00ER45829, National Science Foundation, W-31-100-ENG-38, Reference 1. D. M. Gruen, "Nanostructural Diamond Films", Ann. Rev. Mater. Sci., 29, 211-59, (1999); 2. O. A. Williams, S. Curat, J. E. Gerbi, D. M. Gruen, R. B. Jackman, "n-type Conductivity in Ultrananocrystalline Diamond Films", Appl. Phys. Lett., 89, 1, (2006); 3. L. Naiver, DIMES Technical University, Delft, The Netherlands, Private Communication. 4. P. Zapol, M. Sternberg, L. A. Curtiss, T. Frauenheim, D. M. Gruen, "Tight-Binding McMillan Dynamics Simulate Impurities in Ultrananocrystalline, Diamond Grain Boundaries", Physical Review B., 65, 054543, (2002); 5. Y. M. Lin and M. S. Dresselhaus "Thermoelectric Properties of Superlattice Nanowires" Phys. Rev. B, 68, 075304 (2003). 6. T. E. Hwang and H. Linke, "Electric Potential in Scattering band Structures", Phys. Rev. Lett., 89, 096601 (2007); 7. D. M. Gruen, and W. J. Elam, "NanoTube-Diamond Composites", MRS Fall Meeting, Paper #Q2.3, (December 1-5, 2003).
Vacuum thermionic energy conversion is a process where electrons from a thermionic emitter traversing a vacuum gap are collected by a counter-electrode and thus directly transform thermal into electrical energy. Diamond and doped diamond films exhibit beneficial emission characteristics compared to conventional metal based thermionic emitters. The negative electron affinity (NEA) of hydrogen terminated diamond surfaces means that the vacuum level is located below the conduction band minimum, resulting in efficient emission of conduction band electrons. We present spectra and current vs. temperature results that establish that electron emission from nitrogen doped diamond films is detectable above ~600°C in a zero-field configuration, i.e. where the extraction fields are negligible. The emission current is strongly dependent on the emitter temperature and fitting the data with the Richardson-Dushman equation indicates a low effective work function of <2eV. The thermionic emission spectrum is consistent with this value and a reduction in the work function is observed with increasing temperature. Using these N-doped diamond films in concert with a cooled collector (HI), we measure a voltage and current indicating energy conversion. This research is supported by the ONR under the TEC-MURI project.

4:45 PM F7.9 Properties of direct bandgap Sn₄Ge₁₋ₓ thin films and Quantum Dots, Jordana Blackberg, L. Douglas Bell and Shoule Nikzad; Caltech Jet Propulsion Laboratory, Pasadena, California. Sn₄Ge₁₋ₓ epiayers and quantum dots (QDs) are of great interest as materials that can provide tunable direct band gaps, with the potential for a fully group IV system. Here we report the growth and property studies of Sn₄Ge₁₋ₓ thin films and Sn QDs in direct conversion applications. These materials could be used in a wide range of applications such as thermophotovoltaics (TPV), emitters, and infrared detectors. For thermophotovoltaic applications, Sn₄Ge₁₋ₓ thin films and Sn QDs in direct conversions offer a potentially high payoff in a new and inexpensive material system. This system would be fully tunable varying source temperatures. For example the bandgap of Sn QDs (theoretically tunable from virtually 0 eV and upwards) could be used up to ~0.6 eV where Ge would start absorbing. While Ge is a direct bandgap semiconductor, an indirect to direct transition has been observed with the addition of ~10% Sn in Ge. Quantum confinement effects have been observed for Sn with dimensions < 30 nm. Because Sn₄Ge₁₋ₓ and Sn QDs are direct bandgap materials unlike both Si and Ge, a high infrared absorption cross section would make monolithic thin film TPV devices possible. While there are limitations to the potential applications of TPV are, due to large lattice mismatch and strong surface segregation substantial challenges remain in growth and processing. We have developed a growth process for strained, defect-free epitaxial Sn₄Ge₁₋ₓ thin films with Sn concentrations up to ~15% on Ge (100) using low temperature (~250 °C) Molecular Beam Epitaxy (MBE) and have demonstrated extended long wavelength absorption beyond the Ge band edge using FTIR and photomodulated reflectance spectroscopy. Sn quantum dots (QDs) are formed in these films by annealing at ~750 °C. In order to successfully integrate Sn₄Ge₁₋ₓ into optoelectronic devices, high QY densities, successful elimination of defects, and control over QD size and uniformity will be required. We will discuss several parameters that have been found to affect these properties, including Sn concentration, layer thickness, annealing temperature, and substrate patterning. We will also discuss compositional analysis of quantum dot structures by energy dispersive x-ray spectroscopy as well as Local Electrode Atom Probe (LEAP) nanoanalysis.

SESSION F8: Poster Session: Calochegonides, Shutterides, and Devices Chairs: Ryoji Funahashi, Raphael Herrmann and Qiang Li Wednesday Evening, November 30, 2005 8:00 PM Exhibition Hall D (Hynes)

F8.1 Optical Properties of Thermoelectric Alkalai Metal Chalcogenide Compounds K₂Bi₃S₅, SB₈Se₁₀, and Eu₆P₂H₃O₆, Theodoras Kyratsis¹,², T. Zorbas¹, Konstantinos M. Paraskevopoulos¹ and Mercouri G. Kanatzidis¹.¹ Physics, Aristotle University of Thessaloniki, Thessaloniki, Greece; ²Chemistry, Michigan State University, East Lansing, Michigan; ³Mechanical & Manufacturing Engineering, University of Cyprus, Nicosia, Cyprus.

Research on complex chalcogenide compounds has shown that alkali bismuth chalcogenides (A/Bi/Q A= alkali metal; Q= S, Se, Te) have many attractive features that make these compounds promising for thermoelectric investigations. Potassium members such as K₂Bi₃S₅ have a low symmetry monoclinic structure. The structure framework consists of two different interconnected types of Bi₃Se₆ building blocks of NaCl(100)- and NaCl(111)-type, which give rise to structural tunnels where K⁺ ions reside. The highly anisotropic structure results in a needle-like morphology along the b-crystallographic axis. Their complex crystal structure leads to a very low thermal conductivity. It is possible that in addition to the large, low symmetry unit cell the weakly bound K⁺ ions play an important role via the phonon glass-electron crystal mechanism. In this work, the infrared reflectivity spectra of several alkali metal chalcogenides are reported for the first time. Optical investigations were conducted on crystalline and palletized samples, treated at different conditions. The results from the analysis of the spectra will be presented and discussed in detail.

F8.2 Thermoelectric Properties of K₂Bi₃Se₁₀, S₂, Solid Solutions, Theodoras Kyratsis¹,², Sangeeta Lal², Tim Hogan³ and Mercouri G. Kanatzidis¹.¹ Chemistry, Michigan State University, East Lansing, Michigan; ³Mechanical & Manufacturing Engineering, University of Cyprus, Nicosia, Cyprus; ²Electrical and Computer Engineering, Michigan State University, East Lansing, Michigan.

The solid solutions of β-K₂Bi₃Se₁₀ exhibit very low thermal conductivity and highly anisotropic electrical properties. They can possess high power factors and thus comprise an interesting series of materials for thermoelectric investigations. Up to now substitutions on both the Bi and alkali metal sites have been studied in order to tune the thermoelectric properties. In this work we present the thermoelectric properties of the sulfur-substituted K₂Bi₃S₁₀₋ₓSₓ members with respect to Seebeck coefficient, the electrical and thermal conductivity as a function of temperature. The Seebeck coefficients showed the n-type character of all members while the electrical conductivity shows higher values compared to the other solid solution series of the same type. Hall effect measurements indicate a high
carrier concentration which is typical in the alkali bismuth chalcogenide group of compounds. The lattice thermal conductivity is strongly size-dependent. The temperature dependence of the figure-of-merit ZT shows that these materials have potential for power generation applications.

**F8.3**

**Thermolectric Properties of Tl2Te-Te pseudobinary System.** Keni Kataoka, Ken Kurosaki, Hiroaki Muta and Shinshu Yanamasa: Division of Sustainable Energy and Environmental Engineering, Osaka University, Suita, Japan.

Polycrystalline sintered samples of tellurium compounds, (Tl2Te)x(1-x)(Sb2Te3) (x = 0, 0.3, 1.0, 3.0), have been prepared by melting Tl2Te and Sb2Te3 ingots followed by annealing in sealed quartz ampoules. The thermolectric properties such as the electrical resistivity, Seebeck coefficient, and thermal conductivity have been measured from room temperature to about 900 K. The electrical resistivity of the samples decreases with temperature. The values of the Seebeck coefficient of all the samples are positive, indicating p-type conduction characteristics. The maximum value of power factor is 2.4x10^-2 Wm^-1K^-2 at 580 K obtained for x = 0.5, (Tl2Te)x(1-x)(Sb2Te3), which is about one order lower than those of state-of-the-art thermolectric materials. All the samples have extremely low thermal conductivities, for example that of Tl2Te is around 0.35 Wm^-1K^-1 in the whole temperature range. Although the electrical performance of the samples are not so good, the ZT values are relatively high due to their extremely low thermal conductivities. The maximum ZT value is 0.27 at 574 K for x = 0.5 sample.

**F8.4**

**High Temperature Thermolectric Properties of LnPdX (Ln = lanthanide; X = Sb, Bi) Ternary Compounds.** Takesyluki Sekino, Ken Kurosaki, Hiroaki Muta and Shinshu Yanamasa: Sustainable Energy and Environmental Engineering, Osaka University, Suita, Japan.

Polycrystalline samples of LnPdX (Ln = lanthanide; X = Sb, Bi) ternary compounds were prepared by arc melting the appropriate amounts of the constituent elements. Relatively high density samples (>98% T. D.) could be obtained. The electrical resistivity and thermolectric power of the samples were measured by a four-probe method under helium atmosphere from room temperature to 1000 K. The temperature dependence of the electrical resistivities of ErsPdSb and ErPdBi shows a semiconducting characteristics. The electrical resistivity and the thermolectric power of ErPdSb were larger than those of ErPdBi. The values of the thermolectric power of ErPdSb and ErPdBi are positive in the whole temperature region. On ErPdSb and ErPdBi, the activation energy estimated from the natural logarithm of the electrical resistivity x the inverse of temperature plot is 0.96 ± 0.02 eV, respectively. The difference of the activation energy leads to the magnitude of the thermolectric power and electrical resistivity. The thermal conductivities of ErPdSb and ErPdBi at around temperature is 4.7Wm^-1K^-1 and 5.0Wm^-1K^-1, respectively. The maximum ZT value is obtained for ErPdSb as 0.11 at 987 K. The LnPdX type compounds have a potential to be a high performance p-type thermolectric material.

