SYMPOSIUM F

Materials and Technologies for Direct Thermal-to-Electric Energy Conversion

November 28 - December 2, 2005

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SESSION F1: Thermoelectrics Research Directions & Oxides I
Chairs: Terry Tritt and Jihui Yang
Monday Morning, November 28, 2005
Room 313 (Hynes)

8:00 AM OPENING REMARKS

8:15 AM *F1.1
New Directions for Nanoscale Thermoelectric Materials Research. Mildred S. Dresselhaus[1,2], Gang Chen[3] and Zhifeng Ren[4]; [1]Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; [2]Physics, MIT, Cambridge, Massachusetts; [3]Mechanical Engineering, MIT, Cambridge, Massachusetts; [4]Physics, 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 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 matrix 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 ZrNiSn-based alloys, the thermal conductivities of the materials are depressed significantly. The obtained value of ZT can be as high as 0.7 at 800K. 3) Bi2Te3-based materials with preferred grain orientation have been prepared by Spark Plasma Sintering technique to get materials with good thermoelectric performance as well as excellent mechanical properties for industrial processing. Bending strength as high as 80MPa can be obtained in our laboratory. 4) A novel structure of 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-fiber structure has been fabricated, showing 20 times 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 Near Term to Far Term Potential for High Efficiency Thermoelectric Applications. John Fairbanks, Office of Energy Efficiency and Renewable Energy, US Department of Energy, Washington, District of Columbia.

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 this 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 fuel energy winds up as engine output shaft work. Roughly 55 percent is lost as waste heat including the cooling losses. The primary approach to gain useful work from this waste energy is using high efficiency thermoelectric generators (TEG's). Potential TEG applications include the engine's radiator, lube oil cooler, exhaust gas path, exhaust gas recirculation (EGR) loop, compressor discharge air (engine intake air) and braking. These TEG's provides electrical power which is readily mated with either the "beltless engine concept", wherein all accessories are electric motor driven, or the integrated alternator/motor/starter/damper (ISMAD) 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 compressed gas refrigeration 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 conditioned cars since 1996 is R-134a which has 1300 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, Powertrain, 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. Only in the past 50 years has this technology found its way out of the laboratory and into niche military, space, and commercial products. Most of the profitable commercial products have made their appearance in the past decade. Many of you are working hard to advance the state of the art in thermoelectric materials, and I am sure that you do not want to wait another 180 years, 50 years, or even another decade to commercialize your results. There are many potential ways to commercialize this technology, but the area that I think represents the biggest market is the automotive industry. 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, quantity, and value needed to commercialize thermoelectric technology. Timing to introduce subsystems with this technology is also addressed. Thermoelectric technology has to compete with the existing technologies and other emerging technologies to be successfully commercialized. While it seems out of reach today, there is even the potential that sufficiently advanced thermoelectric materials and device construction could one day replace the internal combustion engine and even rival fuel cells in energy conversion efficiency.

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

There is a growing interest in exploiting charges and spins in cobaltates ($A_xCo_yO_2$) for potential thermoelectric (TE) applications. Cobaltates are oxides in which the Co ions define a layered triangular lattice. At 0 K, the spins remain in a disordered 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.[1] The correlation between the TE properties of an interacting electron system and its effective dimensionality is explored. We demonstrate a successfully growth of c-axis orientated $Ca_3Co_4O_9$ thin films with high thermoelectric power on a variety of substrates, including commercial silicon wafer[2] and glass, which offers the promise of using available state-of-the-art silicon fabrication technology for potential

electronic applications. We describe a few approaches we use to synthesis bulk aligned cobaltates, as well as other oxides for TE applications. Furthermore, we discuss the need of a model, which may have to step beyond the conventional Fermi-liquid theory, in order to explain many exotic behaviors of cobaltates. In collaboration with Y. F. Hu, T. Valla, W. D. Si, P. Johnson, A. Moodenbaugh, and E. Sutter 1) T. Valla, et al, Nature **417** 627 (2002). 2) Y. Hu, W. D. Si, E. Sutter, and Q. Li, Appl. Phys. Lett. **86** 082103 (2005).

11:15 AM F1.6
First Principles Study on Sodium Ordering and its Relation to the Electronic Properties of P2-NaxCoO2 Thermoelectrics.
Ying Shirley Meng[1], Maria K. Y. Chan[1], Anton Van der Ven[2] and Gerbrand Ceder[1]; [1]Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]University of Michigan, Ann Arbor, Michigan.

The unusual electronic properties of NaxCoO2 make it a material of considerable interest. Over a large range of sodium compositions, the system displays an unusual combination of high Seebeck coefficient and low metallic resistance [1]. For low sodium content the hydrated form of the material is superconducting [2]. NaxCoO2 is also an interesting material on which to test our basic understanding of mixed valence transition metals. NaxCoO2 is a mixed valence system with a fraction x CoIV and (1- x) CoIII ions. Because of the high mobility of Na and large vacancy concentration, Na-vacancy ordering is likely in NaxCoO2. This ordering breaks the symmetry on the Co sublattice and may assist in charge ordering of CoIII and CoIV . Mixed CoIII/CoIV systems tend to display rich physics as they are often close to spin transitions and metal insulator transitions, as have been demonstrated in LixCoO2 [3, 4]. Given the potential coupling between the Na-vacancy ordering and the electronic structures, it is important to accurately establish the structure of this material. In this study, we use both standard Density Functional Theory (DFT) in the Generalized Gradient Approximation (GGA) as well as GGA U calculations to investigate the possible Na-vacancy and charge-ordered structure of Na0.75CoO2. We also discuss the electronic/magnetic behavior of the system, which is crucial for understanding the thermoelectric properties of this material and similar mixed valence oxides. References: 1 I. Terasaki, Y. Sasago, and K. Uchinokura, Physical Review B 56, 12685 (1997). 2 K. Takada, H. Sakurai, E. Takayama-Muromachi, et al., Nature 422, 53 (2003). 3 C. A. Marianetti, G. Kotliar, and G. Ceder, Nature Materials 3, 627 (2004). 4 M. Menetrier, I. Saadoune, S. Levasseur, et al., Journal of Materials Chemistry 9, 1135 (1999).

