SYMPOSIUM F
Materials and Technologies for Direct Thermal-to-Electric Energy Conversion
November 28 - December 2, 2005

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* Invited paper
SESSION F1: Thermoelectrics Research Directions & Oxides I

Chairs: Terry Trifil 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. Dresselhaus1,2, Gang Chen2 and Zhifeng Ren2
1Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; 2MIT, Cambridge, Massachusetts;
2Mechanical Engineering, MIT, Cambridge, Massachusetts; 3Physics, Boston College, Chestnut Hill, Massachusetts.

Many of the recent advances in enhancing the thermoelectric figure of merit are linked to nanoscale phenomena whether or not the thermoelectric materials 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.1 ZT. Having shown that reducing the thermal conductivity while maintaining the electric conductivity is a key strategy, research efforts have now evolved 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 material to reduce the lattice thermal conductivity and to improve the thermoelectric performance of the CoSb3-based materials (ZT=1.2-1.3). 2) By introducing iso-electronic alloying for ZnSnSb-based alloys, the thermoelectric properties of the materials are improved 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 polyaniline/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-fibrous structure has been fabricated in this laboratory. It 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 then install them in a device to recover electrical energy from engine's waste heat. Four teams were selected. The BSST Team includes Visteon, 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 the energy winds up as engine output shaft work. Half of that 40 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). Potential TEG applications include the engine's raditor, 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 'beltless' engine concept1, wherein all accessory electric motor are driven by 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 and replacing gas fired air conditioning 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/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 has been known for almost 170 years. Over the past 50 years has this technology found its way out of the laboratory and into nico 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 power generation. 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, process 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 that are already 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 ($A_xCo_3O_y$) for potential thermoelectric (TE) applications. CoO x is one of the few magnets that can form a layered lattice. At 0 K, the spins remain in a doublet quantum state with no discernible pattern (often called a '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 (1-x)Co$_3$O$_4$O$_y$ thin films with high thermoelectric power substrates of commercial silicon wafer and glass, which offers the promise of using available state-of-the-art silicon fabrication technology for potential
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 $ZT = \alpha^2 T / \rho \kappa$, where $\alpha$ is the Seebeck coefficient, $\rho$ electrical resistivity, $\kappa$ 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 materials are subject to 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 characterization techniques and highlights of several systems of materials will be presented. For example, a system of ceramic oxide thermoelectric materials based on NaCoO$_2$, 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 TIs, will also be discussed as well as why this type of structure may well be critical to the development of the next generation of thermoelectric materials. 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 some 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**

**Growth, structural, and transport properties of epitaxial NaCoO$_2$ thin films.** Venmadhab Adya1, A. Soukiasian2, D. A. Tenne1, Qi Li1, X. X. X. X. Li1, D. G. Schloem1, R. Arroyave2, Z. K. Liu2, H. P. Sun1, X. Pan1, M. Lei1 and N. P. Ong1; Physics, Pennsylvania State University, University Park, Pennsylvania; 2Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania.

Layered cobaltate NaNaxO$_2$ has attracted much attention recently due to its exceptional properties, one of which is its unusually high specific heat, magnetic and magnetotransport data. While a concurrence of a small negative thermopower, positive Hall coefficient and large electronic contribution to the specific heat indicates a new form of ferromagnetic metallic perovskites below Tc, the concurrence of negative Hall effect, large positive thermopower and huge electronic contribution to the specific heat characterizes layered NaNaxO$_2$ bronze. 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.
thermoelectric power with low resistivity, and high carrier density. We have studied structural and transport properties of epitaxial Na$_x$Co$_2$O$_4$ thin films on (001) sapphire substrate prepared by topotaxially converting an epitaxial Co$_3$O$_4$ film to Na$_x$Co$_2$O$_4$ 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 on sapphire aligned with [10-10] Na$_x$Co$_2$O$_4$ 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 cut of SrTiO$_3$ is ~70 mW/mK$^2$, which is similar to the single crystal samples of the same composition.

2:15 PM F2.3
Sr$_2$-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$_3$-xSr$_x$RuO$_3$ (0.1 < x < 0.5) polycrystalline samples have been prepared using solid state chemical reaction. The phase constituent, compositional homogeneity and micro-morphology have first been checked by X-ray 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, we measured the dependence of Seebeck coefficient of present compounds was studied in light of the comparison with the strongly correlated system Na$_x$Co$_2$O$_4$ and the relevant model proposed by W. Koshihara. Finally, the potential of using La$_3$-xSr$_x$RuO$_3$ as a practical thermoelectric material is discussed.

3:00 PM F2.4
Synthesis and Thermoelectric Properties of Na$_x$Co$_2$O$_4$ Oxide Materials.
Xiaofeng Tong, Ed Abbott, Joe K. Kolls, Kelvin Aaxon and Thomas Gmitter; Physics & Engineering, Clemson University, Clemson, South Carolina; 2Chemistry, Clemson University, Clemson, South Carolina; 3Physics & Astronomy, Clemson University, Clemson, South Carolina.

In 1997 Terasaki reported that Na$_x$Co$_2$O$_4$ 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$_x$Co$_2$O$_4$ polycrystalline samples, which were prepared by a rapid-heat-up technique, were systematically studied and will be reported here. The anomalous decrease in resistivity with increasing Na concentration of the compounds known to exist of an unknown phase transition, although the thermopower continues to increase with increasing temperature. The thermal conductivity of single crystals Na$_x$Co$_2$O$_4$ grown via typical NaCl flux method was measured by our group and the already reported p-type thermoconductance (PTC) system and was found to be ~5W/mK. Along with the low in-plane resistivity ρ~0.30 mΩ-cm and high thermopower α~100 mV/K, the power factor α$^2$/ρ of Na$_x$Co$_2$O$_4$ single crystals was found to have values of ~10$^3$ mW/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$_x$Co$_2$O$_4$ 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 wire also revealed the semiconducting resistivity behavior, where energy gap E$_F$ was found to be between 0.1 and 0.3eV.

SESSION F3: Poster Session: Nanoengineered Thermoelectrics

Chairs: Haruyuki Inui, Kaoru Kimura and George Nolas
Monday Evening, November 28, 2005

8:00 PM
Exhibition Hall D (Hyves)

F3.1
Abstract Withdrawn

F3.2
Boron-based Nanostructures for High Temperature Energy Conversion.
Syed Amin and Terry Xu; Department of Mechanical Engineering & Engineering Science, The University of North Carolina
at Charlotte, Charlotte, North Carolina.

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 power generation. In this presentation, recent experimental results on synthesis of n-type boron-based TE one-dimensional nanostructures (i.e., Ca$_2$B$_6$, Sr$_2$B$_6$ and Ba$_2$B$_{12}$) will be reported. The nanostructures were synthesized by pyrolysis of diborane (B$_2$H$_6$) over certain metal oxide powders (e.g., calcium oxide (CaO) for synthesis of Ca$_2$B$_6$) at elevated temperature and low pressure. The experiments were performed in a home-built low-pressure chemical vapor deposition (LPCVD) system. Nickel (Ni), Fe, and Bi$_2$Te$_3$ are used for growth of growth of aforementioned hexaboride TE nanomaterials. 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 nanomaterials 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. Marx, Physics, Illinois State University, Normal, Illinois.

Nanometer scale 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 semiconductor 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 well as nanocrystal 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 will be used to exhibit either p-type or n-type behavior. Additionally, we will discuss our 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$_x$Si$_{2-x}$)$_2$ Superlattices - Materials Designed for Low Thermal Conductivity. Ngoc Thanh Nguyen, David C. Johnson, Catalin Chitescu; Chemistry, University of Oregon, Eugene, Oregon; Materials Science, University of Illinois at Urbana-Champaign, Urbana-Champaign, Illinois.

One concept for producing extremely low thermal conductivity superlattices is the combination of materials with different vibrational characteristics. We have prepared superlattices consisting of a variable number of layers of Si$_2$W$_x$ and a 1.5 nanometer layer of W as building blocks. The superlattices were synthesized using modulated electron beam techniques. Altering the thickness layers of Si$_2$W$_x$ and Si were deposited with a 1 to 2 ratio of W to Si and an appropriate thickness to yield an integral number of Si-Si layers of Si$_2$W$_x$ followed by a layer of W to form the repeating unit of the superlattice. An investigation of 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$_{3x}$Bi$_{2-x}$S$_5$ Nanowires. Jana Sommerlatte, Woo Lee, Roland Scholz, Ulrich Gosewolfe, Klaus Bente, Jörg Kornelius Niehsch, Man 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. Sulfides 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 0.2 up to 1.6 eV and exhibit a large variety of crystal structures. Due to the modular crystal structure Pb$_{3x}$Bi$_{2-x}$S$_5$ 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$_{3x}$Bi$_{2-x}$S$_5$ nanowires by electroprecipitation 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 nonaqueous solvent for the electrolyte. The deposition of Bi$_2$S$_3$ and Pb$_{3x}$Bi$_{2-x}$S$_5$ 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 pore filling up to the thickness of the crystal structure. The Bi$_2$S$_3$ nanowires exhibit the bismuthinite phase with a preferential orientation of the caxis 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$_{3x}$Bi$_{2-x}$S$_5$ nanowires which exhibit the cosalite Pb$_2$Bi$_x$S$_5$ for limited Pb$_2$Bi$_x$S$_5$ 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$_2$)$_2$ Superlattices. Mary Smelter, David Johnson, David Cahill and Catalin Chitescu; 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$_2$)$_2$ superlattice thin 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 (TDTTR). A thermal conductivity of 0.230 W/mK was measured for a (Bi$_2$Te$_3$)(TiTe$_2$)$_2$ superlattice, half as low as the value reported by Venkateswaran (J. Appl. Phys. 2001) for (Sb$_2$Te$_3$)(Bi$_2$Te$_3$) superlattices of the same superlattice period. The improvement is thought to be due to a 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. Diana-Kate Bora-Tatnall, Joan Chen, and Andreas Grosz; Rensselaer 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 3ω method on free-standing wires. The specimens under investigation are fabricated through the metalOrganic Chemical Vapor 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 hundred of nanometers 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 0.6 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.

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 model on the effect of porosity on 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 (Sb2Te3)0.7(Te2Se)0.3 Superlattices. Benjamin Schmidt, Clay Mortensen, Raimar Rosiek and David C. Johnson. University of Chemistry, University of Oregon, Eugene, Oregon.

A series of (Sb2Te3)x(Te2Se)3y superlattices with varying ratios of x and y was synthesized by employing the technique of modulated elemental reactants. This system parallels (Bi2Te3)x(Sb2Te3)y and PbTe/PbSnTe nanostuctured 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 Bi2Te3-Based Nanocomposites. Qing Hau1, Bed Poudel2, Yi Ma2, Dezhi Wang1, Wenzhong Wang3, Zhengfu Ren2, Mildred S. Dresselhaus2 and Gang Chen3. 1Department of Materials Engineering, Naval Postgraduate School, Monterey, California; 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 Bi2Te3 nanostructures. Compared with other attempts, nanoparticle composites have shown potentials to improve the ZT value with minimal material cost. The incorporated nanoparticles 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 Bi2Te3-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 (Bi2Te3)0.7(Te2Se)0.3 Superlattice Hot Pressed from Thin Films. Sissi I. L.1, Mary M. Smoller1, Maisha K. Kamunde1, Clay D. Mortensen1, Benjamin A. Schmidt1, David C. Johnson1, Terry M. Tritt2, Brad Edwards2, Nobuyoshi Imaoka3 and Isao Morimoto3. 1Chemistry, University of Oregon, Eugene, Oregon; 2Chemistry, University of Colorado, Boulder, Colorado; 3Chuo University, Chuo, Tokyo, Japan.