**F8.5**

**Thermolectric Properties of AgPb3SbTe5.** Joseph Sootman, 1 Mercuri Kanatzidis,1 Oleg Palchik,2 and Cdirad Uhr2; 1Department of Chemistry, Michigan State University, East Lansing, Michigan; 2Department of Physics, University of Michigan, Ann Arbor, Michigan.

The thermolectric properties of the AgPb3SbTe5 family of compounds with m = 10-18 have shown high figure of merit. These materials possess high power factors and lower than expected thermal conductivity, possibly due to structuring on the nanometer length scale. Nano-structuring has the ability to create interfaces within the material in order to serve as sites for phonon scattering. The compositional fluctuations, if coherent with the matrix, will allow carriers to flow through the lattice unchanged. This decoupling of the thermal and electrical conductivity can yield materials with high power factors and low thermal conductivity. The structure on these length scales has also been shown to have an effect on the band structure of these semiconductors which contributes to the enhanced power factors observed. Nano-structuring of silver antimony telluride within the lead tellurite matrix gives rise to changes in the electronic structure of these materials near the fermi level. The investigation into this family of materials with lower values of m will be discussed. With further incorporation of silver and antimony into the PbTe lattice the transport properties will be measured and analyzed. Thermal conductivity measurements will show if higher concentrations of silver and antimony can further reduce the thermal conductivity of these materials while maintaining the high electrical conductivity and thermopower. High resolution transmission electron microscopy will also be used to determine the changes associated with further addition of silver and antimony and the possible role of nano-structuring in these materials. (Supported by ONR-MURI program)

**F8.6**

**Lead Substitution in the Homolated Family CsPb3Bi5+x Te17-x.** Aurelie Guerguen, Eric Quezada and Mercouri Kanatzidis; Chemistry, Michigan State University, East Lansing, Michigan.

The discovery of new thermolectric materials with superior properties is one of the main challenges in solid state chemistry and physics. One promising candidate for cooling applications is CsBi2Te5. Recently, our effort to produce new materials that resemble to CsBi2Te5 led to the discovery of the homologous series of materials CsPb3Bi5+x Te17-x. The four members of the series (m = 1, 2, 3 and 4) were obtained by introducing various equivalents of PbTe into the layered framework of CsBi2Te5. The CsPb3Bi5+x Te17-x compounds show lower thermal conductivity than that of CsBi2Te5. Preparing analogs of such compounds can be a way to tune the thermolectric performance. We are currently investigating the substitution of lead in CsPb3Bi5+x Te17-x by other elements such as silver, potassium, sodium, barium, strontium and calcium. We will present the new compound Cs3.7K0.7Bi5.7Te9. Single crystal X-Ray diffraction study indicated that this compound is isostructural to CsPb3Bi5Te9 (m = 1) with cell parameters a = 6.3810 (9) Å, b = 28.3263 (41) Å, c = 4.4314 (6) Å in the Cmcn space group. By analogy with CsPb3Bi5Te9, the formula of Cs3.7K0.7Bi5.7Te9 can be rewritten as (Cs9.72K0.28)(K0.7Bi0.5)Bi5Te9. Preliminary electrical conductivity and thermopower measurements indicate n-type behavior. Further experiments on preparing other analogs in the homologous series will be presented.

**F8.7**

**Synthesis, Structures, and Magnetic Properties New Ternary Europium and Ytterbium Pnictogen Chalcogenides.** Geng Bang Jin,1 Shane J. Crerr,2 Arthur Mar2 and Thomas E. Albrecht-Schmitt1; 1Chemistry and Biochemistry, Auburn University, Auburn, Alabama; 2Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada.

In this poster we will present recent results from our group on the preparation, single crystal X-ray diffraction studies, and magnetic property measurements on several new europium and ytterbium pnictogen sulfides and selenides. In the europium/Pn (Pn = Sb, Bi)/S or Se system, we will demonstrate the propensity of these compounds for containing Eu in the divalent state, whereas Yb is trivalent in these compounds. These Eu compounds undergo antiferromagnetic ordering at low temperatures. Our work on the Yb/Sb/Se system at some doubt on a previous formulation of a mixed-valent ytterbium sulfide, which may in fact be trivalent defect system. Some of these compounds are semiconductors and might be useful for thermoelectric applications. Results along these lines will be presented.

**F8.8**

**Electronic Properties of CeO4Sb12.** Donald H. Galvan and Cuauhtemoc Samaniego; Fisico Quimica de Superficies, Centro de Ciencias de la Materia Condensada-UNAM, Ensenada, Mexico.

Electronic structure calculations were performed on CeO4Sb12 filled skutterudite. The energy bands show a semiconductor behavior with a forbidden energy gap of 0.45 eV. Strong hybridization among Ce 4f, with Os d-, p, p with Sb p-orbitals occur. This hybridization, together with the existence of a mini gap are likely responsible for the heavy Fermion behavior, as well as to consider CeO4Sb12 as a candidate for thermoelectric applications.

**F8.9**

**Characterization of Thermolectric Power Generation Modules Made from New Materials.** Farrold L. Short; 1Jonathan D. Beegle,1 Michael A. Pajak, Adam D. Deering, Edward Tinny2; 1Electrical and Computer Engineering Department, Michigan State University, East Lansing, Michigan; 2Chemistry Department, Michigan State University, East Lansing, Michigan.

Lead-Antimony-Silver-Tellurium (L-A-S-T) materials synthesized at Michigan State University show promising thermolectric properties at high temperatures for use in power generation applications. Recent scaled-up quantities of L-A-S-T show a ZT=1.4 at 700 K approaching the figure of merit for samples made in small quantities [1]. These materials are of great interest for applications with a hot side temperature in the range of 600-800 K. Developing these materials into working devices requires minimization of the thermal and electrical parasitic contact resistances, so various fabrication methods
are under investigation to achieve the calculated efficiencies. To examine each method, a new measurement system has been developed to characterize devices under temperature and temperature gradients [2]. An introduction to the system will be presented, as well as results for devices made of the L-A-S-T materials.

F8.10 Investigation of Low Resistance Contacts to Pb-Sb-Ag-Te (LAST) Materials for Module Fabrication.
Jonathan James D’Angelo1, Jarrod Short1, Adam Downey1, Michael Fager2, Edward Timm2, Harald Schock2, Mercouri Kanatzidis4 and Timothy Hogan1; 1Electrical and Computer Engineering, Michigan State University, East Lansing, Michigan; 2Chemistry, Michigan State University, East Lansing, Michigan; 3Mechanical Engineering, Michigan State University, East Lansing, Michigan.

Low electrical contact resistance is essential for the fabrication of high efficiency thermoelectric generators. These contacts must be stable to high temperature thermal cycling. Here we present the fabrication procedure and characterization of several contact materials including tungsten, antimony, tin, nickel, and a bismuth antimony based solder to lead antimony silver tellurium (LAST) quaternary compound. The contacts were typically deposited by an electron beam evaporation method after careful preparation of the sample surface. The resistances were measured by using the transmission line model, and ohmic behavior was verified through current vs. voltage measurements. Contact resistivities of less than 20 μΩcm have been measured for annealed antimony to n-type LAST samples. We present the procedures for fabricating low resistance contacts and the use of these procedures towards the fabrication of high efficiency thermoelectric generator modules.

F8.11 Development of thermoelectric generating modules and systems. Tsunehiro Oka, Kouchi Fujita and Chikco Tokunaga; Ishikawajima-Harima Heavy Industries, Yokohama, Japan.

IHI is investigating application of thermoelectric conversion systems on the usage of residual heat for industrial processes. The thermoelectric module units receive the heat originating from the insulator by means of radiation. In this work, we show the develop a method of receiving heat and materials for receiving radiation. Experimental results are related to the mechanical characteristics, as well as a performance of module based on the heat transmission and thermoelectric conversion characteristic. The results of these experiments will be presented at the conference.

SESSION F9; Half-Heuslers, Thallium Tellurides, and Skutterudites
Chairs: Thierry Cullat and Jeff Sharp
Thursday Morning, December 1, 2005
Room 313 (Hynes)

8:00 AM F9.1
L. Poen1, S. Culp1, N. Soroka2 and Terry M. Britt2; 1Physics, University of Virginia, Charlottesville, Virginia; 2Physics & Astronomy, Clemson University, Clemson, South Carolina.

The TiNiSn related compounds have recently been discovered as potentially efficient materials for power generation applications. Investigations on the ternary intermetallic compounds ABC (A = Ti, Zr, Hf; B = Ni, Cu, Pt; C = Sn, Sb) have been carried out in order to optimize the electronic and thermal properties. Trends in the Seebeck coefficient, resistivity, and thermal conductivity in the temperature range 5 K to 800 K are examined as a function of chemical substitution on the various fcc sub-lattices. Discussions will be based primarily on substitutions on the Ti site with varying Zr and Hf concentrations which aide in controlling the lattice thermal conductivity and small amounts of Sb on the Sn site to control the power factor. Both Hf and Sb concentrations are also found to aid in controlling the high temperature rollover in the thermopower, where minority charge contributions start to become apparent. In addition, small amounts of Pt substitution on the Ni site have been able to yield a lower lattice thermal conductivity in these materials. The half Heusler alloys remain one of the truly promising high temperature thermoelectric materials, due to two key factors: their high power factors which are evident to temperatures in the 400 to 900 °C range and their high chemical stability at temperatures as high as 1000 °C.