Using the modulated elemental reactant method, thin films of (Bi2Te3)0.7(Te2Se)0.3 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 analysis. A 0.3092g bulk pellet was prepared by hot-pressing the thin films at 520°C and 7000 psi for 24 hours. The thermal and electrical properties of this bulk pellet are presented.


Bulk Bi2Te3 is one of the best known thermoelectric materials with a ZT ~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 Bi2Te3 nanosheets by ablating a rotating Bi2Te3 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 nanosheets. Alternatively, we have also prepared Bi2Te3 nanosheets by subliming Bi2Te3 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 (Ti1-xVx)(Ti2x)0.7(Bi2Te3)0.3 Superlattices. Clay Mortensen, Benjamin Schmidt, Raimar Rosiek and David C. Johnson. Department of Chemistry, University of Oregon, Eugene, Oregon.

We explored TiTe2 as a diffusion barrier between Bi2Te3 and Sb2Te3 to limit interdiffusion of Sb and Bi. A series of (Ti1-xVx)(Ti2x)0.7(Bi2Te3)0.3 superlattices has been synthesized using modulated elemental reactants. Interdiffusion of Bi and Sb as a function of TiTe2 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 (Bi2Te3)(Sb2Te3) layered structures.

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

Chairs: Mercouri Kanatzidis and Winnie Wong-Ng

Tuesday Morning, November 29, 2005

Room 313 (Hynes)


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 PbTe/PbTe-quantum dot superlattice (QDSL) 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-salt QDSL materials (~1.5 at 300K), the rapid rate of progress confirms the favorable mirror-image band structure of the Pb-chalcogenides and validates our expectation that comparable p- and n-type figures of merit will be obtained from Pb-based QDSL materials. In addition to the QDSL 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 PbSnSeTe/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 unipolar devices, we have obtained a power density of ~2 W/cm2 for both n- and p-type QDSL materials, with a temperature difference across the devices of approximately 220 K at Tcold = 310K.

We will discuss these unipolar device measurements as well as the on-going development of fabrication techniques suitable for producing multiple unipolar arrays in QDSL materials. 1. T. C. Harman, M. P. Walsh, 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. Ichiro M. Ziegler, Genghong Zeng, Je-Hyeong Baik, John E. Bowers, Wooshul Kim, Arun Majumdar, Ali Shakouri and Art C. Gossard1. 1Materials, University of California, Santa Barbara, Santa Barbara, California; 2Electrical and Computer Engineering, University of California, Santa Barbara, Santa Barbara, California; 3Mechanical 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 semiconductor 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 large number of factors, such as the Seebeck coefficient, electrical conductivity, and thermal conductivity. These factors depend on the material properties, and the material properties can be tuned by the incorporation of nanoparticles. In this talk, we will discuss the growth, characterization, and potential applications of III-V semiconductors containing nanoparticles.
controlled during growth. We present experimental results on the incorporation of Er ions into various compositions of InGaAlAs (lattice matched to InP) in superlattices. The Er concentration in the superlattices is varied, and we measure the optical and electrical properties. In GaAs/AlAs, the Fermi level at 77K is pinned ~400meV below the conduction band edge, and so the carriers serve as a buried Schottky barrier. By carefully choosing the composition of the InGaAs/AlAs superlattices, we can increase the electron density in the superlattices and reduce the barrier height. This results in a decrease signal ringing due to parasitics and achieve short time resolution (<1 micro seconds) in the current measurements. Direct ZT measurements are compared with independent measurements of the cross-plane thermal conductivity and Seebeck coefficient.

9:15 AM F4.5
A Band Structure Phase Diagram Calculation of 2D BiSb Films. Ming Y. Tang1 and Mildred S. Dresselhaus2,3. 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. BiSb alloys have been of particular interest for thermoelectric application in the temperature range of 70K to 100K. In bulk form, a BiSb alloy can either be either a semimetal or a semiconductor, depending on the alloy composition. Moreover, semimetalllic BiSb alloys can be made semiconducting by using the low dimensionality quantum confinement concept. With the help of previous concept and alloy composition, calculations of the band structure of BiSb nanowires by Rabin, Lin, and Dresselhaus (Appl. Phys. Lett., 79, v.2, p.81-83, we now examine the corresponding effect of the Sn concentration and the wire diameter on the semimetallic or semiconducting phase of BiSb alloys nanowires by Rabin, Lin, and Dresselhaus. (Appl. Phys. Lett., 79, v.1, p.81-83), we now examine the corresponding effect of the Sn concentration and the wire diameter on the semimetallic or semiconducting phase of BiSb alloys nanowires by Rabin, Lin, and Dresselhaus. (Appl. Phys. Lett., 79, v.2, p.81-83), we now examine the corresponding effect of the Sn concentration and the wire diameter on the semimetallic or semiconducting phase of BiSb alloys nanowires by Rabin, Lin, and Dresselhaus. (Appl. Phys. Lett., 79, v.1, p.81-83), we now examine the corresponding effect of the Sn concentration and the wire diameter on the semimetallic or semiconducting phase of BiSb alloys nanowires by Rabin, Lin, and Dresselhaus. (Appl. Phys. Lett., 79, v.2, p.81-83). In this paper, we describe in detail the test device and methodology we used to characterize the cross-plane Seebeck coefficient of a in a temperature range of 100-600K.

9:30 AM F4.6
Thermoelectric Transport Properties of Bi2Te3 Nanoparticles. Seong Yul Kim1, Erin Dunbar2, Daniel Tsang1, Abhishek Jain3, Arup Purkayastha2, Ganapathiraman Ramana2 and Theodoros Boreas Tegelaer1. 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 nanostructures has emerged as a candidate for factorial enhancements in the thermoelectric figure of merit. This work explores thermoelectric transport in films of self-assembled Bi2Te3 nanoparticles. The nanoparticles are grown with control over size and size distribution using a new room temperature synthesis method from microenclosures. Nanoparticles 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 microelectrodes 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. Direct Seebeck coefficient of the film can be extracted from the slope of S=ΔV/ΔT. Electrical conductivity is determined using a two probe technique. A linear I-V characteristic is obtained for the films indicating ohmic behavior. Temperature dependence of electrical measurements are obtained 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 andBulk Materials. Nicola Pernot1, Oliver Eibl1, and Joachim Nurnsch1. 1University of Tuebingen, Institute for Applied Physics, Tuebingen, Germany; 2Fraunhofer Institut Physikalische Metstechnik, Freiburg, Germany.

Multiquantum well structures of Bi2Te3 are predicted to show an
enhancement of the thermoelectric figure of merit of ZT [1]. Bi2Te3/Bi2Te(0.85Sb0.15)3 superlattices (SL) with a layer thickness of 12 nm grown on BaF2 substrates by molecular beam epitaxy 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 interference of the fundamental reflections of the superlattice reflections of the substrate. The period length of the SL is 13.1+/-0.4nm. The SL is slightly bent with an amplitude of 30nm and a wavelength of 400nm. Threading dislocations were found with a density greater than 10^8 cm^-2. The superlattice interfaces are strongly bent by several degrees in the region of the threading dislocations, undisturbed regions have a maximum lateral size of 500nm. A structural modulation (nm) parallel to the (1,0,1)-planes with a wave length of 1nm was found. This modulation (nm) was also observed in n-type Bi2Te(0.35Se)3 and p-type (Bi,Sn)2Te3 bulk material and turned out to be of general character for Bi2Te3 materials. The (nm) did not show bending due to the superlattice and vice versa. Therefore, the structure is a nanoscale superlattice of the original superlattice (nm) and the structural modulations (nm). The structural modulation was analysed in n-type bulk material in detail. The (nm) consists of parallel dislocation lying on (1,0,1)-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 darkfield microscopy. The investigations showed the presence of none, one or two (nm). Particularly the heat conductivity should be significantly decreased due phonon scattering on the (nm) with its high dislocation density. We assumed that the heat conductivity the (nm) could yield a reduced dimensionality and localization and anisotropic behaviour in the basal plane. Cubic AgPumSbTe2+4 bulk materials also showed such (nm) and an enhancement of the thermoelectric efficiency [1] [7]. [1] Venkatakrishnan, R., Nature, vol. 413 (2001), pp. 597-602. [2] Lamprecht A. et al., Proc 20th Int. Conf. on Thermoelectrics, Beijing, P.R.China (2001), pp. 335-338. [3] Parzone N. et al., Proc 29th Int. Conf. on Thermoelectrics, Boulder, USA (2004), in press [4] Kue-Fang Hsue, Science, Vol. 303 (2004), pp. 818-821.

10:30 AM E4.10
Large Area Quantum Well Thermoelectric Generator, Harry Efstatiadis1, Tianhua Yu1, Frank Ramos1, Pradeep Haldar1, Saedd Ghamaty2 and Norbert Elsner2,1; College of Nanoscale Science and Engineering, University at Albany, Albany, New York; 2Hi-Z Technology, Inc., San Diego, California.

Recent development in thermoelectric conversion, especially in the area of quantum well (QW) thin film materials, have 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 exterrirtorial 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 demonstrate a new approach to the development of large area QW films of N-type SiC/Si layered with P-type B5/C6 alloy, 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 a novel deposition process on a defective substrate. The deposition process is expected to be scalable and 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 their surface uniformity, thickness, growth rate, composition, resistivity, and thermoelectric performance on an atomic scale using 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, thin film contamination, and crack formation lowering the device performance will be presented and correlated to device efficiency.

10:45 AM E4.12
Fabrication and Characterization of Si-Ge Nanocomposite for Thermoelectric Applications. Dezhri Wang1, Wenzhong Wang2, Shuo Chen1, Zhifeng Ren1, Hollynn Lee2, Gang Chen1, Ming Tang1, Mildred Dresselhaus1,2, Pawan Gogna3, Jean-pierre Fleurial1 and Bradley Klotz41; Physics, Boston College, Chestnut Hill, Boston, MA 02168; 2Massachusetts Institute of Technology, Cambridge, Massachusetts; 3Electrical Engineering, MIT, Cambridge, Massachusetts; 4Physics, MIT, Cambridge, Massachusetts; JPL, Pasadena, California; 5Dynamic 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 superlattices 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 nanocomposites, nano SiGe alloy particles in SiGe alloy matrix. The Si-Ge nanocomposite was made of nano silicon and germanium particles by hot-press. A unique hot-press procedure was developed in order to make the nanocomposite 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 nanoparticles 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 carrier effective mass, and the thermal conductivity, which is modeled by a power law r = γT n. In order to determine these four unknowns each at a particular temperature, four measurements are taken: the electrical conductivity, and the Hall, Seebeck and transverse Nernst-Ettingshausen coefficients. A linearleast squares analysis concludes that the increased Seebeck coefficient in samples with nanoscale inclusions is due to an increase in the scattering parameter r. The mobility of the sintered samples is much lower than that of the metallic Pb material, while the situation in samples containing nanopracticipants is more favorable. No decrease in lattice thermal conductivity is measured in binary PbTe with nanocomposites.