8:15 AM F9.2
High-Performance of Half-Heusler MnNiSn (M=Hf,Zr) Single-Phase Thermoelectric Alloys Fabricated using Optical Floating Zone Melting. Yoshihito Kimura1, Tomoya Kuri2, Akihisa Zama2, Yasufumi Shibata3 and Yoshinao Mishima1; 1Materials Science and Engineering, Tokyo Institute of Technology, Yokohama, Japan; 2Graduate School of Science and Engineering, Tokyo Institute of Technology, Yokohama, Japan; 3Higashifujits Technical Center, Toyota Motor Corporation, Susono, Japan.

Thermoelectric materials allow us to directly convert waste heat to clean electric energy without sacrificing the environment. Half-Heusler type intermetallic compound is one of attractive candidate thermoelectric materials that are applicable at high temperatures up to several 1000 K. It is well known that Half-Heusler MnNiSn (M=Hf,Zr,Sn) compounds exhibit n-type semi-conducting behavior excellent thermoelectric properties, especially high Seebeck coefficient and low electrical resistivity. A drawback of relatively high thermal conductivity can be improved for instance by several modification effects through substituting the M site with Hf, Zr and Sn atoms thus forming continuous solid solution. In the present work, we have focused on the fabrication of Half-Heusler MnNiSn (M=Hf,Zr) single-phase alloys, or alloys having almost evaluated thermoelectric properties. We believe that the fabrication of single-phase Half-Heusler alloys using optical floating zone melting (OFZ) is effective to improve thermoelectric properties not only because of single-phase microstructure but also of suppression of solidification defects such as micro cracking induced by the thermal stress. It was successful to grow almost single-phase Half-Heusler (Hf1−x,Zrx)NiSn alloys, where x varies from 0 to 1, using OFZ with the solidification rate of 5 to 10 mm/h under slightly positive pressure of flowing Ar gas. As we have expected, (Hf1−x,Zrx)NiSn alloys grown by OFZ exhibit tremendously excellent power factor of 1.85 electrical figure of merit, ranging around 3.0 to 3.6 mW/K2 m, in a temperature range from 700 to 1000 K. These values are three or four times higher than those of the alloys with same compositions which have been prepared by conventional arc-melting, high-frequency and spark plasma sintering. It is interesting that HfNiSn alloy has quite high thermoelectric power exceeding 400 μV/K and that ZrNiSn alloy shows electrical resistivity lower than 50 μΩm at room temperature. A temperature range from 700 to 1000 K, (Hf1−x,Zrx)NiSn alloys exhibit about 200 μV/K of thermoelectric power and about 50 mW/mK of electrical resistivity regardless of Hf and Zr concentrations ratio. Thermal conductivity of OFZ (Hf1−x,Zrx)NiSn alloys strongly depends on the Hf and Zr concentrations ratio. The solid solution effect on lowering thermal conductivity is maximized at alloy. The thermal conductivity (Hf0.5,Zr0.5)NiSn alloy is effectively lowered around 3 W/mK which is about a half of the values of HfNiSn and ZrNiSn alloys.

Consequently, the dimensionless thermoelectric figure of merit, ZT, of (Hf0.5,Zr0.5)NiSn alloy reaches as high as 0.9. It should be emphasized that further improvement of thermoelectric performance is possible through optimization of carrier concentration by the addition or substitution of elements, since ZT=0.9 has been achieved based on simple HfZr-Ni-Sn quaternary alloy composition.
reduction was achieved by the impurity phonon scattering.

8:45 AM F9.4
Fivos K. Drymiotis, Amy Pope, Nicoleta Soroica and Terry Tritt; Physics and Astronomy, Clemson University, Clemson, South Carolina.

Half-Heusler alloys are excellent candidates for high-temperature thermoelectric. Although several members of these alloys have been investigated extensively, the work done has been mainly on polycrystalline samples. However because of the intricacies of the half-Heusler lattice, mainly the existence of an ordered vacancy, polycrystalline samples might not be the appropriate choice. For the sake of comparison, we have investigated the properties of several single crystalline half-Heusler alloys. In particular we find that single crystalline TiCoSb is metallic whereas polycrystalline TiCoSb exhibits semi-metallic behavior. The Seebeck coefficient (S), electrical resistivity (ρ), and thermal conductivity (κ) were measured from room temperature to around 700 K, and evaluated the thermoelectric figure of merit. A maximum power factor (S^2/ρ) is 3.8×10^-5 W m^-1 K^-2 at 700 K. Although its electrical performance is not very high, Ag_2TiTe_5 exhibits an excellent thermoelectric figure of merit because of its extremely low thermal conductivity (around 0.25 W m^-1 K^-1). Its highest ZT value is 1.23, obtained at 700 K. Ag_2TiTe_5 combines extremely low thermal conductivity and relatively low electrical resistivity, making it a very interesting high-performance thermoelectric material.

10:15 AM *F9.8
Xun Shi, Yan Xu, Wenqing Zhang and Lidong Chen; Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China.

Filling fraction of impurities in the voids of CoSb₃ affects significantly the thermoelectric performance of the filled-skutterudite compounds. Over years, it has been observed that there exists a filling fraction limit (FFL) for each impurity in CoSb₃. However, no physical understanding for the FFL has been obtained to our knowledge. By combining density functional simulations and thermodynamic consideration, we studied the filling fraction limits for various impurities in CoSb₃. The calculated FFLs for the reported filler atoms in CoSb₃ are in reasonable agreement with experimental data. Our model also provides a deep physical understanding for the factors that determine the FFL of an impurity in CoSb₃. These results lead to some simple rules for selecting filler atoms to get new filled-skutterudites with potential better thermoelectric performance.

10:45 AM F9.9
New Skutterudite-based Thermoelectric Materials for Power Generation. 
Tao He; DuPont CR&D, Wilmington, Delaware.

Tao He, Jiazhong Chen, T. Calvarrese, J. J. Krajewski, M. A. Subramanian DuPont CR&D, Experimental Station, P.O. Box 80328, Wilmington, DE 19880 USA Recent advances in synthesis, theory and understanding of structure/property relationships of materials have increased the possibility of finding higher efficiency thermoelectrics. Here we will show our efforts at DuPont in designing and developing new skutterudite-based TE materials with enhanced ZT. They have high Seebeck coefficients and low thermal conductivities, with optimal operating temperature in the range of 600-800 K. These materials are promising for applications in power generation.

11:00 AM F9.10
Synthesis and Thermoelectric Properties of Ce₀.₅Ru₁₋₀.₅Ir₀.₀Sb₂ Filled Skutterudite Compounds. 
April D. Jewell and Thierry Caillat; Jet Propulsion Laboratory, Pasadena, California.

Radioisotope Thermoelectric Generators (RTGs) have proved to be reliable, long-lived sources of electrical power that have enabled the conduct of a number of important U.S. missions since 1961. Past RTGs have used two types of thermoelectric materials: PbTe/TaGe and SiGe. In an effort to further improve both the thermoelectric efficiency and specific power of the next generation of RTGs, JPL is investigating a number of potential high temperature thermoelectric materials that could operate at a hot-side temperature of up to 1275K. Among these materials being studied are the refractory Ce₀.₅Ru₁₋₀.₅Ir₀.₀Sb₂ filled skutterudites compounds. We have synthesized polycrystalline samples for ≤ 1.5 by a powder metallurgy technique. Dense samples have been hot-pressed from the pre-reacted powders and characterized by a variety of techniques including electron probe microanalysis, differential scanning calorimetry and thermogravimetric analysis. Seebeck coefficient, electrical resistivity, Hall coefficient, and thermal conductivity measurements have been conducted on the samples from room temperature to 1275K. Results show that the samples are phase stable up to 1275K. The results of the transport property measurements are presented and discussed.

11:15 AM F9.11
Combined experimental and theoretical studies of plasma resonance and the dielectric function of binary skutterudites. 
Oystein Prytz, Ole Martin Lovvik and Johan Tafto; Centre for Materials Science and Nanotechnology, University of Oslo, Oslo, Norway.

We acquire electron energy loss spectra of the binary skutterudites Co₃P, Co₃As, Co₃Sb and Ni₃P, and observe multiple narrow plasmon peaks similar to those previously observed for simple metals and semiconductors. While the metals tend to exhibit plasmon energies
11:30 AM F0.12
The Synthesis and Characterization of CoS1.5Te1.5, CoGe1.5Se1.5, and Partially Filled CoGe1.5Se1.5
Arwyn Smalley 1, 2, Qiyin Lin 3, David C. Johnson 1, Joshua Martin 3 and George S. Nolas 1
1Chemistry, University of Oregon, Eugene, Oregon; 2Chemistry, Norwich University, Northfield, Vermont; 3Physics, University of South Florida, Tampa, Florida.

We have synthesized the skutterudite-like compounds CoGe1.5Se1.5 and CoS1.5Te1.5 using ultra-thin film elemental deposition techniques. We have also used both the elemental deposition technique and a traditional, high-temperature technique for synthesizing CoGe1.5Se1.5 compounds that are partially filled with various lanthanide elements. This is the first report of filling the CoGe1.5Se1.5 compound. We used X-ray diffraction and Rietveld refinement to verify that the samples were partially filled with the lanthanides. Regardless of the amount of lanthanide present during synthesis, we found that the maximum that could be incorporated into the lattice was ~15% using high-temperature methods, and ~20% using the elemental deposition method. We also used Rietveld refinement to study the amount of crystalline material present in the samples, and determined that both methods produced samples that were not completely crystalline.

11:45 AM F0.13
Abstract Withdrawn

SESSION F10: Cathode and New Measurement Techniques
Chairs: Tim Hogan and David Johnson
Thursday, December 1, 2005
Room 913 (Hynes)

1:30 PM F10.1
The Dynamics of the Caged Guests in Filled Germanium Clathrates. 1
Hermann 2, 3, 4, Perrine Granjaune 1, Veerle Keppens 5, Werner Schweika 3, George S. Nolas 1, David G. Mandrus 1, Brian C. Sales 5, Hans M. Christen 5, Pierre Bonville 6 and Gary J. Long 1
1Department of Physics, University of Georgia, Athens, Georgia; 2Div Condensed Matter, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 3Service de Physique de l'Espace Condense, Centre d'Etudes de Saclay, Gif-sur-Yvette, France; 4Department of Chemistry, University of Missouri-Rolla, Rolla, Missouri.

Atomic motion in solids typically takes place with frequencies in the terahertz range that is usual for phonons. However, when the atoms are weakly bound in atomic cages, multiple minima in the potential energy can appear, causing the guests of the cages to move off-center. As a consequence of such a multiple well potential a tunneling splitting of the energy levels takes place. The dynamics of the caged guests then exhibits similarity with the atomic dynamics in molecules that present tunneling behavior such as NaN3. In the filled gallium-germanium clathrates R3Ga16Ge30, where R is Ba, Sr, or Eu, the guest atoms are located in two large cages and are weakly bound to the crystalline framework. The prominent feature of the dynamics of the caged guest is that they exhibit a localized vibrational mode, i.e., they behave as localised Einstein oscillators. Such a “tunneling” behavior provides an efficient mechanism in reducing the thermal conductivity. Such materials are promising candidates for thermoelectric applications, because they behave as an electron-crystal and a phonon-glass. Inelastic neutron scattering and nuclear elastic scattering measurements have yielded the phonon density of states in R3Ga16Ge30. The obtained Einstein oscillator energies are in good agreement with those obtained by other techniques such as atomic displacement parameters, heat capacity, Raman scattering, and resonant ultrasound spectroscopy measurements. Neutron diffraction studies show that the guests in the larger cage are located off-center, and it was proposed that their jumping about the four off-center locations is responsible for the observed glasslike thermal conductivity at temperatures below 10 K. Ultrasonic attenuation in Sr3Ga16Ge30 indicates a high density of tunneling states below ~1 K. Because the off-centering of the Eu guests is larger than for the Sr guests, the Eu dynamics is likely to be governed by tunneling instead of thermally activated hopping, even at higher temperatures. The jump of such slow guest motion is challenging because the typical time and energy scales involved are ca. 4 ns and 1 μeV, respectively. We have studied the europium dynamics by europium-151 Mössbauer spectroscopy—a technique that presents the advantage of specifically detecting the behavior of Eu guests and we have measured the radio-frequency absorption in Eu3Ga16Ge30. Both results indicate that the europium atoms are tunneling with a frequency of ~500 MHz. I. Sales B.C., Nolas B.C., Mandrus B.C., Jir. J., Thompson J.R., Mandrus D., Phys. Rev. B 63, 245113 (2001); 2. Nolas G. S., Kendziora C. A., Phys. Rev. B 62, 7157 (2000); 3. Zerer I., Keppens V., McGuire M. A., Mandrus D., Sales B. C., and Thalmeier P., Phys. Rev. Lett. 89, 185502 (2002); 4. Keppens V., Sales B.C., Mandrus D., Chakoumakos B.C., Laermans C., Phil. Mag. Lett. 80, 907 (2002).

1:45 PM F10.2
Transport Properties of Type II Sodium-Silicon Clathrates. 1
Matt Beekman 2, Jan Gryko 3 and George S. Nolas 1
1Department of Physics, University of South Florida, Tampa, Florida; 2Department of Physical and Earth Sciences, Jacksonville State University, Jacksonville, Alabama.

Inorganic clathrate materials are comprised of covalently bonded frameworks, in which framework polyhedra enclose various atomic guest species. Some type I clathrates have been shown to possess very low thermal conductivities, in addition to favorable electrical properties, resulting in the current investigation of these materials for thermoelectric applications by several groups. A promising aspect of type II clathrates is the ability to form non-stoichiometric compounds in which the framework polyhedra are partially occupied, offering an avenue for tuning the transport properties in these materials. We have synthesized and characterized a series of Na3S13x clathrates, where x has been varied between the minimum value of 0 and maximum value of 24. Transport measurements are presented, and the prospects of these materials for thermoelectric applications will be discussed.

2:00 PM F10.3
Dual-laser Deposition of Type I Clathrate Films. 1
Sarah Witanachchi, P. Mukherjee, H. S. Nagaraja, R. Hyde, M. Beekman, H. F. Rubin and G. S. Nolas
Physics, University of South Florida, Tampa, Florida.

The clathrates Sr8Ga16Ge30 and Ba8Ga16Ge30 are promising materials for thermoelectric applications due to their low thermal conductivity, high electrical conductivity and relatively high thermopower. Formation of stoichiometric films of these complex materials has been challenging. Laser ablation of the composite targets of these materials produced films with stoichiometries closer to the starting material. However, very low ablation thresholds (<1 J/cm2) for these materials require the ablation to be carried out at low uv laser fluences to avoid molten particulate ejection. Low laser fluence leads to low plasma temperatures and variations in stoichiometry that adversely affect the quality of the film. We have used a dual-laser ablation process to deposit films of these compounds from stoichiometric hot-pressed targets. A pulsed CO2 laser that is synchronized with the pulse laser ablation has its intensity tuned to energize the plasma. Under optimum conditions high plasma temperatures and broader expansion profiles have been observed. The results of a systematic study to investigate the effect of the second laser on the quality of the deposited clathrate films will be discussed.

2:15 PM F10.4
Splitting of Guest Atom Sites and Lattice Thermal Conductivity in Ba-Ga-Ge Clathrate Compounds. 1
Norihiko O. Okamoto, Katsushika Tanaka and Haruyuki Imai
Department of Materials Science and Engineering, Kyoto University, Kyoto, Kyoto, Japan.

The very low thermal conductivity is one of characteristics of clathrate compounds, which is believed to result from rattling motion of guest atoms in the large polyhedral cages. The rattling motion is monitored as anomalously large atomic displacement parameters (ADPs) at guest atom sites in X-ray and/or neutron diffraction.
measurements. When values of ADPs are considerably large, the split-site model is sometimes employed for structure analyses. Then, the analogous values of ADPs based on the single-site model can be interpreted as a sum of two kinds of thermal motion; one is thermal vibration around split sites (ADP$_{split}$) and the other is thermal jump among the split sites. Upon allowing for Ga, values of lattice thermal conductivity $\kappa$ of type-I and -II compounds increase with increasing Ga content. However, values of ADPs based on the single-site model for type-I compounds decrease with increasing Ga content while those for type-III compounds increase. This indicates that the value of ADP$_{split}$ on the single-site model does not predict how lattice thermal conductivity is reduced. Values of ADPs based on the split-site model (ADP$_{split}$) for both type-I and -III compounds decrease with the increase in the Ga content, indicating that the value of ADP$_{split}$, obtained on the single-site model does not predict the tendency for reduction of lattice thermal conductivity. On the other hand, the distance between split sites for both type-I and -III compounds increases with the increase in the Ga content. The fact the split distance inversely correlates with the value of lattice thermal conductivity indicates that thermal jump among the split sites is a key factor for reducing lattice thermal conductivity in clathrate compounds.

2:30 PM F10.5
Thermoelectric Properties of Two-phase Mixtures of Type-I and -III Ba-Ga-Ge Clathrate Compounds. Jung-Hwan Kim, Norihiko I., Okamoto, Ryosuke Takara, Katsuki Tanaka and Haruyuki Imai; Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan.

Intermetallic clathrate compounds, in particular type-I and -III clathrates, have been considered as potential thermoelectric materials because of their low thermal conductivity and high electric conductivity. Type-I clathrate compounds, $M_{x}Ca_{2}Si_{12}$ (M=alkali or alkaline earth metals, $X=Si$, Ge), are composed of two kinds of cages designated as $M_{4}$(1200) tetrahedron and $X_{20}$-dodecahedron whereas type-III clathrate compounds, $M_{2}Ca_{10}X_{2}$, are composed of three kinds of cage structures designated $X_{20}$-pentagonal dodecahedron, $X_{20}$-open cage and distorted cube. Although, extensive rattling of the guest atoms is expected also to occur in type-III clathrate lowering the thermal conductivity, the thermoelectric properties, especially at high temperatures, have not been studied yet. In this research, we have investigated the thermoelectric properties of ternary type-II clathrate compounds in the Ba-Ga-Ge system. Upon substituting Ge atom with Ga atom, the thermoelectric power factor increases while the thermal conductivity decreases, which enhances the thermoelectric figure of merit significantly. For further increasing the thermoelectric figure of merit, we have also investigated the thermoelectric properties of two-phase mixtures of type-I and -III Ba-Ga-Ge clathrate compounds. Two-phase mixtures exhibit much lower thermal conductivity than single phase compounds of type-I or -III, while their electrical resistivity is not much different from that of single phase compounds. Such low thermal conductivity in two-phase mixtures is discussed in terms of mismatch in rattling phonon modes between type-I and -III clathrate compounds. One of the two-phase mixtures of type-I and -III exhibits a thermoelectric figure of merit as high as unity.

3:15 PM F10.6
Cross-plane Thermoreflectance Imaging of Thermoelectric Elements. Peter Mayer and Rajeev Ram; Research Lab of Electronics, MIT, Cambridge, Massachusetts.

This paper presents the first cross-plane thermoreflectance image of the temperature distribution in a thermoelectric element under bias. Using the technique of lock-in CCD thermoreflectance imaging [1], we can map the temperature distribution of an operational device with submicron spatial resolution and a temperature resolution of 10 mK. The spatial resolution is demonstrated to be approximately equal to the electron energy relaxation length within the thermoelectric. As such it provides a direct picture of the equilibrium transport within the device. The submicron resolution of the thermoreflectance image enables clear determination of localized heating due to interfaces - for example due to contact resistance - and thermal impedance mismatch within samples. The high spatial resolution is ideal for the characterization of thin-film thermoelectric materials where data from conventional techniques (such as the transient Harman method) are difficult to interpret. This paper also presents the first thermoreflectance image of a BiTe-based material system. Identification and separation of the Pelcier and Joule components of the heating are possible, and finite difference simulations of the devices are presented for comparison with experiment. In addition, it is possible to acquire information about the Seebeck coefficient, electrical conductivity, and thermal conductivity of the thermoelectric material. The measurements demonstrate the feasibility of non-contact thermal measurements at the sub-micron scale [1].