11:30 AM E4.11
Abinitio study of electronic structure of Defects in Narrow Band-Gap Semiconductor PbTe*. Sahibeh Mohammad Ahmad1, S. D. Mahanti2 and M. G. Kanatzidis2,3; Physics and Astronomy, Michigan State University, East Lansing, Michigan; 2Department of Chemistry, Michigan State University, East Lansing, Michigan.

A novel class of quaternary compounds AgPb0.85Sb0.15Te2.24, denoted as LAST-m have attracted considerable attention during last two years because of their large thermoelectric figure of merit at high temperatures[1]. Abinitio electronic structure calculations have shown that the compound has a potential band gap of PbTe2.24. This gives 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 resistance on ZT. Recently, Na91-Pb83Sb0.16Te0.84 materials have been found to exhibit p-type conduction over a wide temperature range and for Na91-Pb85Sb0.16Te2.24, 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 MPb90-xTexp x (n=10), where M is a defect which can be a Pb vacancy, a monovalent atom (alkali atoms, Cu), a divalent atom (type H* Zn, Cd, Hg and type IVA Sn, 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 their influence increases (n-type thermoelectric) over 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 Sn because their valence configurations are nearest neighbors, respectively, to Sn, Ga, and In, hence they increase the DOS near the top of the valence band (good for p-type thermoelectric), whereas Ga and TI the impurity induced states are resonant with the valence band.


11:45 AM E4.12
Thermoelectric Properties of Hot-pressed core-shell
Nanoparticles Having the Shell of InSb. Seiji Take1, Kikuo Okuyama2 and Yukio Yamaguchi3; 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 proposed 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) 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 allowing a big amount 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 resulted from the progress 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”.

SESSION F5: Low Dimensional Structures II (Bulk: Pressed and Self Assembled)
Chairs: Ryoji Funahashi and Joseph Poohn Tuesday, 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. Tritt; 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 nm, 200 nm 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. Suvankar Sen Gupta, Bao B. Revaz, Troy Pensl1, J. R. Schorr1, Jennifer Nelson2, Julie Anderson2, James H. Adair2 and Norbert Elsner3; 1MetaMateria Partners, Columbus, Ohio; 2Penn State University, University Park, Pennsylvania; 3Hi-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 PbS. The resulting coated particles, as well as uncapped 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 Poudel1, W. Z. Wang1, D. Z. Wang1, Y. Ma1, Z. F. Ren1, Q. Hao2, H. Lee2, G. Chen2 and M. S. Dresselhaus3; 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 P900 die and samples, with almost 100 percent 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 dispersed with different elements, for example Se, 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, D. Edwards, D. Thompson, J. He and Terry M. Tritt; 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 constitutively based on good bulk thermoelectric materials. The character has been to achieve higher performance 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 comparison techniques in order to yield a bulk system composed of these nano-structured materials. Measurements of the thermoelectric parameters of a material are problematic in general, and the nanostructured samples present their own 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. AgPbSnTe2+m (LAST-m). Meroufi G. Kanatzidis, Michigan State University, East Lansing, Michigan.

The family of chalcogenide lead-based compounds, AgPbSnTe2+m, or LAST-m materials (LAST for Lead Antimony Silver Tellurium), comprises of several members which exhibit large ZT values up to ~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 nano scale with at least two coexisting well defined phases. Electron microscopy examination revealed endotaxially dispersed quantum nanodots (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 PbS/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 AgSb1-xMxTe2 (M=Pb, Sn) Compounds - Implications for Thermoelectric Properties*. Khyang 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 μ. It has been suggested that resonant structures in the neighborhood of μ can indeed give rise to enhanced thermoelectric figure of merit[1]. Ab initio electronic structure calculations can shed some light on the possibility of finding such resonant structures[2]. Recently, quaternary compounds AgSb1-xMxTe2 (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 by means of density-functional theory (generalized-gradient approximation for exchange-correlation) using
PAW method[6]. Results for a monolayer structure of M=pb and m=14 (one layer of Ag$_2$Te$_2$ sandwiched between 7 layers of Pb$_2$Te$_2$) show the existence of a band gap of 2.8 eV at high temperatures as a function of the layer that give rise to a peak (width ~0.25 eV) in the density of states near but above the valence band. This behavior persists for a bilayer structure of the same M and m. For M=pb and m=2, which consists of alternating layers of Ag$_2$Te$_2$ and Pb$_2$Te$_2$, 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 Ag$_2$Sn$_3$Te$_4$ we find again the same 1D-like structures in the density of states at high temperatures as in Ag$_2$Te$_2$. 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 large positive thermoelectric power) in Ag$_2$Sn$_3$Te$_4$.4. Supplied by OCN-MURI. References [1] G. D. Mahan and J. O. Sofo, Proc. Natl. Acad. Sci. USA 93, 7436 (1996). [2] D. Bilc et al., Phys. Rev. Lett. 93, 146401 (2004). [3] K. F. Hsu et al., Solid State Commun. 136, 607 (2004). [4] A. Androulakis et al. (to be published) [5] K. Hoang, K. Desai and S. D. Mahanti, Phys. Rev. B (to be published 01 July 2005). [6] P. E. Blöchl, Phys. Rev. B 50, 17963 (1994).

4:15 PM F5.7 Thermoelectric Materials AgPb$_6$Sn$_9$Te$_{21+m}$ (LAST-m) with High Figure of Merit. Structural Evidence Breaking the Myth of Solid Solution. Eric Quarez1, N. Frankel2, E. K. Polychroniadou3, Kuei-Fang Hsu1, Robert Pcionek1, Jonathan D’Angelo2, Adam Downey2, Joseph Sootsman3, Robert J. Pcionek1, Zhenhua Zhou4, 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, Michigan State University, East Lansing, Michigan; 3Department of Physics, University of Michigan, Ann Arbor, Michigan.

The effects of the variation of Sb and Se contents on the thermoelectric properties of Pb$_6$Sb$_4$Te$_{29-2x}$Se$_x$ in the intermediate temperature range were investigated. The Pb$_6$Sb$_4$Te$_{29-2x}$Se$_x$ family was derived from Pb$_6$Sb$_4$Te$_{30}$ (cubic, Fm-3m) by isoelectronic substitutions in anion positions of Te by Se. Sb-free samples start from a huge positive thermopower values at room temperature, show a maximum around 500 K and decrease rapidly to negative values at high temperature. The change of the sign of thermoelectric effect from positive to negative values indicates a transition from p- to n-type conduction. Such behavior may be caused by the difference of mobility between thermally excited electrons and holes at high temperatures. Samples with Sb = 0.10 and Se = 0.01 (y=0.2) showed n-type conduction in the entire temperature range. The value of the thermopower decreases with increasing of Se content. For Pb$_6$Sb$_4$Te$_{29-2x}$Se$_x$, a maximum figure of merit of ZT~0.8 was observed around 600 K. High resolution transmission electron microscopy of Pb$_6$Sb$_4$Te$_{29-2x}$Se$_x$ samples revealed the presence of nanoscale inhomogeneities inside PbTe crystalline matrix. Increasing the Sb content to y = 0.4 results to 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 needs to be engineered 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 these conclusions 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-xGex Ordered Nanowire Composites. Ming Y. Tang1, Mildred S. Dresselhaus2,3, Ronani Yang2 and Gang Chen2. 1Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; 2Mechanical Engineering, MIT, Cambridge, Massachusetts; 3Physics, MIT, Cambridge, Massachusetts.

Thermoelectrics 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 designs. 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 increase in phonon scattering 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-Si<xGex system, a field emission scanning electron microscope (SEM, JOEL-6340F), and a field emission transmission electron microscope (TEM; HRTEM, 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.

8:45 AM F0.3
Synthesis of Bi2Se3 Nanowires Using a Hydrothermal Method. Yi Ma, Wenzhong 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 diffractometer (XRD), a Raman spectrometer, a Scanning electron microscope (SEM, JOEL-6500F), and a Transmission electron microscope (TEM). The as-prepared Bi2Se3 nanowires were then used as the active material in thermoelectric devices.

9:00 AM F0.4
Thermoelectric performance of pulse-deposited bismuth telluride nanowire arrays. Lynn Tran1,1 Jeff Sharp2 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 electrodedeposited into porous alumina templates using pulsed-potentiostatic methods. The pulsed-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 changing the scan rate of the pulse potentiostatic electrochemical deposition system. We also show that by using the templates as a starting material, bismuth telluride nanowire arrays 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 F0.5
Incorporation of Bismuth Antimony Nanowire Arrays into Thermoelectric Couple, Jennifer Keyan1, J. W. Sharp2 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−xSb1−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−xSb1−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 few micrometres. The width has been controlled to be approximately 100 nm diameter pores for alloy compositions of 0.07 < x < 0.30. Metal contacts were electrodepored 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 F0.6
Thermoelectric Properties of Bi and Bi1−xSb 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 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 alloy under 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 Bi1.75Sb0.25 nanowires is comparable with that of Bi nanowires. The possible explanation of unusual thermoelectric properties of these nanowires is presented.

10:15 AM F0.7
Electronic States of Ti3S2, 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 Ti3S2, MoS2, and Mo-doped Ti3S2. Also, nanotubes have been grown of both Ti3S2 and MoS2, and their properties measured. To understand the properties of these materials, we have calculated the electronic states of Ti3S2 and MoS2 in various geometries, as well as Mo-doped Ti3S2. The calculations are performed within the framework of the projection method using the Vienna Ab initio (PAW) scheme. 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 F0.8
Rhenium Silicide as a New Class of Thermoelectric Material. Hayakawa Inui, Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan.

Silicide formed with rhenium is of interest owing to potentials as a promising candidate material for thermoelectric applications. The silicide is a direct silicide 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 C112 lattice. Binary ReSi1.75 exhibits significantly anisotropic thermoelectric properties such that the value of Seebeck coefficient along [100]c\[110] is positive (230μV/K at 330K) while it is negative (-300μV/K at 600K) along [011](c\[110], which 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 0.707 at 1073 K when measured along [001] while the ZT value along [100] is moderate. We have made some efforts to improve the thermoelectric properties of ReSi1.75 by adding some other transition metals, 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 lower, 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 expected from the high value of the 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 F0.9
Highly Anisotropic Thermoelectric Properties of ReSi1.75 Single Crystal. Min Wook Oh1, Katsuji Tanaka2, Haruyuki Inui2, Myung-Hoon Oh3 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
Science and Engineering, Kumoh National University of Technology (KNUT), Gumi, South Korea.

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 and thermal 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 Seebeck coefficient of electrical transport (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, while also indicating that the thermoelectric power showed highly anisotropic behaviors. The value of the thermoelectric power along [100] is positive (+150 μV/K at 600 K) while it is negative along [001] (−300 μV/K at 600 K). These peculiar orientational 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 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.

SESSION F7: Thermionics and Photovoltaics

11:15 AM F8.10 Thermoelectric Properties of Icosahedral Cluster Solids. Kaoru Kimura$^{1,2}$, Junpei Tamura Okada$^{2}$, Hongki Kim$^{3}$, Takehiro Hamamatsu$^{1}$, Tomohiro Nagata$^{4}$ and Kazuhiro Kirihara$^{2}$; $^{1}$Department of Advanced Materials Science, The University of Tokyo, Chiba, Japan; $^{2}$Department of Applied Physics, The University of Tokyo, Tokyo, Japan; $^{3}$Department of Materials Science, The University of Tokyo, Tokyo, Japan; $^{4}$Nanochalcogenides Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan.