3:30 PM F10.7
Application of transmission line theory for modeling of a thermoelectric module in multiple configurations for AC electric current measurements. Darrell Dow, 1, Ken T. Hogan1, Edward Timm2, John Androulakis2, Eric Queroz2, Ferdinand Poudevo2, Mercouri G. Kanatzidis2 and Harold Schock3; 1Electrical and Computer Engineering, Michigan State University, East Lansing, Michigan; 2Chemistry Department, Michigan State University, East Lansing, Michigan; 3Department of Mechanical Engineering, Michigan State University, East Lansing, Michigan.

Measurements of assembled thermoelectric modules commonly include investigations of the module output power versus load resistances. Such measurements include non-ideal effects such as electrical and thermal contact resistances. Using an AC electrical measurement, two models for a thermoelectric module have been developed utilizing electrical circuits for both the thermoelectric and electrical modules. Measurements were taken over the frequency range of 1mHz to 500Hz using lock-in amplifiers. We present data showing the extraction of ZT from such measurements on commercially available modules. By knowing either the heat capacity of the module or the average module Seebeck coefficient, determination of the thermal conductance can also be achieved. This first model proposed here provides a simple equivalent circuit which can be analyzed using an electrical simulator such as SPICE. This model makes use of the magnitude and phase of the electrical impedance measured by the lock-in amplifiers at the input terminals of the module and includes finite electrical elements of the Seebeck, electrical resistance, thermal resistance, contact conductance, heat capacitance, and module Seebeck coefficient. Here we extend upon a simple RC model by utilizing transmission line theory in electrical circuits to explain the thermal activity in a thermoelectric module. This model includes the clathrate module such as nickel traces and ceramic end caps, and makes use of their corresponding thermal conductivities, thermal capacitance, and density. This model can then be applied to unipolar sources and to individual p or n legs of the module. Data is presented showing the advantages of both models. Measurements on new thermoelectric materials and modules will be presented.

3:45 PM F10.8
Nano-instrumentation for Structure and Property Characterizations of Individual Nanowire Thermoelectric Materials. Anastassia Mavroidelis1, Jinshua Zhou1, JaeHun Seol2, Feng Zhou3, Michael Thompson Pettes4, Li Shi5, Chuangli Jin2 and Xiaoguang Li6, 1Mechanical Engineering & Center for Nano and Molecular Science and Technology, University of Texas at Austin, Texas, 2Department of Materials Science and Engineering, Hefei National laboratory for Physical Science at Microscale, Hefei, China.

Several theoretical studies [1,2] and our previous measurements [3] have suggested that nanowire materials may have large thermoelectric figure of merit $ZT$=S$^2$κ/T=$\kappa$,$\sigma$S, where S is the Seebeck coefficient, $\kappa$ is the electrical conductivity, $\sigma$ is the thermal conductivity, and T is the temperature. It was found in our measurements that the thermoelectric properties of individual electro-deposited bismuth telluride nanowires are largely influenced by the crystal structure including crystalline quality, chemical composition and surface roughness of the nanowires. The thermoelectric properties and crystal structure were characterized on different nanowires so that the correlation between the crystal structure and thermoelectric properties could not be established. In this paper, we report the development of a nano-instrument that allows us to characterize and correlate the structure and properties of the same individual nanowires. The nano-instrument is based on an improved design of our microfabricated suspended device which were reported earlier [4]. The current design of the device includes two suspensions with each suspended by six 400-800 $\mu$m long SiN beams. A platinum serpentine line is patterned on each membrane and used as an electrical heater and/or resistance thermometer. Two additional Pt electrodes are patterned on each membrane to allow for four-probe electrical measurement of a nanowire trapped between the two membranes. The temperature on each membrane can be measured during the four-probe resistance measurement so that the Seebeck voltage can be subtracted from the measured voltage difference between the two middle voltage probes in order to obtain the accurate four-probe resistance. The ZT can be calculated from the electrical conductivity obtained from the measured four-probe resistance as well as the Seebeck coefficient and thermal conductivity obtained from the suspended device [4]. A通过hole is etched in the substrate of the suspended device to allow for transmission electron microscopy (TEM) and energy dispersion spectroscopy (EDS) measurements of the nanowire. The obtained crystalline quality, surface roughness, and

4:00 PM F10.0
Thermoelectric Transport Measurements of Bi2Te3 Nanostructured Films using a Scanning Hot Probe Technique. Claudia Lopez, Shunsuke Araki, Yukako Nakayama1,2, Ganapathiraman Ramathan3 and Tohderian Borca-Tasciuc1,2,1Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York; 2Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

A scanning hot probe technique was developed for thermoelectric transport measurements of films. In this method a resistively heated Wollaston wire thermoprobe mounted on an Atomic Force Microscope (AFM) is brought in contact with the sample surface giving rise to a temperature gradient and a Seebeck voltage in the specimen. The average temperature rise of the probe is determined from the change in its electrical resistance. The heat transfer rate between the probe and the sample is estimated using a heat transfer model that takes into account the major heat transfer mechanisms in the system. The thermal conductivity is determined from the measured thermal resistance of the film and the Seebeck voltage determined using the measured temperature drop and the Seebeck voltage developed in the plane of the sample. Experimental results are presented for Bi2Te3 nanostructured films. Nanoparticles of 1-5 nm diameter and rod-shaped rhombohedral nanocrystals of 20-85 nm diameter are grown using wet chemistry methods. The Bi2Te3 nanostructures are functionalized with desired termini for re-dispersion and controlled assembly. Films are obtained by spin-coating or drop-casting and drying the dispersed and functionalized structures on glass substrates. The work will present the effect of growth and annealing conditions on the thermoelectric properties of the films measured at room temperature.

4:15 PM F10.10
Probing the Local Thermopower Using a Scanning Tunneling Microscope Tip in the Tunneling and Contact Regimes. Carolina Eshra, Li Shi, Sarah Ruch and Feng Zhou; Mechanical Engineering, University of Texas, Austin, Texas.

In 1990, Williams and Wickramasinghe reported a Scanning Chemical Potential Microscopy (SCPM) method for the mapping of the thermovoltage formed at the tip-sample gap of a scanning tunneling microscope (STM) [1]. To explain their results, Stovneng and Lipavsky [2] proposed a model based on Bardeen’s formula for tunneling current and Tersoff and Hamann’s approximations to predict the tunneling thermovoltage as $V = \frac{2kT}{e(\Phi)} \left[ \frac{d}{dx} \ln(\Phi(x, y)) + \frac{d}{dx} \ln(\Phi(x, y)) \right] + \frac{e}{4\pi \hbar} \ln \left( \frac{\Phi(x, y)}{\Phi(x, y)} \right)$ (1) where subscripts t and s denote the tip and sample, respectively, $e$ is the electron charge, $\Phi$ is the local electronic density of states, $\Phi(x, y)$ is the electron energy, $x$ is the tip-sample separation, $m$ is electron mass, $h$ is Planck’s constant, and $\Phi$ is the work function for vacuum tunneling barrier height. The logarithmic derivative of the density of states depends on the lateral x and y position and is evaluated at the Fermi level. This formula shows the dependence of the tunneling thermovoltage on tip-sample separation, which has not yet been experimentally verified. Lyco et al. [3] have recently developed a Scanning Thermoelectric Microscopy (SThEM) method to probe the local thermopower of nanostructured materials. A key difference between the SThEM and SCPM is that the tip makes a nano-contact with the sample surface. While the tip and the sample were kept at two different temperatures in the SCPM because of a large tip-sample thermal resistance due to the tunneling gap, the contact of a room-temperature tip and a warm sample created a localized temperature difference on the sample surface. The temperature gradient in the sample leads to a thermovoltage proportional to the spatial average of the local thermopower (or Seebeck coefficient, S(x, y) inside the non-uniform temperature zone of the sample, i.e., $V = S(x, y)(T_c - T_s)$ (2) where $T_c$ is the temperature at the contact point, $T_s$ is the temperature at the backside of the sample. The thermovoltage formed in the STM tip made of tungsten has been ignored because the Seebeck coefficient of tungsten is close to zero. In this paper, we report a detailed investigation of the sample thermovoltages as a function of the tip height in both the tunneling and contact regimes. The measurement results are compared with the calculation results from Eqs. 1 and 2 to better understand the different physics involved in the SThEM and SCPM. Additionally, we report the use of the SThEM method to probe the local thermopower of nanostructured materials including nanowires and thin film superlattices. REFERENCES [1] Williams, C. C. and Wickramasinghe, H. K. Nature 344, 317 (1990). [2] Stovneng, J. A. and Lipavsky, P. Phys. Rev. B 42, 9214 (1990). [3] Lyco, H. K. et al. Science 303, 816 (2004).

4:30 PM F10.11

Measurements of thermoelectric power have been reported on many inorganic materials. In oxides, composition changes occur during measurement when subjected to variations in temperature and/or oxygen partial pressure. If a composition gradient exists across sample, due to imposed temperature gradient, an electromotive force (EMF) arises, known as Soret effect. In recent years to minimize effects of composition gradients, a modified technique has been used in which the average temperature is maintained constant. The composition changes that occur when subjected to various temperatures and atmospheres require chemical diffusion of oxygen in or out of the sample. Over the typical temperature range, diffusion kinetics is usually very sluggish. Thus, equilibration of sample composition under imposed conditions rarely occurs during the course of a typical experiment. Thus, measurements made on dense oxide samples often do not correspond to equilibrium conditions, and thus are not representative of the true thermoelectric power. To obtain accurate values of thermoelectric power of oxides corresponding to imposed conditions, measurements in this work were performed on porous samples instead of dense samples. Time required for compositional equilibration under diffusion, is proportional to the square of diffusion distance, and inversely proportional to the chemical diffusion coefficient of diffusing species. In dense samples, diffusion distance is half the thickness of the sample, typically 1 mm or less. By contrast, in porous bodies, diffusion distance is typically the diameter of individual particles, typically a micron. Thus, time required for equilibration is about six orders of magnitude smaller in porous samples than in dense bodies. To test the hypothesis, thermoelectric power measurements were made on dense and porous samples. Two materials were selected: Silver and Gd0.1Ce0.9O2-δ (GDC10). Silver does not change composition when heated in air, since it does not oxidize and does not exhibit compositional changes. It was observed that both dense and porous samples equilibrated in about same time, and measured thermoelectric power was also about the same. It was also observed that over the temperature range, time required for equilibration in porous GDC10 was several minutes. By contrast, time required for equilibration in dense GDC10 was several hours. The thermoelectric power on dense GDC 10 did not agree well with those on porous GDC 10 below ~600°C. Also, at low temperatures, EMF in dense samples did not equilibrate. Based on this work, it is concluded that thermoelectric power measured on dense samples is unreliable, especially at low temperatures. It is proposed that thermoelectric power measurements on oxides should be done on porous samples and not on dense.