Boron- or Aluminum-rich icosahedral cluster solids (ICS) consist mainly of B12 or Al12 icosahedral clusters. In the ICS, a slight change of the structure of icosahedral metal clusters can initiate metallic-covalent 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 the electron cloud 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/Rietveld, we successfully obtained the clear image of the electron density distribution for $\alpha$-AlReSe$_4$ approximant crystal. The bond strength distributes widely from weak metallic to strong covalent band, and the intra-cluster bonds are stronger than the inter-cluster ones. This means that $\alpha$-AlReSe$_4$ is located at the intermediate stage 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 quasicrystals. 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 of 10% Re. The higher thermal transport is lower than that of boron, 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 negative value of $\kappa$ is decreased. The maximum and n-type ZT value is obtained and is approaching to that of B4C, which is considered to have the largest and p-type ZT value in boron-rich ICS.

11:45 AM F6.11 Improving Thermoelectric Figure of Merit: Investigation of Zn-doped Yb$_{14}$Mn$_{53}$Sb$_{11}$. Shawn R. Brown$^1$, Susan M. Kauzlarich$^1$, G. Jeff Goodenough$^2$, and Rachel Gasior$^1$; $^1$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$_{53}$Sb$_{11}$, have shown a high figure of merit at elevated temperatures (900-1275 K). The Zn-doped analog, Yb$_{14}$Mn$_{53-x}$Zn$_x$Sb$_{11}$ with $x = 0.17$, 0.35, 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$_{53}$Sb$_{11}$ by adding disorder and lowering the thermal conductivity. Recent microprobe, single crystal diffraction, DSC/DTA, 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.

1:30 PM F7.1 Thermionic Energy Conversion. Ali Shokouri, 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°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 investigated. Measurements of emission, electrical 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. Zhe Liang and Ali Shokouri; 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 $S^2\sigma$ compared to thermionic devices. In conventional 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 by the parasitic heat flow from the hot side to the cold side. One shortcoming of planar barriers is that they only transmit hot electrons whose kinetic energy in the direction perpendicular to the barrier is large enough. 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 help 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.
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 the same throughout the device. 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. One might expect that there may in fact be an optimum design for solid-state refrigerators and power generators which incorporates elements of both ballistic and diffusive transport. This expectation in based on the fact that the two types of devices can be combined in a single device to optimize 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 refrigeration device 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 greater 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 a band mean-free path, it is expected that most electrons move ballistically through the barrier whenever the electron mobility is low 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 described with either purely ballistic or purely diffusive formalism. 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. An important aspect of this work which we will report on at the conference is the determination of the correct treatment for the density of states and dispersion relation for electrons in a material with a periodicity on the order of an electron mean-free path.

3:30 PM F7.4 Metal-Semiconductor Nitride Multilayers for Solid-state Thermionic Energy Conversion. Vijay Rao1; H. JoYoung Kim2 and Timothy Sand1, 2, 1 Materials Engineering, Purdue University, West Lafayette, Indiana; 2 Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana; 3 Physics, Purdue University, West Lafayette, Indiana.

Solid-state thermionic direct energy conversion devices based on metal-semiconductor nitride multilayers are predicted to exhibit optimal thermoelectric figures of merit (ZT) for Schottky barrier heights in the range of 0.3 to 1.0 K/T (ref. 1). The band gap of diamond is between 2.8 to 3.8 eV. For applications requiring moderate to high temperatures (300 - 700 °C), the multilayers must be stable against corrosion, decomposition, and interdiffusion. The nitrides meet these criteria, and offer potential materials combinations for metal-semiconductor nitride multilayers with tunable electronic and thermal transport properties. Nitrides such as TiN, ZrN, VN, and TaN are metals whereas GaN, InN, and AlN 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 ambient at substrate temperatures ranging from 550-700 °C. TiN/V/AlN/V/AlN/Au 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 of the Fermi level due to electron mobility. Evaluation 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 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 InN/GaAs will permit tuning of the barrier height in the range of 200 to 500 meV range. Electrical and 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/5 nm TiN periods at a TiN layer thickness of 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 PowerFactor in Metal – Base Superlattices, D. Vashaa and A. Shakouri, Phys. Rev. Lett. 92, 106103 (2004).


Improving the performance of a vacuum thermionic energy conversion device (VTEC) 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 a vacuum 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 thermionic energy converter (VTEC) with and without an 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 for five 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 Electron and Phonon Transport in Nanostructured Carbons. Darryl M. Green and Paola Bruno, Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

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 (HE), we measure a voltage and current indicating energy conversion. This research is supported by the ONR under the TEC-MURI project.

This research paper will investigate the use of the Bass diffusion models for predicting life cycles and penetration of PV and CdTe market sales of new products until 2020. A MWdive, the current world photovoltaic power capacity is about 744 megawatts (MW) a year in 2004. It is worth about $1 billion. However, a yearly production of 10,000 MW is required to sustain the photovoltaic capacity that can contribute just 5% to the current electricity capacity. To fulfill the need of photovoltaic devices, a substantial increase in manufacturing volume is needed. There are serious limitations on the manufacturing costs and availability of the feedstock materials, which prevent the now dominant technology from expanding further. The addition of relatively small amounts of manufacturing capacity with other manufacturing technologies has proven slow and expensive. The expansion of the use of photovoltaic manufacturing volume and time for peak sales is a difficulty in adding new manufacturing capacity with future needs. A 2 MW CdTe prototype production system is being manufactured at Colorado State University. We will use this prototype to feed into a 2.0 to 3.0 GW factory solar park. This 2.0 to 3.0 GW factory production facility has the potential to significantly increase the photovoltaic volume over typical CdTe factories are expected. The conceptual design methods will investigate the high volume manufacture of CdTe thin film modules required for transformation of continuous processes, which will allow motion of the substrate for the start to the end. The laminating and confectioning will require a completely new solution. A laminator module will be designed so as it can be manufactured in multiple modules at the same time in one process cycle. This work will be done at the Engineering Research Center at Colorado State University. The areas that will be investigated: Objectives 1. Model photovoltaic devices using CdTe materials, production and market sales data. Fabricate CdTe low raw material costs: To review the raw material cost for the fabrication of photovoltaic devices. Fabricate CdTe modules with greater than 15% collection efficiency on in-line continuous manufacturing processes 2. Develop Manufacturing process research for economically producing these solar photovoltaic cells. Use High Throughput Equipment Design and Process simulation to up to 100 times faster than other photovoltaic technologies Integrated, all in line production processes Demonstrate Lean and high production manufacturing of CdTe modules.
carrier concentration which is typical in the alkali bismuth chalcogenide group of compounds. The lattice thermal conductivity is strongly affected by the Se/S ratio. The temperature dependence of the figure-of-merit ZT shows that these materials have potential for power generation applications.

F8.3 Thermoelectric Properties of Tl2Te-Sb2Te3 Pseudo-Binary System. Keita Goto, Ken Kurosaki, Hiroaki Muta and Shinusuke Yamana; Division of Sustainable Energy and Environmental Engineering, Osaka University, Suita, Japan.

Polycrystalline-sintered samples of thallium compounds, (Tl2Te)x(1-x)(Sb2Te3)x (x = 0.2, 0.3, 1.0, 3.0), have been prepared by melting Tl2Te and Sb2Te3 ingots followed by annealing in sealed quartz ampoules. The thermoelectric properties such as the electrical resistivity, Seebeck coefficient, and thermal conductivity have been measured from room temperature to around 1000 K. The electrical resistivities of these samples decrease 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^{-6} Wm^{-1}K^{-2} at 580 K obtained for x = 0.9, (Tl2Te)0.1(Sb2Te3)0.9, which is about one order lower than those of state-of-the-art thermoelectric materials. All the samples have extremely low thermal conductivities, for example that of Tl2Te is around 0.3 Wm^{-1}K^{-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 Thermoelectric Properties of LnPdX (Ln = lanthanide; X = Sb, Bi) Ternary Compounds. Takeyuki Sekiguchi, Ken Kurosaki, Hiroaki Muta and Shinusuke Yamana; 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 thermoelectric power of the measured four-probe method under helium atmosphere from room temperature to 1000 K. The temperature dependence of the electrical resistivities of ErPdSb and ErPdBi shows a semiconducting characteristics. The electrical resistivity and the thermoelectric power of ErPdSb were larger than those of ErPdBi. The values of the thermoelectric power of ErPdSb and ErPdBi are positive in the whole temperature range. On ErPdSb and ErPdBi, the activation energy estimated from the natural logarithm of the electrical resistivity vs the inverse of temperature plot is 0.96 and 0.50 eV, respectively. The difference of the activation energy leads to the magnitude of the thermoelectric power and electrical resistivity. The thermal conductivity of ErPdSb and ErPdBi at around 200 K is 4.7 Wm^{-1}K^{-1} and 5.0 Wm^{-1}K^{-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 thermoelectric material.

F8.5 Thermoelectric properties of AgPb5SbTe5. Joseph Sootsman1, Mercouri Kanatzidis1, Oleg Palchik2 and Ciritad Uher2; 1Department of Chemistry, Michigan State University, East Lansing, Michigan; 2Department of Physics, University of Michigan, Ann Arbor, Michigan.

The thermoelectric properties of the AgPb5SbTe5 family of compounds with values of 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 structuring 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 telluride 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 Homoeclectite Family CePb10Bi2Te12+δ. Aurelle Guerguiev, Eric Querez and Mercouri Kanatzidis; Chemistry, Michigan State University, East Lansing, Michigan.

The discovery of new thermoelectric materials with superior properties is one of the main challenges in solid state chemistry and physics. One promising candidate for cooling applications is CsBi2Te6. Recently, our effort to produce new materials that resemble to CsBi2Te6 led to the discovery of the homologous series of materials CsPb8Bi3Te20+δ. 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 CsBi2Te6. The CsPb8Bi3Te20+δ compounds show low thermal conductivity comparable to that of CsBi2Te6. Preparing analogs of such compounds can be a way to tune the thermoelectric properties. We are currently investigating the substitution of lead in CsPb8Bi3Te20+δ by other elements such as silver, potassium, sodium, barium, strontium and calcium. We will present the new compound Cs87.5K0.75Bi3Te6. Single crystal X-Ray diffraction study indicated that this compound is isostructural to CsPbBi12Te6 (m = 1) with cell parameters a = 6.3810 (9) Å, b = 28.3263 (41) Å, c = 4.4134 (6) Å in the Cmcm space group. By analogy with CsPbBi12Te6, the formula of Cs87.5K0.75Bi3Te6 can be rewritten as (Cs87.46K0.54)2Bi3Te6. Preliminary electrical conductivity and thermopower measurements indicate n-type behavior. Further experiments aimed at preparing other analogs in the homologous series will be presented.


In this paper 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) 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/Bi system cast 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 CeOs4Sb12. 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 CeOs4Sb12 filled skutterudite. The energy bands show a semiconductor behavior with a forbidden energy gap of 0.45 eV. Strong hybridization among Ce-5d, with Os-5d, 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 CeOs4Sb12 as a candidate for thermoelectric applications.

F8.9 Characterization of Thermoelectric Power Generation Modules Made from New Materials. Jarrod L. Short, Jonathan D. Robles1, Michael A. Pajak1, Adam D. Deady and Edward Time1; 1Electrical and Computer Engineering Department, Michigan State University, East Lansing, Michigan; Chemical Engineering Department, Michigan State University, East Lansing, Michigan; 2Mechanical Engineering Department, Michigan State University, East Lansing, Michigan.

Lead-Antimony-Silver-Tellurium (L-A-S-T) materials synthesized at Michigan State University show promising thermoelectric 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 materials under high 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 Pajer2, Edward Timm2, Harald Schock2, Mercouri Kanatzidis2 and Timothy Hogan1; 1Electrical and Computer Engineering, Michigan State University, East Lansing, Michigan; 2Chemistry, Michigan State University, East Lansing, Michigan; 2Mechanical 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 and high electric field. Here we present new advances in the fabrication procedure and characterization of several contact materials including tungsten, antimony, tin, nickel, and a bismuth antimony based solders 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 20µΩcm2 were 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.


IHI is investigating application of thermoelectric conversion systems on the usage of natural heat for industrial use. 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 presented related to the mechanical characteristics, as well as a performance of module based on the heat transmission and thermoelectric conversion characteristic. The results from 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 Effect of Substitutional Doping on the Structural, Electronic and Thermal Properties of TiNiSn-Based Half-Heusler Compounds. J. Poem1, S. Culp1, N. Soroka2 and Terry M. Tritt2; 1Physics, University of Virginia, Charlottesville, Virginia; 2Physics, University of Kentucky, Lexington, Kentucky.

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 thermoelectric properties. Trends in the Seebeck coefficient, electrical transport and thermal conductivities in the temperature range 5 K to 800 K are examined as a function of chemical substitution on the various fcc sub-lattices. Discussion will be based primarily on substitutions on the Ti site with varying Zr and Hf concentrations which aim in controlling the lattice thermal conductivity and small amounts of Sn on the Sn site to control the power factor. Both Hf and Sn 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 shown 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 MnSiN (M=Hf,Zr) Single-Phase Thermoelectric Alloys Fabricated using Optical Floating Zone Melting. Yoshihato Kimura1, Tomoya Koji2, Akhisa Zama2, Yasufumi Shibata2 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; 3Higashifujii Technical Center, Toyota Motor Corporation, Suzuki, 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 around 1000 K. It is well known that Half-Heusler (M=Hf,Zr) alloys exhibit excellent thermoelectric properties, especially high Seebeck coefficient and low electrical resistivity. A drawback of relatively high thermal conductivity can be improved for instance by so-called non-ordinary effects through substituting the M site with Hf, Zr and Ti atoms as forming continuous solid solution. In the present work, we have focused on the fabrication of Half-Heusler MnSiN alloys (M=Hf,Zr) single-phase alloys, or alloys having almost similar 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,2x)Zr1-xNiSn alloys, where x width 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, Zr)NiSn alloys grown by OFZ exhibit tremendously excellent power factor, i.e., electrical figure of merit, ranging around 3.6 to 3.9 mW/m°K, 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, hot pressing and spark plasma sintering. It is interesting that HfNiSn alloy has quite high thermoelectric power exceeding 400 µW/K and that ZnNiSn alloy shows electrical resistivity lower than 50 µm at room temperature. In a temperature range from 700 to 1000 K, (Hf1-x, Zr)NiSn alloys exhibit about -230 µV/K of thermoelectric power and about 50 mW/m°K of electrical resistivity regardless of Hf and Zr concentrations ratio. Thermal conductivity of OFZ (Hf1-x, Zr)NiSn alloys strongly depends on the Hf and Zr concentrations ratio. The solid solution effect on lowering thermal conductivity is maximal at (Hf0.5, Zr0.5)NiSn alloys. Moreover, the thermal conductivity of (Hf0.5, Zr0.5)NiSn alloy is effectively lowered around 3 W/mK which is about half of the values of HfNiSn and ZnNiSn 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, such as Zn, Te, etc. In the present work, we have achieved a high ZT=0.9 based on simple Hf-Zr-Si-Ni quaternary alloy composition.

8:30 AM F9.3 Substitution effect on the thermoelectric properties of ZrNiSn based half-Heusler compounds. Hiroaki Mutai, Takahiro Kanemitsu, Ken Kuroasaki and Shinjiro Yamanaka; Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka, Japan.

ZrNiSn based half-Heusler compounds are prospective as n-type thermoelectric materials for middle range temperature utilization. The reported power factor was reached 3 mW/m°K at 600 K. However, the thermal conductivity was rather high as a thermoelectric material, thus substitutions for both Zr and Ni sites were tried to reduce the thermal conductivity. In this study, the substitution effects on the thermoelectric properties were investigated for quaternary phases: substitution of titanium for zirconium, palladium for nickel and silicon for tin. The samples were prepared by arc melting followed by spark plasma sintering (SPS) technique. Before SPS, the ingots were annealed at 700 °C for 12 hours. The electrical conductivity, the Seebeck coefficient, and the thermal conductivity were measured from room temperature to 1000 K. Small impurity phases were observed especially for titanium and silicon substituted samples. The phases were identified to hexagonal titanium-tin alloy and pure tin element from XRD analysis. All the samples showed n-type semiconducting behavior. Pure ZnNiSn had lowest electrical conductivity and largest Seebeck coefficient. The substituted samples generally followed Seebeck coefficients with higher electrical conductivity, indicating the carrier electrons were generated by the substitutions. The electrical conductivity increased with increasing the SPS temperature without the deterioration of the Seebeck coefficients. The result indicates high SPS potential of ZrNiSn desirable for the thermoelectric material. The maximum power factor was obtained for partially titanium substituted sample. The value reached about 4 mW/m°K at 700-800 K. Titanium and palladium substitutions effectively reduced the thermal conductivities. The calculated Debye temperature was similar for the samples, thus the
reduction was achieved by the impurity phonon scattering.

8:45 AM F9.4 Properties of Some Single-Crystalline Half-Heusler Alloys and Their Potential as High Temperature Thermoelectrics. Fivos K. Drymiotis, Amy Pope, Nicoleta Sorbacea and Terry Trit; Physics and Astronomy, Clemson University, Clemson, South Carolina.

Half-Heusler alloys are excellent candidates for high-temperature thermoelectrics. Although several members of those 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, polycrystallinity 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 thermal conductivity of the semiconductor is half that of the metallic sample. Small additions of V on the Ti site and Fe on the Co site drive the system to a semiconducting ground state. The metallic ground state though can be recovered with carrier density conserving equal additions of V and Fe. Our measurements indicate that short range disorder plays the dominant role in the transport behavior of this family of compounds. Single crystals allow us to control the amount of disorder more precisely than arc-melted samples by simply controlling the purity of the constituent elements and the cooling rates of the growths. We expect that the increase of electrical conductivity resulting from the decrease in short range disorder combined with a reduction in the thermal conductivity due to alloy scattering will result in increased thermoelectric performance.

9:00 AM F9.5 Extremely Low Thermal Conductivity Substances as Novel Thermoelectric Materials. Shinichi Yamanaka, Ken Kurosaki, Atsuko Kosuga, Keita Goto and Hiroaki Muta; Sustainable Energy and Environmental Engineering, Osaka University, Suita, Osaka, Japan.

Thallium compounds have been a focus of attention as new thermoelectric materials because they have very low thermal conductivities. We have prepared many kinds of thallium compounds and measured the thermal conductivities. The most remarkable point of the thermoelectric properties of thallium compounds is the extremely low thermal conductivity. The state-of-the-art thermoelectric materials such as BiTeI and TaGS materials indicate relatively low the thermal conductivities, around 1.5 W/mK. However, the thermal conductivities of our thallium compounds are below 0.5 W/mK. Especially those of silver thallium tellurides are around 0.25 W/mK at room temperature. These extremely low thermal conductivities lead a great advantage for thermoelectric materials. In this paper, we report on the properties of some kinds of thallium compounds selected for study as novel thermoelectric materials. One of these compounds seems to have a thermoelectric figure of merit comparable to those of state-of-the-art materials.

9:15 AM F9.6 Thermoelectric properties of Ti-X-Te (X=Ph, Sn, Ge) systems. Atsuko Kosuga, Ken Kurosaki, Hiroaki Muta and Shinshu Yamanaka; Sustainable Energy and Environmental Engineering, Osaka University, Suita, Osaka, Japan.

We recently focused the attention on Ti compounds due to their low thermal conductivity. In this study, some compounds of Ti-X-Te (X=Ph, Sn, Ge) systems were prepared by a solid-state reaction. The thermoelectric properties were evaluated by using the measured electrical resistivity, Seebeck coefficient, and thermal conductivity in the temperature range from room temperature to 700 K. The thermophysical properties such as Young’s modulus and Debye temperature were also evaluated at room temperature. All the samples show p-type conduction characteristics and have a large Seebeck coefficient. The dimensionless figure of merit of all the samples is comparable to that of the state-of-the-art materials due to their extremely low thermal conductivity (about 0.5 W/mK). It can be said that the compounds of Ti-X-Te (X=Ph, Sn, Ge) systems have a possible candidate as a good thermoelectric material.


We have studied the thermoelectric properties of thallium compounds as novel thermoelectric materials. Especially, we focus on the Ag-Ti-Te ternary semiconductor. In this paper, we report on a high performance thermoelectric material whose formula is Ag$_2$TlTe$_5$. We prepared a polycrystalline sample of the compound by melting the appropriate amounts of Ag$_2$Te and Tl$_2$Te in a sealed silica tube. The electrical resistivity (ρ), Seebeck coefficient (S), 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 3.8x10$^{-6}$ W/mK$^2$ at 700 K. Although its electrical performance is not very high, Ag$_2$TlTe$_5$ exhibits an excellent thermoelectric figure of merit because of its extremely low thermal conductivity (around 0.25 W/mK). Its highest ZT value is 1.23, obtained at 700 K. Ag$_2$TlTe$_5$ combines extremely low thermal conductivity and relatively lower electrical resistivity, making it a very interesting high-performance thermoelectric material.


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 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.


Tao He, Jiazhong Chen, T. Calverase, 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 rather high Seebeck coefficients and low thermal conductivities, with optimal operating temperature in the range of 600 - 800 K. Those materials are promising for applications in power generation.

11:00 AM F9.10 Synthesis and Thermoelectric Properties of Ce$_2$(Ru$_{1-x}$Ir$_x$)$_3$Sb$_2$ 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: PtTe/TaGS 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 Ce$_2$Ru$_{1-x}$Ir$_x$Sb$_2$ filled skutterudites compounds. We have synthesized polycrystalline samples for x = 0.5 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 Lovik and Johan Taft; Centre for Materials Science and Nanotechnology, University of Oslo, Oslo, Norway.

We acquire electron energy loss spectra of the binary skutterudites CoP$_3$, CoAs$_3$, CoSb$_3$ and NiP$_3$, and observe multiple narrow plasmon peaks similar to those previously observed for simple metals and semiconductors. While the metals tend to exhibit plasmon energies
slightly below the values derived from the free electron model [1], the experimental plasmon energies of semiconductors, and even more so of the skutterudites, are found to be above the calculated values. We attribute the increased plasmon energies of semiconductors and skutterudites to a reduced mass of the valence electrons that participate in the plasmon oscillations. This reduction more than compensates for the decreased plasmon energy caused by core polarization [2]. We furthermore investigate the complex dielectric function of the skutterudites through a Kramer-Kronig analysis of the low loss region of the EELS spectra [3] and first principle band-structure calculations. Our theoretical calculations are in good agreement with the experimentally determined dielectric function, successfully predicting their plasmon energies and serving as a valuable test of the first principle calculations. References [1] H. Haether, Excitation of Plasmons and Interband Transitions by Electrons, Vol. 88 of Springer Tracts in Modern Physics. Berlin: Springer-Verlag (1980). [2] D. Finot, Collective energy losses in solids, Rev. Mod. Phys. 28, 184-190 (1956). [3] B. F. Egerton, Electron Energy Loss Spectroscopy in the Electron Microscope. New York: Plenum Press (1986).