4:45 PM ORGANIZER COMMENTS

SESSION F11: Poster Session: Oxides and Other High Temperature Materials
Chairs: Tim Hogan, Hsin Wang and Wenqing Zhang
Thursday Evening, December 1, 2005
8:00 PM
Exhibition Hall D (Hynes)

F11.1
Pulsed Laser Deposition of Thermoelectric Cobaltate Thin Films. Weidong Si1, Sang-moon Park2, Yufeng Hu2, Qiang Li2 and Eli Sutter1; 1Physics, Brookhaven National Laboratory, Upton, New York; 2Materials Science, Brookhaven National Laboratory, Upton, New York; 3Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York.

Recently cobaltates have been discovered to have very large thermoelectric power, which shows that it may be used in potential integrated heating spread cooling solution. Sodium cobaltate was also found to be superconducting at certain sodium concentration after intercalated with water. We have successfully grown c-axis oriented thin film cobaltates on various substrates, including polycrystalline and (0001) sapphire, (100) and (111) Silicon wafer, even glass, by pulsed laser deposition. We found they have very good thermoelectric properties from the transport and magnetic measurements. We also found c-axis aligned crystal structure even on glass by cross-section transmission electron microscopy. A self-assembly mechanism may interpret the result.
F11.2 Thermoelectric properties of cubic perovskite-type manganite oxides: Yasushi Inamura, Hiroaki Muta, Ken Kurosaki and Shinzuke Yamanaka; Division of Sustainable Energy and Environmental Engineering, Osaka University, Suita, Osaka, Japan.

Several perovskite-type oxides have been studied for high temperature thermoelectric material. In this study, thermoelectric properties of cubic perovskite-type SrMnO\textsubscript{3} were investigated. This compound takes on a hexagonal structure by the ordinal synthesis method in air. By sintering in a reducing atmosphere, we obtained a cubic structure because of the oxygen deficient. Polycrystalline Sr\textsubscript{1-x}La\textsubscript{x}MnO\textsubscript{3-δ} and SrMn\textsubscript{1-x}Nb\textsubscript{x}O\textsubscript{3-δ} (x = 0, 0.05, 0.1) were synthesized by solid state reaction of two-step method. In first step, oxygen deficient perovskites were obtained by heating in a reducing atmosphere at about 1723 K. Then it was ball milled and pressed into a pellet, and sintered at same condition. In the second step, oxygen-deficient samples were annealed in air at 773 K. The thermoelectric properties of non-annealed samples were compared with each other. The crystal structure and lattice parameter were evaluated by XRD analysis. The electrical conductivity and Seebeck coefficient were measured under He atmosphere. The thermal conductivity was evaluated as the product of the thermal diffusivity, the heat capacity, and the experimental density at room temperature. The figure of merit was calculated from the above.

F11.3 Fabrication of Grain-Aligned Bulks and Thick Films of Misfit Layered Cobalt Oxides by a Magneto-Scientific Process: Shigeru Hori1, Tatsi Okamoto2, Toshiaki Kumagai2, Tetsuo Uchihashi1, Toshiro Suzuki1, Yoshio Saka1, Jun-ichi Shinoya1 and Kohji Kaku1; 1Department of Chemistry, University of Tokyo, Tokyo, Japan; 2NIMS, Tsukuba, Japan.

Misfit layered cobalt oxides, Ca3Co4O7 (Ca349) and Bi2Sr2CoO\textsubscript{4+\delta} (BiSr222), are promising candidates as practical materials for thermoelectric power generation at high temperatures in air because these dimensionless Figures of Merit show over 1 in single crystals. However, improvement of thermoelectric properties is required in polycrystalline form. We report the fabrication of 100% polycrystalline films at 773 K. In order to improve the functionality, one can recognize that useful processes are grainorientation and densification. Furthermore, taking generation of voltage with an order of volt into account, integration of thermoelectric modules is also required. In this study, for the Ca349 phase possessing an easy axis for magnetization along the c-axis, we tried to prepare thick films with the size of sub millimeter in thickness using an electrophoretic deposition (EPD) method under high magnetic fields. Grain-oriented thick films have been successfully fabricated, and the c-axis directions of aligned Ca349 grains were able to be controlled independently of the surface of a substrate by control of angle of an electric field and an applied magnetic field. Additionally, we report the development of generation of magnetic moment of a-axis by a-axis to c-axis by a crystallographic process in BiSr222 with the easy axis along the a-axis for magnetic c-axis grain-alignment.

F11.4 Power Factor of Sr Doped LaCoO\textsubscript{3}: Kouta Iwasaki1, Tsuyoshi Itoh1, Masahito Yoshino1, Tsuneo Matsui1,2, Takakori Nagasaki1 and Yuji Arita3; 1Department of Materials, Physics and Energy Engineering, In Air atmosphere, Nagoya University, Nagoya, Japan; 2Department of Material Science Institute, Nagoya University, Nagoya, Aichi, Japan.

LaCoO\textsubscript{3} has perovskite structure consisting of corner-sharing CoO\textsubscript{6} octahedra. Sr-doped La-CoO\textsubscript{3} (La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3}) has been reported to exhibit high power factor more than 1×10\textsuperscript{-3} Wm\textsuperscript{-1}K\textsuperscript{-2}[1, 2]. The thermoelectric properties of (La\textsubscript{1-x}Sr\textsubscript{x})CoO\textsubscript{3} are of interest, however, the relation between the power factor and carrier density has not been investigated. In this study, polycrystalline (La\textsubscript{1-x}Sr\textsubscript{x})CoO\textsubscript{3} [0\textless x \textless 0.09] were prepared by a solid state reaction in air, and the electrical conductivity, Seebeck coefficient and the power factor were investigated. La\textsubscript{0.5}Sr\textsubscript{0.5}O\textsubscript{3} (4N) and Co\textsubscript{0}O\textsubscript{3} (4N) were used as starting materials. These powders were weighed with the appropriate amounts (the metal ratio was La Sr-Co=1:2:1). The powders were mixed and pressed into a pellet form. The pellet was heated at 1273 K for 20 h in a nitrogen atmosphere. The samples were ground and re-heated at 1673 K for 20 h under the same conditions. Electrical conductivity was measured by the direct-current four-probe method in the temperature range of 300 to 1100 K in air, Seebeck coefficient was measured by the method of the least square fitting, and the power factor was calculated from the difference of temperature (∆T) (thermal electromagnetic force), and the contribution of lead wires (∆P) was subtracted. The electrical conductivity (σ) of (La\textsubscript{1-x}Sr\textsubscript{x})CoO\textsubscript{3} [0\textless x \textless 0.09] increased with increasing Sr content, and showed semiconducting behavior below 700 K. Seebeck coefficient of (S) of (La\textsubscript{1-x}Sr\textsubscript{x})CoO\textsubscript{3} was positive at 0.01 ≤ x, and decreased with increasing Sr content. On the other hand, Seebeck coefficient of LaCoO\textsubscript{3} was negative below 350 K. The power factor (σS) of (La\textsubscript{1-x}Sr\textsubscript{x})CoO\textsubscript{3} showed temperature dependence. The power factor tended to decrease with increasing temperature above 650 K. The highest value of the power factor was 3.1×10\textsuperscript{-4} Wm\textsuperscript{-1}K\textsuperscript{-2} for x=0.08 at 300 K. [1] T. Ohtani et al., J. Appl. Phys., 94 (2003) 05759. [2] J. Androulakis et al., Appl. Phys. Lett., 84 (2004) 1069.

F11.5 Synthesis and Thermoelectric Power Factor of LSCO Perovskites: Julio E. Rodriguez, Department of Physics, Universidad Nacional de Colombia, Bogota, Colombia.

Measurements of Seebeck coefficient, S(T) and electrical resistivity, ρ(T) on polycrystalline La\textsubscript{2-x}Sr\textsubscript{x}CuO\textsubscript{4+x} (LSCO) (0≤x<0.2) samples are reported. The Seebeck coefficient is positive in whole the measured temperature range (between 77K and 300K) and decreases with Sr content. At room temperature S(T) changes from 300 to 500 µV/K for the samples with the highest levels of Sr. The behavior of S(T) fit to the Heikes model which describes the behavior of Seebeck coefficient in systems where the correlated hopping is present. The electrical resistivity shows a linear behavior with the temperature and it took values from 10\textsuperscript{-2} to 10\textsuperscript{-3} Ωm. From the S(T) and ρ(T) measurements the thermoelectric power factor, PF was obtained. The maximum values for PF were about 25 µW/K\textsuperscript{2}cm in the samples where x=0.05, which are comparable to the typical values of conventional thermoelectric semiconductors. The structural and morphological properties of the samples were studied by x-ray diffraction analysis and Scanning Electron Microscopy, and Transmission Electron Microscopy, respectively. The behavior of transport properties opens up the possibility of including factors of perovskite as thermoelectric material that work below room temperature.

F11.6 Fabrication and Properties of Thermoelectric Generator with Half-Heusler Compounds: Shinya Sakurada1, Naoki Shuto1, Shinzuke Hirono1 and Masami Okumura2; 1Corporate R&D Center, Toshiba Corporation, Kawasaki, Japan; 2Development Dept., Toshiba Materials Co., Ltd., Yokohama, Japan.

Half-Heusler compounds with the cubic MgAs-type structure have become of great interest due to their application as thermal power generation. Previously, we have investigated the effect of Ti substitution on the thermoelectric properties of (Zr, Hf)Ni(Sn, Sb) and revealed that substitution of Ti for (Zr, Hf) sites significantly reduced the thermal conductivity κ and increased the Seebeck coefficient a. Moreover, it was also found that Sn doping at Sn sites reduced the electrical resistivity r and enhanced the power factor correspondingly. The combination of the low k and the high power factor resulted in a high ZT value. A maximum ZT value of 1.5 was achieved at 700 K for (Zr, Ti, Hf)(Sn, Nb)Sb\textsubscript{2} compounds. These compounds showed n-type behavior in the temperature range of 300 K to 773 K. In thermoelectric applications, p-type compounds with high ZT values are required for constructing high performance thermoelectric modules. In this study, we fabricated half-Heusler compounds, Xia et al. have investigated ZrCoSb-based compounds and obtained an α of +0.13 mV/K, a r of 1 to 2 m cm, and a k of about 3 W/mK at 300 K for Zr(Co, Pt)(Sn, Sb) compounds. In this study, we investigated the thermoelectric properties of (Ti, Zr, Hf)CoSb compounds with three kinds of p-type dopants, namely Er, Fe, and Sn at the (Ti, Zr, Hf), Co, and Sb sites, respectively. The thermoelectric measurements were conducted at 300-773 K. Undoped (Ti, Zr, Hf)CoSb shows a ZT value of 0.3 at 300-773 K and r for this compound is about 100 m cm at 700K. In contrast, when the doping concentrations are 5 at. %,(Ti, Zr, Hf)(Co, Sb) exhibits n-type behavior with an α of more than +0.35 mV/K at 700 K for all dopants. Also, as the doping concentration is increased, r decreases. In particular, a marked decrease of r is observed in the case of Sn-doping. For the Sn-doped compound (Ti0.3Zr0.3Hf0.35)(Co0.6Sb0.6Sn0.15), an α of +0.31 mV/K, a r of 2.8 m cm, and a k of 2.7 W/mK, corresponding to
a ZT = 0.9, are obtained at 700 K. On the other hand, the ZT values obtained for Er- and Fe-doped compounds are less than 0.2. Next, we fabricated a thin-film half-Heusler device. This module consists of a large number of bar-shaped p-type and n-type materials connected electrically in series and sandwiched by two plates of thermally conducting but electrically insulating ceramics to form a module. The size of this module is 40 mm x 40 mm x 5 mm. The (Ti,Zr,Hf)Co(Sb,Sn) and (Ti,Zr,Hf)Ni(Sn,Sb) compounds referred to above are respectively used for the p-type and the n-type materials. Heat is supplied to one surface of the module and is emitted at a lower temperature from the opposite surface. The module generates an output power of 20 W under the thermal conditions of Th = 823 K (temperature at the surface where heat is supplied) and Td = 445 K (temperature difference between the two surfaces).

**F11.7 Effects of SPS Condition on Thermoelectric Properties of \( \text{ZrNiSb} \) Based Half-Heusler Compounds, Takeshi Kanemitsu, Mitsuhiro Mutai, Yuko Yosanaka and Shinjiro Yamada**

Recently, extensive studies have been carried out on ZrNiSb based half-Heusler compounds as a thermoelectric material due to its high power factor, high mechanical strength and non-toxicity. The thermoelectric properties are very sensitive to the preparation condition and the stoichiometry in the compounds. In this study, the effects of sintering condition on thermoelectric properties were investigated. The samples of \( \text{Zr}_{0.5} \text{Ti}_{0.5} \text{Sb}_{2} \text{Sn} \) and \( \text{Zr}_{0.5} \text{Ti}_{0.5} \text{Sb}_{3} \) were prepared by spark plasma sintering (SPS) technique, and the temperature in the range of 1273-1473 K after annealing at 1073 K for one week. The thermoelectric properties were measured from room temperature to about 1000 K. In addition, the sound velocity of the samples was measured by the ultrasonic time-of-flight (TOF) method. The electrical lattice thermal conductivity of the samples. We found that the electrical conductivity drastically increased with increasing the sintering temperature. While the Seebeck coefficient was independent of the temperature, thus high power factor was obtained for the sample sintered at high temperature. The value for \( \text{Zr}_{0.5} \text{Ti}_{0.5} \text{Sb}_{3} \) sintered at 1473 K was larger than that of pure ZrNiSb, reached 4 mW/mK above 800 K. There were no impurity peaks in XRD patterns, however, the peaks of half-Heusler were broad for the annealed sample. The peaks for the sample sintered at high temperature were sharper than those of the only-annealed sample. Thus SPS at high temperature appeared to be effective for preparation of thermoelectric samples. The thermal conductivity of substituted samples was lower than that of the pure ZrNiSb. The value for \( \text{Zr}_{0.5} \text{Ti}_{0.5} \text{Sb}_{3} \) prepared by SPS at 1473 K was 5 W/mK, about half of the pure ZrNiSb. The sintering temperature effect was small and unclear for the thermal conductivity. The dimensionless figure of merit increased with increasing the SPS temperature, the value for \( \text{Zr}_{0.5} \text{Ti}_{0.5} \text{Sb}_{3} \) sintered at 1473 K was about 0.48 at 900 K.

**F11.8 Thermoelectric Properties of \( \text{Bi}_2 \text{Sr}_2 \text{Co}_3 \) Tellurium-Doped Single Crystalline Whiskers, X. Tang1, K. Aaron1, T. Merritt, D. Bourne2, J. Barnes3 and J. Payne1**

Tellurium-doped single crystalline whiskers were synthesized using tellurium-doped precursors. The length of these whiskers varies from less than 1 mm to 9 mm. The thermopower and resistivity were found to be 148 µV/K and 5.5±0.4 cm respectively at 325 K. Thermopower was measured using a differential technique, while resistivity was measured by a standard four-probe method.

**F11.9 Thermoelectric and Structural Properties of the \( \text{Ba}_2 \text{ZnCu}_3 \text{O}_7 \) Solid Solution, Winnie Kwai-Wah Wong1,2, Yufeng Hu2, Zhi Yang2, Qing Huang2, Qiang Li2 and Martin Green1**

The search of thermoelectric materials for power generation and for solid-state cooling has led to interest in cobalt-containing oxides because of their thermal stability at high temperature and their desirable thermoelectric properties. The paper examines the effect of substitution of Co in the layered perovskite, \( \text{Ba}_2 \text{ZnCu}_3 \text{O}_7 \). The polycrystalline \( \text{Ba}_2\text{ZnCu}_3\text{O}_7 \) (x = 0.3, 0.4, 0.5, 0.6, 1.0) samples were prepared in air using conventional high temperature solid state techniques. Thermoelectric properties of these \( \text{Ba}_2\text{ZnCu}_3\text{O}_7 \) samples were studied in the temperature range of 10K to 390K. It was found that the resistivity of these samples increases as x increases, and among the \( \text{Ba}_2\text{ZnCu}_3\text{O}_7 \) compositions, the x = 0.4 member gives the highest ZT of 0.017 at 270K. Structural investigations using neutron diffraction showed that Co substitutes for Cu in two different sites in the \( \text{Ba}_2\text{ZnCu}_3\text{O}_7 \) structure on the x value. Results of the structural/property study will be discussed.

**F11.10 Thermoelectric properties of polycrystalline \( \text{Si}_{1-x} \text{Ge}_x \) \( (x=0.4-0.7) \) by die-casting vertical Bridgman growth technique, Takashi Baba, Tetsuomi Iida, Hiashi Hiraizumi and Yoshikuni Takashiri**

Alloys of silicon and germanium \( \text{Si}_{1-x} \text{Ge}_x \) are ecologically friendly semiconductors and important materials not only for microelectronic devices but also for solid-state energy systems such as solar cells and thermoelectric devices. This is mainly due to chemical stability, mechanical strength at elevated temperatures, and a close match of the \( n/p \)-type alloys in terms of their thermal and electrical characteristics enable better device operation with no noticeable variation in efficiency. For thermal-to-electric energy-conversion, \( \text{Si}_{1-x} \text{Ge}_x \) with \( x \approx 0.3 \) to 0.8 can minimize the thermal conductivity due to the random ordering of the constituent atoms in the crystal. However, since the Si-Ge system shows a complete series of solid solutions with a phase relationship, it is not easy to precipitate crystals possessing a certain composition of silicon or germanium selectively by using conventional Bridgman or Czochralski methods. To conduct a bulk crystal growth of \( \text{Si}_{1-x} \text{Ge}_x \), we applied a die-casting growth technique combined with an advanced version of the Bridgman method. The grown samples were coin-shaped \( \text{Si}_{1-x} \text{Ge}_x \) polycrystalline crystals with a diameter of 16 mm and a thickness of 2 mm. Using die-casting combined with Bridgman growth brought about \( \text{Si}_{1-x} \text{Ge}_x \) precipitation in a form completely different from that predicted by the Si-Ge phase diagram. By combining this growth with subsequent heat treatment of the precipitated sample, \( \text{Si}_{1-x} \text{Ge}_x \) with \( x = 0.4 \) to 0.8 were obtained. For the concentration variation in \( \text{Si}_{0.5} \text{Ge}_{0.5} \), the deviation of the obtained germanium content was within ±3%. We describe the preparation of the crystals by the die-casting growth process and effects of post-annealing heat treatment of the grown samples, in terms of changes in the compositional fraction. For the grown samples, thermoelectric properties such as Seebeck coefficient, electrical conductivity, and thermal conductivity were measured over a range of room temperature to 873 K. We present the results of the calculated dimensionless figure of merit, ZT, for the grown \( \text{Si}_{1-x} \text{Ge}_x \) as a function of the composition, x, ranging from 0.4 to 0.7.