11:30 AM E9.12
The Synthesis and Characterization of CoS11.5Te1.5, CoGe1.5Se1.5, and Partially Filled CoGe1.5Se1.5.
Arwyn Smalley1,2, Qiyan Lin1, David C. Johnson1, Joshua Martin3, and George S. Nolas4; 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 CoS11.5Te1.5 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 lanthanides. 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 E9.13
Abstract Withdrawn

SESSION F10: Clathrates and New Measurement Techniques
Chair: Tim Hogan and David Johnson
Thursday afternoon, December 1, 2005
Room 151 (Hynes)

1:30 PM F10.1
The Dynamics of the Caged Guests in Filled Germannium Clathrates.
G. W. B. Hermann2, Ferras M. Granjeaud1,2, Pierre Keppe2, Werner Schweik2, George S. Nolas2, David G. Mandrus2, Brian C. Sales5, Hans M. Christen6, Pierre Bonville7, and Gary J. Long8; 1Dept of Physics, Universite de Liege, Liege, Belgium; 2Materials Science and Engineering, The University of Tennessee, Knoxville, Tennessee; 3Institut fuer Festkoerperforschung, Forschungszentrum Juelich, Juelich, Germany; 4Dept of Physics, University of South Florida, Tampa, Florida; 5Div Condensed Matter, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 6Service de Physique de I'Etat Condense, Centre d'Etudes de Saclay, Gif sur Yvette, France; 7Dept 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 NH3. In the filled gallium-germanium clathrates RaGa16Ge30, 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 guests is that they exhibit a localized vibrational mode, i.e. they behave like Einstein oscillators. Such a "trapping" 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-crystal. Inelastic neutron scattering and nuclear elastic scattering measurements have yielded the phonon density of states in RaGa16Ge30. 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 diffusion studies have shown 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. Each of such slow guest motion is challenging because the typical time and energy scales involved are ca. 4 ps and 1 µeV, respectively. We have studied the euryon dynamics by euryparticle-151 Mössbauer spectroscopy – a technique that presents the advantage of specifically identifying the behavior of the guests and we have measured the radio-frequency absorption in EuGa16Ge30. Both results indicate that the euryon atoms are tunneling with a frequency of 550 MHz, I. Sales B.C., Nolas B.C., Jin R., Thompson J.R., Mandrus D., Phys. Rev. B 63, 245113 (2001). 2. Nolas G. S., Kendziora C. A., Phys. Rev. B 62, 17517 (2000). 3. Zerec I., Keppe2ns V., McGuire M. A., Mandrus D., Sales B. C, and Thalmeier P., Phys. Rev. Lett. 92, 185502 (2004). 4. Keppe2ns V., Sales B. C., Mandrus D., Chakoumakos B. C., Laermanns C., Phil. Mag. Lett. 80, 907 (2002).

1:45 PM F10.2
Transport Properties of Type II Sodium-Silicon Clathrates.
Matt Beeman1, Jan Gryko2 and George S. Nolas1; 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 Na3,Si133 clathrates, where z 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.
Sarath Witanachchi1, P. Mukherjee2, H. S. Nagaraja3, R. Hyde4, M. Beeman5, H. F. Rubin2 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 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 pulsed laser ablation has been used 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 presented.

2:15 PM F10.4
Splitting of Guest Atom Sites and Lattice Thermal Conductivity in Ba-Ga-Ge Clathrate Compounds.
Norihiko O. Kaneto1, Katsuaki Tanaka1 and Haruyuki Imi2; 1Department 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 measured 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 non-anomalous 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 (ADPs$_{split}$) and the other is thermal jump among the split sites. Upon alloying with Ga, values of lattice thermal conductivity of type-I and -II compounds decrease 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 ADPs$_{split}$ based on the single-site model does not predict how lattice thermal conductivity is reduced. Values of ADPs based on the split-site model (ADPs$_{split}$) for both type-I and -III compounds decrease with the increase in the Ga content, indicating that the value of ADPs$_{split}$ based on the split-site model does predict how lattice thermal conductivity is reduced. 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, Ryooyuki Takara, Katsuki Tanaka and Haruyuki Inui; Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan.

Intermediate 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, $M_{12}$X$_{48}$ (M=allali or alkali earth metals, X=Si, Ge), are composed of two kinds of cage structures designated $T_{16}$ and $X_{20}$-dodecahedron whereas type-III clathrate compounds, $M_{24}$X$_{100}$, 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-III 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 electric 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 Rajvee 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 can be used to measure the equilibrium temperature 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 data we are aware of for BiTe-based material systems. Identification and separation of the Pettier and Joule components of the heating are possible, and finite difference simulations of the devices are presented for comparison with experiment. Finally, it is possible to extract 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] D.Lueken, J. Huddles, P. Mayer, R.J. Ram. "Non-Scale Thermoreflectance With 10 mK Resolution Using Stochastic Resonance" *, Semitherm, 15-17 March 2005

3:30 PM F10.7 A new transmission line theory for modeling of a thermoelectric module in multiple configurations for AC electrical measurement. Darryl Downey, David L. Hogan, Edward Tunn, John Androulakis, Eric Queroz, Ferdinand Poulen, Mercouri G. Kanatzidis and Harold Scoheck; 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 resistance. 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 electronic circuits for both the thermal and electrical aspects of the module. Measurements were taken over the frequency range of 1mHz to 500Hz using lock-in amplifiers. We present data showing the extrapolation 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 fits of the electrical resistances, the Seebeck 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 a 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 pn unipolar 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. Anastassios Pavyvakolas, Jianhua Zhou, JaeHun Se0, Feng Zhou, Michael Thompson Pettette, Li Shi, Chuanqi Jin and Xiaoguang Li; 1 Mechanical Engineering & Center for Nano and Molecular Science and Technology, University of Texas at Austin, Austin, Texas; 2 Department 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=α^2S^2/kT, where S is the Seebeck coefficient, α is the electrical conductivity, k 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 single 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 consists of two suspended membranes each suspended by six 400-800 μm 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 measured on the suspended device [4]. A through 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

A scanning hot probe technique was developed for thermoelectric transport measurements of films. In this method a resistively heated Wollaston wire thermal probe 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 probe temperature rise of the film. The Seebeck voltage is 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 1-5nm diameter and rod-shaped rhombohedral nanocrystals of 20- to 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 nanocrystalline 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 Microscopic Tip in the Tunneling and Contact Regimes. Calo Fidalgo, Li Shi, Sarah Burch and Feng Zhou; Mechanical Engineering, University of Texas, Austin, Texas.

In 1999, 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, Stonveng and Lipavsky [2] proposed a model based on Bardeen’s formula for tunneling current and Tenneoff and Hanonoff’s approximations to predict the tunneling thermovoltage as

\[ V = \frac{2\pi kT}{2(\Phi/2)\xi} + \frac{h(2m/\Phi)}{2}\xi/S(\text{y}) \]

where subscripts t and s denote the tip and sample, respectively, e is the electron charge, \(\Phi\) is the local electronic density of states at the electron energy, \(\xi\) is the tip-sample separation, \(m\) is electron mass, \(h\) is Planck’s constant, and \(S\) 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] has 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 using the AFM. 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 gradient. The temperature of the sample lead 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., \(V(x,y) = \frac{S(x,y)T(x,y)}{2}\) (where \(T(x,y)\) 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 on investigations of the tip-sample thermovoltage 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] Stonveng, J. A. and Lipavsky, P. Phys. Rev. B 42, 9214 (1990). [3] Lyco, H. K. et al. Science 303, 816 (2004).


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 Seebeck 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 in this case, 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 half 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 the 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 porous 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 Hu3, Ling 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 spreading 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 films of Sodium and Cobalt cathodes on various substrates, including polycrystalline and (0001) sapphire, (100) and (111) Siliccon 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.
E1.1.2 Thermoelectric properties of cubic perovskite-type manganese oxides. Yasushi Inamura, Hironari Mutu, Ken Kurosaki and Shinusuke Yanamasa; 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$_3$ were investigated. This compound takes on a hexagonal structure by the ordinal synthesis method in air. By sintering perovskite oxides at different sintering temperatures, the thermoelectric properties of the cubic structure because of the oxygen deficient. Polyctralline Sr$_{1-x}$La$_x$MnO$_3$ and Sr$_{1-x}$Ni$_x$O$_{3-x}$ (x = 0, 0.05, 0.1) were synthesized by solid state reaction of two-step method. In first step, oxygen-deficient Sr$_{1-x}$La$_x$MnO$_3$ and Sr$_{1-x}$Ni$_x$O$_{3-x}$ were obtained by sintering at 1500 °C in Ar 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 were thermal conductivity 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. No impurity phase was observed in the X-ray diffraction pattern for all the samples. We confirmed that the non-annealed and annealed samples had cubic structure. The doping of La and Nb increased slightly the lattice parameter. The electrical conductivity improved, which increasing the La and Nb content and temperature. As for La-doped system, the Seebeck coefficient was negative in whole temperature range, which indicated n-type conduction characteristic of samples. The electrical conductivity of the annealed sample was higher than that of non-annealed sample and appeared to be independent of the temperature. The absolute value of Seebeck coefficient for annealed samples was higher than that of non-annealed samples which had a large amount of oxygen deficient. The resistivity in this carrier gas and annealed gas was lower than that of the carrier gas and the non-annealed sample system by increasing annealed. The value was about ten times higher than that for the non-annealed samples.

E1.1.3 Fabrication of Grain-Aligned Bulk and Thick Films of Misfit Layered Cobalt Oxides by a Magneto-Scientific Process. Shigeru Horii$^{1}$, Taichi Okamoto$^{1}$, Toshiaki Kumagai$^{2}$, Tetsuo Uchikoh$i^{3}$, Tōhru Suzuki$^{4}$, Yosioh Sakada$^{5}$, Jun-ichi Shimoyama$^{6}$ and Kohji Tada$^{6}$; Division of Applied Chemistry, University of Tokyo, Tokyo, Japan; $^{1}$NIMS, Tsukuba, Japan.$^{4}$

Misfit layered cobalt oxides, Ca$_3$Co$_4$O$_7$ (Ca348) and Bi$_2$Sr$_2$Co$_2$O$_{y}$ (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 for practical point of view. In order to improve the functionality, one can recognize that useful processes are grain-orientation 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 Ca348 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 Ca348 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. We additionally measured the power output of magnetization from a-axis to c-axis by a crystallochemical process in BiSr222 with the easy axis along the a-axis for magnetic c-axis alignment.

E1.1.4 Power Factor of Sr Doped LaCoO$_3$. Kouta Iwasaki$^{1}$, Tsuyoshi Itoh$^{2}$, Masahito Yoshino$^{3}$, Tsuneo Matsui$^{4}$, Takaroni Nagasaki$^{2}$ and Yuji Arita$^{5}$; Department of Materials, Physics and Energy Engineering, in Ar atmosphere, Nagoya University, Nagoya, Japan; $^{1}$Kakusho Science Institute, Nagoya University, Nagoya, Aichi, Japan.

LaCo$_3$O$_7$ has perovskite structure consisting of corner-sharing CoO$_6$ octahedra. Sr-doped LaCoO$_3$ (La$_{1-x}$Sr$_x$CoO$_3$) has been reported to exhibit high power factor more than $10^{-3}$ Wm$^{-1}$K$^{-2}$. The thermoelectric properties of (La$_{1-x}$Sr$_x$CoO$_3$) are of interest, however, the relation between the power factor and carrier density has not been investigated. In this study, polycrystalline (La$_{1-x}$Sr$_x$CoO$_3$) $[0<\leq x \leq 0.09]$ were prepared by a solid state reaction in air, and the electrical conductivity, Seebeck coefficient and the power factor were investigated. La$_2$O$_3$ (4N) and Co$_2$O$_3$ (4N) were used as starting materials. These powders were weighed with the appropriate amounts (the metal ratio was La: Sr=1:2:1:1). The powders were mixed and pressed into a pellet form. The pellet was heated at 1273 K for 20 h in air. The samples were ground and reheated 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 calculated by the least square fits. The slope of the power factor of the 30K temperature difference $\Delta V$ (temperature electromotive force), and the contribution of load wires (Pt) was subtracted. The electrical conductivity $\sigma$ of (La$_{1-x}$Sr$_x$CoO$_3$) $[0<\leq x \leq 0.09]$ increased with increasing Sr content, and showed semiconducting behavior below 700 K. Seebeck coefficient $S$ of (La$_{1-x}$Sr$_x$CoO$_3$) was positive at 0.01 $\leq x \leq 0.05$ and decreased with increasing Sr content. On the other hand, Seebeck coefficient of La$_2$O$_3$ was negative below 350 K. The power factor $(\rho\sigma^2)$ of (La$_{1-x}$Sr$_x$CoO$_3$) showed the maximum value below 350 K and tended to decrease with increasing temperature above 650 K. The highest value of the power factor was $3.1 \times 10^{-4}$ Wm$^{-1}$K$^{-2}$ 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.

E1.1.5 Synthesis and Thermoelectric Power Factor of LCSO Perovskites. Julio E. Rodríguez, Department of Physics, Universidad Nacional de Colombia, Bogota, Colombia.

Measurements of Seebeck coefficient, S(T) and electrical resistivity, \(\rho(T)\) on polycrystalline La$_{2-x}$Sr$_x$CuO$_{4+y}$ (LSCO) (0.5$\leq x \leq$0.2) 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 800 $\mu$V/K for the samples with the highest Sr 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 $10^{-2}$ to $10^{-3}$ cm. From the S(T) and \(\rho(T)\) measurements the thermoelectric power factor, PF was obtained. The maximum values for PF were about 25 mW/K$^2$cm in the samples where $x=0.03$, 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, respectively. The behavior of transport properties opens the possibility of considering this family of perovskites as a thermoelectric material that work below room temperature.

E1.1.6 Fabrication and Properties of Thermoelectric Generator with Half-Heusler Compounds. Shinya Sakurada$^{1}$, Naoki Shuto$^{2}$, Shinusuke Hiroto$^{3}$ and Masami Okumura$^{4}$; $^{1}$Corporate R&D Center, Toshiba Corporation, Kawasaki, Kanagawa, Japan; $^{2}$Development Dept., Toshiba Materials Co., Ltd., Yokohama, Japan.

Half-Heusler compounds with the cubic MgAgAs-type structure have become of interest due to these material as thermal power generators. Previously, we have investigated the effect of Ti substitution on the thermoelectric properties of (Zr, Ti)Ni(Sn)Nb and revealed that substitution of Ti for (Zr, Ti)Ni(Sn)Nb significantly reduced the thermal conductivity, and increased the Seebeck coefficient. Moreover, it was also found that Sn doping at Sn sites reduced the electrical resistivity and enhanced the power factor correspondingly. The combination of the low k and high power factor resulted in a high ZT value. A maximum ZT value of 1.5 was achieved at 700 K for Zr(Ti, Zr)NiSn(Sb). 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, half-Heusler compounds, Xia et al. have investigated ZrCoSb-based compounds and obtained an 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)(Sb,Sn) compounds. In this study, we investigated the thermoelectric properties of (Zr, Ti)CoSb compounds with three kinds of p-type dopants, namely Er, Fe, and Sn at the (Zr, Ti), Co, and Sb sites, respectively. The thermoelectric measurements were conducted at 300-773 K. Undoped (Zr, Ti)CoSb shows ZT=$\sim$0.01 at 300-773 K and for this compound is about 160 m cm at 700K. In contrast, when the doping concentrations are 5 at. %, (Zr, Ti)CoSb(Sb,Sn) exhibits n-type behavior with an a 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 ($\rho/\sigma$)$\sim$3500 S/m(350 S/m) at 300 K, a of $+0.31$ mV/K, a r of 2.8 m cm, and a k of 2.7 W/mK, corresponding to

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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 ternary half-Heusler module. 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)HfCo(Sb,Sb) and (Ti,Zr)HfNi(Sb,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 T_h = 823 K (temperature at the surface where heat is supplied) and T_c = 445 K (temperature difference between the two surfaces).

### F11.7 Effects of SPS Condition on Thermoelectric Properties of ZrNiSn Based Half-Heusler Compounds

Takamori Kanemitsu, Mutsuo Yosaka and Shinya Yamanaka

Recently, extensive studies have been carried out on ZrNiSn 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 nonstoichiometry in the compounds. In this study, the effects of sintering condition on thermoelectric properties were investigated. The samples of Zr_{0.5}Tio_{3}Sn and Zr_{0.5}Tio_{5}Sn were prepared by spark plasma sintering (SPS) technique. SPS was conducted in the range of 1273-1473 K 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 ultrasonic measurement as an indirect means of diagnosing 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, higher power factor was obtained for the sample sintered at high temperature. The value for Zr_{0.5}Tio_{3}Sn sintered at 1473 K was larger than that of pure ZrNiSn, reached 4 mW/mK above 800 K. There were no impurity peaks in XRD patterns, however, the peaks of half-Heusler compound were broad for the annealed sample. The peaks of the sample sintered at high temperature were sharper than those of the only-annealed sample. SPS at high temperature appeared to be effective for preparation of pure crystalline samples. The thermal conductivity of substituted samples was lower than that of the pure ZrNiSn. The value for Zr_{0.5}Tio_{5}Sn prepared by SPS at 1473 K was 5 W/mK, about a half of the pure ZrNiSn. 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 Zr_{0.5}Tio_{3}Sn sintered at 1473 K was about 0.48 at 900 K.

### F11.8 Thermoelectric Properties of Bi_{1.2}Sr_{1.2}Co_{1.2}O_{4+δ} Tellurium-Doped Single Crystal Whiskers

X. Tang, K. Aaron, T. M. Tritt, D. Bourne, J. Barnes and J. Payne

Clemson University, Clemson, South Carolina

Long single crystal whiskers were synthesized using tellurium-doped precursors. The length of these whiskers varies from less than 1mm to 9mm. The thermopower and resistivity were found to be 148V/K and 5mΩcm respectively at 325K. Thermoelectric power was measured using a differential technique, while resistivity was measured by a standard four-probe method.

### F11.9 Thermoelectric and Structural Properties of the Ba_{2}Zn_{3}Cu_{3}O_{7-δ} Solid Solution

Winnie Kwai-Wah Wong, N.G., Yufeng Hu, Zhi Yang, Qiang Huang, Li Qiang and Martin Green

1 Ceramics Division, NIST, Gaithersburg, Maryland; 2 Reactor Division, NIST, Gaithersburg, Maryland; 3 Applied Science, BNL, Upton, New York.

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. This paper examines the effect of substitution of Cu in the layered perovskite, Ba_{2}Ni_{2}CuO_{7-δ}. The polycrystalline Ba_{2}Zn_{3}Cu_{3}O_{7-δ} (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 Ba_{2}Zn_{3}Cu_{3}O_{7-δ} 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 Ba_{2}Zn_{3}Cu_{3}O_{7-δ} 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 different sites in the Ba_{2}Zn_{3}Cu_{3}O_{7-δ} structure. This work demonstrates the importance of understanding the structural and electronic properties of these materials for their application as thermoelectric devices.

### F11.10 Thermoelectric Properties of Polycrystalline Si_{1-x}Ge_{x} (x=0.4-0.7) by Die-Casting Vertical Bridgman Growth Technique

Takashi Baba, Tsutomu Iida, Hisashi Hiraara and Yoshishimi Takamori

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Alloys of silicon and germanium (Si_{1-x}Ge_{x}) are ecologically friendly semiconductors and important materials not only for microelectronic devices but also for solid-state energy devices 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, Si_{1-x}Ge_{x} with x=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 Si_{1-x}Ge_{x}, we applied a die-casting growth technique combined with an advanced version of the Bridgman method. The grown samples were coin-shaped Si_{1-x}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 Si_{1-x}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, we evaluated the dimensionless figure of merit, ZT, for the grown Si_{1-x}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

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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 and in high temperature resistance, 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-CH4-H2 gas mixture, in an impinging jet CVD reactor. The impingement on the substrate surface is important in minimizing the effect of many random limitations on the reaction rates. The chemical analysis of the reactor outlet stream was done by FTIR and formation of BHC12 and HCl 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 BHC12 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.
Magnesium silicide (Mg2Si), 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 power generation is the vanishing thermoelectric power of Mg2Si likely is to be slightly lower, but it is still believed to be adequate for realizing thermoelectric power generation. Due to its environmentally friendliness, Mg2Si also provides safe handling and device electrical use. At the stoichiometric Mg2Si, the conditions for growing high-quality and single crystals are required to achieve more efficient thermoelectric conversion. The Mg2Si crystal growth was derived from a congruent melt that was initiated from the stoichiometric Mg2Si powder. A conventional vertical Bridgman method was used for the growth. For Mg2Si, the grown crystals were single-crystal and showed n-type conductivity in undoped condition. Although the high reactivity of molten or vapor Mg2Si at elevated growth temperatures resulted in sticking of the melt Mg2Si to the crucible material and increased contamination of the grown ingot, a use of highly pure crucible materials and purification of the source Mg metal brought about a lower level of the unintentional impurity doping from contaminants. Under this growth condition, a systematic incorporation of carbon was performed to form Mg2Si-C. An intentional carbon incorporation in the grown crystals formed resulting in an increase in the Seebeck coefficient and the power factor, as compared with the sample with no carbon doping. The highest power factor obtained was 1.1 x 10⁻⁶ W/cmK² at 373 K when the composition x=0.03. We present the effects of carbon incorporation into Mg2Si in terms of the thermoelectric properties by measuring the Seebeck coefficient, electrical conductivity, and the thermal conductivity.

F11.17
Thermoelectric Properties of Mg2Si-Cr Crystals Grown by the Vertical Bridgman Method. Masanori Higuchi, Tutomu Iida, Kenichiro Makino and Yoshinori Takahashi; Materials Science and Technology, Tokyo University of Science, Noda, Japan.

Center, Akita, Japan.