**F11.11 Mechanism And Characterization Studies on Boron Carbides Deposited by Chemical Vapor Deposition Technique, Mustafa Karakaya, Hilmi Oruced Engelze, Nam A. Sezgi and Timur Dogu**

Due to its excellent mechanical, thermal, chemical and electrical properties superior to many refractory materials, boron carbide (B4C) finds a vast industrial demand at the present and will find many new uses in the future. The main uses are in the nuclear industry as neutron absorber, in production of armour with its high hardness, and in semiconductors, in metal coatings with its low surface friction properties. It has a potential use in direct thermoelectric energy conversion due to high Seebeck coefficient, low thermal and high electrical conductivity. Recently, boron carbide is gaining importance in semiconductor industry as a p-type semiconductor material in the manufacture of heterojunctions and diodes. The need for high quality boron carbide with high purity makes chemical vapor deposition process an attractive method especially in microelectronic applications. Boron carbide based materials are widely deposited by CVD. Boron carbides are produced from BC3-H4-H2 gas mixture, in an impinging-jet CVD reactor. The impingement on the substrate surface is important in minimizing the effect of mass transport limitations on the reaction rates. The chemical analysis of the reactor outlet stream was done by FTIR and formation of BHC2 and HC1 was verified experimentally from the FTIR spectra. There are two reactions occurring in the reactor: one is the B4C formation reaction and the other one is the BHC2 formation reaction. Effect of substrate temperature and composition of reactor inlet stream on the rates, conversions and selectivities of these two reactions were analyzed and the results showed a complex reaction mechanism. The purpose of this study is to find a reaction mechanism which is in best accord with the experimental results. The parameters of the model rate expressions that are derived from the proposed reaction mechanisms are found statistically using nonlinear regression procedure.

**F11.12 Abstract Withdrawn**
Magnesium silicide (Mg$_2$Si), an ecologically friendly semiconductor, is a promising thermoelectric material at temperatures ranging from 500 to 800 K. One of the most important aspects of this material for thermoelectric generation is its high electrical conductivity, which is 5% of that for Mg$_2$Ge is likely to be slightly lower, but it is still believed to be adequate for realizing thermoelectric power generation. Due to its environmentally friendliness, Mg$_2$Si also provides safe handling and device electrical use. A stoichiometric Mg$_2$Si single crystal grown by the Czochralski method was investigated for the Seebeck coefficient and electrical conductivity. The Seebeck coefficient of Mg$_2$Si is 100 µV/K, and the electrical conductivity is 100 S/cm. This study showed that Mg$_2$Si is a promising thermoelectric material for power generation.
thermoelectric devices and prevent contamination of sublimed materials during operation. Silica gels in JPL were synthesized with a two-step annealing and nitric oxide gas treatment in vacuum. The silica gels were dried in an anodic stainless steel autoclave. Reducing shrinkage is key when considering aerogel as a cast-in-place sublimation suppression coating/thermal insulation. By minimizing shrinkage, intimate contact can be made between the thermoelectric elements and the sublimation suppression coating (aerogel)/thermal insulation, thus providing efficient sublimation suppression and thermal insulation. A new, improved process for integrating aerogel as a sublimation suppression agent and thermal insulation for the thermoelectric technology has been developed. The process involves the fabrication of composite aerogels, which are primarily composed of oxide powders, and the silica aerogel works as a binder 'gluing' the particles together. The primary purpose for adding the oxide powder is to reduce shrinkage during gelation and the supercritical drying process. This process provides another advantage by allowing more flexibility in the fabrication process, which enables the properties of aerogel for better sublimation suppression/thermal insulation. For example, this method enables casting high density aerogel with little shrinkage (typically associated with fabrication of higher density aerogel 1-100 mg/cc). Devise shows that the higher the aerogel coating density the greater the reduction in sublimation suppression. Preliminary results with pure Si at 500 °C indicated that this composite aerogel can suppress Si sublimation by as much as 10,000 times. We also investigated the thermal stability of aerogel at high temperatures. Aerogels exhibit around 10% shrinkage in the beginning of 1000 °C isotherm and become stable without further shrinkage for more than 200 hr. The shrinkage in the beginning of isotherm was up to 2%. After casting in a vacuum chamber together, we are reporting a novel process, which will offer substantial improvements over the processes used to integrate aerogel into thermoelectric technology. This process will enable casting of high density aerogel, control of cracks and offers improved sublimation suppression in practically all thermoelectric technologies used for power generation.

8:45 AM F12.2
High Efficiency Thermoelectric Power Converter.
Donald F. Byrnes and Ben Heshmatpour; Teledyne Energy Systems, Inc., Hunt Valley, Maryland.

Recent efforts at Teledyne Energy Systems, Inc. have lead to significant improvements in thermoelectric (TE) materials and power conversion devices. A number of improved formulations were identified for standard n-type PbTe and p-type TAGS. The preliminary testing results appear to show nearly 50% improvements in the dimensionless figure-of-merit, ZT, for these two TE materials. The new material formulations also exhibit lower sublimation rates which allow use of these materials at higher heat source temperatures and thus result in higher Carnot efficiencies. The combination of higher ZT and higher Carnot efficiency allows achievement of exceptionally high thermoelectric conversion efficiencies with reasonably conservative changes to proven technology. For example, a thermoelectric conversion device which uses segmented BiTe/modified PbTe/modified TAGS thermoelectric couple design and operates between 300K and 900K will have a conversion efficiency of approximately 17%. Effort is continuing to optimize the preliminary results and validate the materials fabrication processes. A number of improvements have also been made in the TE device fabrication processes and assembly techniques which have reduced the internal thermal and electrical losses, increased conversion efficiency, enhanced reliability and reduced manufacturing cost for the thermoelectric devices.

9:00 AM F12.4
Progress on the Fabrication and Characterization of High Efficiency Thermoelectric Generators.
Timothy P. Hogan, Adam D. Downey, Jarrod L. Short, Jonathan J. D’Angelo, Ed Timm, Kimberly A. Sarbo, Eric Quarez, John Androlakis, Pierre F. P. Foudel, Harold J. Schock, Tom Shih and Mercouri G. Kanatzidis; Materials Research and Computer Engineering Department, Michigan State University, East Lansing, Michigan; 2 Mechanical Engineering Department, Michigan State University, East Lansing, Michigan; 3 Department of AerospaceEngineering, Iowa State University, Ames, Iowa; 4 Chemistry Department, Michigan State University, East Lansing, Michigan.

High efficiency thermoelectric modules are of great interest for power generation applications where high temperature environments of approximately 800K exist. The fabrication of such modules requires a multidisciplinary effort for the optimization of the material compositions, the engineering of the module systems, modeling and fabrication of the thermoelectric and constant element modules for characterization. Pb-Sb-Ag-Te compounds are among the best known materials for this temperature range. Modeling of these materials and possible cascaded structures shows efficiencies of 14% can be achieved for low resistance contacts. Using automated technology, we have achieved contact resistivities less than 20 μΩ-cm². Here we give a detailed presentation on the procedures used in the fabrication of thermoelectric generators based on new materials. We also present the characterization systems and measurements on these generators.

9:15 AM F12.5
Thermoelectric Modules For High Temperature Waste Heat.
Ryoji Funahashi, Yoshihisa Hira, and Naoki Nabeshima; 1 National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka, Japan; 2 CREST, Japan Science and Technology Agency, Kagawa, Saitama, Japan; 3 Osaka Electro-Communication University, Neyagawa, Osaka, Japan.

Thermoelectric generation systems can convert heat energy directly into electrical energy irrespective of source size. The requirements placed on thermoelectric materials, however, are not easily satisfied. Not only must they possess high conversion efficiency, but must also be composed of non-toxic and abundantly available elements having high chemical stability in air even at high temperature. Ca₃Co₄O₉ (Co₃Sb₃) with a layered structure is a good p-type thermoelectric compound at high temperature in air. Moreover recently, perovskite LaNiO₂ (Ni-133) has been reported to show negative Seebeck coefficient (S) and low resistivity (ρ) values. Different versions of thermoelectric unipolar compounds composed of Co-Sb and Ni-113 bulks were prepared. In the unipolar p- and n-legs are connected using Ag paste. Open-circuit voltage (Vₜ) of the unipolar reaches 100 mV at a hot-side temperature (Tₜ) of 1073K and a temperature difference (ΔT = T – Tₜ) of 500K in air. Internal resistance (Rₑ) can be suppressed to 14Ωm at Tₜ of 1073K in air and decreases with increasing temperature. Maximum output power (Pₜ) increases with Tₜ and reaches 177mW at Tₜ of 1073K (ΔT = 500K). This corresponds to a volume power Vₜ of 0.610W/cm³. A small thermoelectric module consisting of 140 couples were fabricated using the same method with the unipolar. We show how power can be generated using a small thermoelectric module composed of 140 pairs of thermoelectric unipolar bulks. A weight of 0.9 g and dimensions are 53 mm long, 32 mm wide, and 5.0 mm thick. The hot-pressed thermoelectric oxide bulk materials used were connected with an Ag paste and Ag electrodes. The module’s Vₜ increases with increasing hot-side temperature (Tₜ) and reaches 4.5 V at a Tₜ of 1072 K in air. No deterioration in output power was seen when power generation was carried out ten times at a Tₜ of 723 K with intermediate cooling to room temperature. The module was successfully used to charge a lithium-ion battery in a mobile phone.

9:45 AM F12.7
ErAs/InGaAs superlattice thin film power generator.
Gehong Zeng, Je-Hyeong Bakh, John E. Bowers, Joshua Zide, Arthur Gossard, Yan Zhang and Ali Shakouri; 1 Electrical and ComputerEngineering, University of California, Santa Barbara, California; 2 Materials Department, University of California, Santa Barbara, California; 3 Electrical Engineering Department, University of California, Santa Cruz, California.

InGaAs with embedded ErAs nanoparticles is a promising material for thermoelectric applications. The incorporation of erbium arsenide metallic nanoparticles into the semiconductor can provide both charge carriers and create scattering centers for phonons. Electron filtering by heterostructure barriers can also enhance the Seebeck coefficient by selective emission of hot electrons. The thin film power generators consist of 200 n-p coupled InGaAs/ErAs superlattices elements, which were grown on InP substrate using molecular beam epitaxy. The elements are 5 μm thick and 200 μm x 200 μm in size. There are a total of 400 thermoelectric elements that are packaged within 650 μm thick AlN plates via flip-chip bonding. The output powers over 0.5 milliwatts were measured at 255 temperature difference across the whole device package. Simulations show that the output power density can reach up to 1W/cm² with a heating source at 700K and heat sink temperature at 350K.

10:00 AM CLOSING REMARKS