Zinc oxide and the related materials have been studied as a candidate for high performance thermoelectric materials. Although it is known that Al-doped ZnO shows fairly high potentiality at high temperatures around 100 K, further development in property of this system is required for practical purpose. In this study, we investigated the effects of doping of rare-earth ions (Ce, Pr, Nd, Sm, and Er) on the thermoelectric properties of ZnO, especially Seebeck coefficient. The samples were prepared by a wet sol-gel process: mixed aqueous solutions of zinc acetate and rare-earth metal chlorides with the molar ratio of 0.4 % was hydrolyzed at room temperature; the recovered mixed hydroxide was washed and calcined at 500 °C, followed by sintering at 1400 °C for 10 hrs. The Seebeck coefficient and electric conductivity were measured in the temperature range from 100 °C to 300 °C. For reference, Al-doped ZnO samples with Al content of 0.1 - 0.4 % were also prepared and measured in the same way. The data were scattered more or less depending on the doping species, but it was confirmed that the rare-earth doped samples showed higher Seebeck coefficients with compared to those for Al-doped samples. The highest values were observed for Nd-doped ones ranging from -360 to -4000 μV/K, in the temperature range observed, the values for Pr-doped ZnO were twice or more as much as that for Al-doped one. Further results at x=0.01 and 0.02 doping is effective for enhancement of thermoelectric power of ZnO.

F11.14
Thermal Conductivity of Novel Rare Earth Boron-Rich Cluster Compounds. Takeo Mori, National Institute for Materials Science, Namiki 1-1, Tsukuba 305-0044, Japan.

Boron-rich cluster compounds are attractive materials for their stability under high temperature and unfriendly (e.g. acidic) environments. Magnetic properties of some rare earth boron cluster compounds have recently attracted increasing interest, being magnetically dilute, insulating/segregating materials but displaying a wide range of properties with relatively strong magnetic coupling. Interestingly, it has been indicated that the B4<sub>x</sub>C<sub>10</sub>icosahedral clusters play an important role in mediating the magnetic interaction which is a novel phenomenon. Boride compounds such as the well known metal-doped β-boron have been previously investigated as possible thermoelectric materials and used in catalysis and energy conversion applications [1] and we have recently shown that the rare earth boride REB<sub>4</sub>S<sub>12</sub> appears to be a promising system at high temperatures [2]. Boron cluster compounds have generally exhibited low thermal conductivity [3], actually exhibiting a glass-like conduction for the boron cluster compound, for example. In this work, the thermal conductivities of the recently discovered rare earth boron cluster compounds are investigated in detail. The framework of these rare earth boron cluster compounds is basically composed of boron clusters while heavy rare earth atoms reside in spaces among the clusters, and we note that they have substantially lower thermal conductivities compared to simple β-boron. REB<sub>4</sub>S<sub>12</sub> has a similar low thermal conductivity to the YB<sub>4</sub>Nb<sub>12</sub> system, which is approximately 27 W/mK and the temperature dependence of thermal conductivity at high temperature is approximately 300 K, while boron metal actually decreases α by 200 K. Effects on the other thermoelectric properties will also be discussed. This work was supported by the Japan Science and Technology Agency. [1] T. Mori and A. Leith-Jasper; Phys. Rev. B 66 214119 (2002), [2] T. Mori and H. Mamiya, Phys. Rev. B 68 214422 (2003), [3] T. Mori, J. Appl. Phys. 98, 73021 (2004). [4] W. Bercht, R. Schoenel, V. Fuef, and T. Lundstrom, J. Alloys Comp. 262-263, 372 (1997), T. Nakayama, J. Shimizu, K. Kinuma, J. Solid State Chem. 154 13 (2000); [3] T. Mori, J. Appl. Phys. 93, 065703 (2005). [5] E. G. Cahill, H. E. Fischer, S. R. Woodson, R. J. fulfil, J. S. Sanders, J. Appl. Phys. 80 3254 (1998).

F11.15
Effect of Rare-Earth Cation Doping on Enhancement of the Thermoelectric Power of Zinc Oxide. Kiyoshi Fuda and Seikosuke Sugiyama; 1 Akita University, Akita, Japan; 2 Akita Pref. Ind. Tech. Center, Akita, Japan.

Radiosotope 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/TAGS and SiGe. Reducing mass and improving the efficiency of power generation are of great interest to RTGs would further expand their potential for space applications. A straightforward way to improve the efficiency is to use advanced thermoelectric materials with higher ZT values than those of state-of-the-art PbTe/TAGS and SiGe alloys. This paper will review the various requirements that advanced materials should meet both in terms of thermoelectric and physical properties to be potential candidates for integration into future generation of RTGs. In particular, the temperature stability constraints will be described as well as typical methods for minimizing sublimation of thermoelectric materials at high temperatures of operation. The development status of advanced thermoelectric materials and unicouples at the Jet Propulsion Laboratory (JPL) will be summarized. To date, a maximum conversion efficiency of ~14% has been demonstrated for a skutterudite/Bi2Te3 unicouple operating at a hot-side temperature of 975 K and a cold-side temperature of 300 K. This result fully validates the predicted unicouple performance based on the thermoelectric properties of the materials used in the unicouple. Progress made in the fabrication, characterization, performance and lifetime materials and unicouples testing will be reported. 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 1275 K. Refractory skutterudites such as CeH<sub>x</sub>Fe<sub>12</sub>Cr<sub>12</sub>Si<sub>12</sub> and CeRu<sub>x</sub>Si<sub>3</sub> are among the materials being studied. Transport properties for polycrystalline samples and the potential of these materials for thermoelectric power generation will be presented and discussed.

F11.22
Aerogels for Thermoelectric Power Systems. Jong-Ah Paik, Steven M. Jones, Jean-Pierre Fleurler, Thierry Caillet and Jeffrey S. Sakamoto; Jet Propulsion Laboratory, Pasadena, California.

Aerogels with high porosity and tortuous pathway exhibit the most promising results as a thermal insulation or sublimation suppression layer for thermoelectric power systems. Sublimation phenomenon of thermoelectric materials is one of major causes for the degradation of thermoelectric materials. Therefore, thermoelectric power systems need some sublimation barriers in order to maintain the efficiency of
thermoelectric devices and prevent contamination of sublimed materials during operation. Silica gels in JPL were synthesized with a two-step p-process: a tetranitrite as a metal and the resulting nitride dried in an acetonitrile supercritical 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 aerogel, 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 $>1000$g/cc). It is noted that the higher the aerogel coating density the greater the reduction in sublimation suppression. Preliminary results with pure SB at 500 oC indicated that this composite aerogel can suppress SB sublimation by as much as 10,000 times. We also investigated the thermal stability of aerogel at high temperature. Aerogels exhibit around 10% linear shrinkage in the beginning of 1000 oC isotherm and become stable without further shrinkage for more than 200 hrs. The shrinkage in the beginning of isotherm was determined to be significant by using a technique in vacuum. Together, we are reporting a novel process, which will offer substantial improvements over the processing used to integrate aerogel into thermoelectric technology. This process will enable casting of high density aerogels without cracks and offer improved sublimation suppression in practically all thermoelectric technologies used for power generation.

8:45 AM F12.5
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 test 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 3000K and 9000K will have a conversion efficiency of approximately 17%. Effort is continuing to improve the preliminary test 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 Quarze, John Andoulakis, Pierre F. P. Fouled, Harold J. Schock, Tom Shih and Mercouri G. Kanatzidis; 1Department of Chemistry and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Illinois; 2Department of Chemical Engineering and Materials Science, University of California at Santa Barbara, California; 3Materials Department, University of California, Santa Barbara, California; 4Department of Electrical and Computer Engineering, University of California, Santa Barbara, California.

High efficiency thermoelectric modules are of great interest for power generation applications where hot side temperatures 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 elements, and constant feedback from the characterization. Pb-Sb-Ag-Tc 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 antimony we have achieved contact resistivities less than 20 $\mu$-ohm-cm. Here we give a detailed presentation on the procedures used in the fabrication of thermoelectric generators based on these 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, Yoichi Mihara, Manabu Hirai, and Naoki Nabe, National Institute of Advanced Industrial Science and Technology, Ibaraki, Osaka, Japan; CREST, Japan Science and Technology Agency, Saitama, Japan; 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 at high temperature. $Ca_2Cu_4O_9$ (Co-349) with a layered structure is a good p-type thermoelectric compound at high temperature in air. Moreover recently, perovskite LaNiO3 (Ni-113) has been reported to show negative Seebeck coefficient (S) and low resistivity ($\rho$) values. Different versions of thermoelectric unicouples composed of Co-349 and Ni-113 bulks were prepared. In the unicouples p- and n-legs are connected using Ag paste. Open-circuit voltage ($V_c$) of the unicouples reaches 100mV at a hot-side temperature ($T_H$) of 1073K and a temperature difference ($T_H - T_C$) of 500K in air. Internal resistance ($R_{int}$) can be suppressed to 14m$\Omega$ at $T_H$ of 1073K in air and decreases with increasing temperature. Maximum output power ($P_{max}$) increases with $T_H$ and reaches 17mW at $T_H$ of 1073K ($\Delta T = 500K$). This corresponds to a volume power density of 0.01W/cm$^3$. A small thermoelectric module consisting of 140 couples were fabricated using the same method with the unicouples. We show how power can be generated using a small thermoelectric module composed of 140 pairs of Co-349 and Ni-113 unicouples. The weight of 19.8 g and dimensions of 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 $V_c$ increases with increasing hot-side temperature ($T_H$) and reaches 4.5 V at a $T_H$ of 1072 K in air. No deterioration in output power was seen when power generation was carried out ten times at a $T_H$ of 723 K with intermediate cooling to room temperature. The module was successfully used to charge a lithium-ion battery in a mobile phone.

9:30 AM F12.6
ErAs/InGaAs superlattice thin film power generator.
Gehong Zeng, Jie-Hyeong Bahk, John E. Bowers, Joshua Zide, Arthur Gossard, Yan Zhang and Ali Shakouri, 1Department of Electrical and Computer Engineering, University of California, Santa Barbara, California; 2Materials Department, University of California, Santa Barbara, California; 3Engineering 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 couples of ErAs/InGaAs superlattices elements, which were grown on InP substrate using molecular beam epitaxy. The elements are 5 $\mu$m thick and 200 $\mu$m x 200 $\mu$m large in size. There are a total of 400 thermoelectrical elements that are packaged within 650 $\mu$m thick AlN plates via flip-chip bonding. The output powers over 0.5 milliwatts were measured at 255K temperature difference across the whole device package. Simulations show that the output power density can reach up to 1W/cm$^2$ whereas with a heating source at 700K and heat sink temperature at 350K.

9:45 AM F12.7
Thermal Diodes for Heat-to-Electricity Conversion.
Yan Kucherenko, Peter Hagelstein, Victor Sevstyanenko, Harold Brown, Sivaraman Guruswamy and Deepak Thimmegowda, UNESCO, Inc., Salt Lake City, Utah; MIT, Cambridge, Massachusetts; University of Utah, Salt Lake City, Utah.

A few years ago we introduced a new type of energy converter based on barrier layers on thermoelectric materials. Efficiencies exceeding 40% of ideal Carnot cycle were demonstrated experimentally, but the understanding of underlying physics lagged. Only recently it reached acceptable level. We will present dependence of thermal diode performance on materials, barrier shape, carrier scattering length.

10:00 AM CLOSING REMARKS