11:30 AM F1.7
Cobaltites as perspective thermoelectrics.
Jiri Hejtmanek[1], Zdenek Jirak[1], Karel Knizek[1], Hiroyuki Fujishiro[2], Bertrand Lenoir[3] and Christine Bellouard[3]; [1]Department of Magnetics and Superconductors, Institute of Physics, Academy of Sciences of the Czech Republic, Praha, Czech Republic; [2]2 Dept. of Materials Science and Technology, Faculty of Engineering, Iwate University,Morioka, Morioka, Japan; [3]LPM, Ecole Nationale Superieure des Mines de Nancy, Nancy, France.

The recent material research of mixed cobalt oxides is strongly motivated by the potential of some of them to be used as chemically stable high temperature thermoelectric material. This fact together with both the theoretical and experimental ambitions to fulfill the severe criteria needed for efficient thermoelectric conversion intensified both their theoretical and experimental research. Nonetheless, despite the intensive investigations of the prototype materials represented by 3D perovskites Ln1-xAxCoO3 (Ln = La, Y, rare-earth, A = alkaline-earth) and 2D cobaltites of NaxCoO2 type, the concise physical background of their transport and magnetic properties remain still a matter of debate. This is likely due to a fact that cobalt ions can be stabilized either in low-spin state (diamagnetic for "pure" Co3+), with filled t2g levels and empty eg states, or magnetic ones, with filled eg states. As the energy difference between respective states is due to comparable strength of crystal field and Hund's energies rather small, the thermodynamically most stable ground-state, with eventually different character of charge carriers, can be critically influenced by an interplay of additional degrees of freedom - orbital and charge. The challenge for unequivocal theoretical model represents e.g. the thermoelectric power of mixed cobaltites where, up to now, somewhat ambiguous models based either on "classical" approach, associated with diffusion of itinerant charge carriers, or more exotic - based on configurational entropy of quasi-itinerant carriers - are often used for similar materials. Simultaneously, the open question remains the assessment of the dominant mechanism of phonon scattering in 2D cobaltites which can "confirm" or "rule-out" the theoretically postulated "phonon-glass electron -crystal" behaviour insinuated for NaxCoO2 bronzes. Consequently, in a present paper we focus on the comparative experimental study of highly conducting 3D and 2D cobaltites. Using a complex structural, magnetic, transport and thermal characterization in a wide range of temperatures we analyze and discuss the thermoelectric power, specific heat, magnetic and magnetotransport data. While a concurrence of a small negative thermopower, positive Hall coefficient and huge electronic contribution to the specific heat is observed in ferromagnetic metallic perovskites below Tc, the concurrence of negative Hall effect, large positive thermopower and huge electronic contribution to the specific heat characterizes layered NaxCoO2 bronzes. This fact point to a complex character of the Fermi surface while further experiments insinuates that the large positive thermopower can be linked with strong electron correlations.

11:45 AM F1.8
Thermoelectric Properties and Microstructure of c-axis Oriented Ca3Co4O9 Thin Films.
Yufeng Hu[1], Qiang Li[1], Weidong Si[2] and Eli Sutter[3]; [1]Materials Science Department, Brookhaven National Laboratory, Upton, New York; [2]Physics Department, Brookhaven National Laboratory, Upton, New York; [3]Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York.

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

SESSION F2: Oxides II and New Directions
Chairs: Joseph Heremans and George Nolas
Monday Afternoon, November 28, 2005
Room 313 (Hynes)

1:30 PM *F2.1
New Directions in Bulk Thermoelectric Materials Research.
Terry M. Tritt[1], J. He[1], B. Zhang[1], N. Gothard[1], D. Thompson[1], E. Weeks[1], T. Xiaofeng[1], K. Aaron[1], X. Ji[1] and J. W. Kolis[2]; [1]Physics & Astronomy, Clemson University, Clemson, South Carolina; [2]Chemistry, Clemson University, Clemson, South Carolina.

The focus in this talk will be on some new directions in bulk thermoelectric materials research that we have recently been pursuing. The requirements for a potential thermoelectric material will be discussed and how these relate into giving a favorable figure of merit, ZT, defined as ZT = α^2T/$\rho\kappa$ where α is the Seebeck coefficient, ρ electrical resistivity, & κ thermal conductivity and T is the temperature in Kelvin. Thermoelectric materials are inherently difficult to characterize and a short discussion of these difficulties will be part of the presentation. These difficulties are magnified at high temperatures and many challenges remain. Specific materials will be discussed, and especially those results in bulk materials that exhibit favorable properties for potential high temperature power generation capabilities. A brief discussion of the synthesis techniques, the characterization techniques and highlights of several systems of materials will be presented. For example, a system of ceramic oxide thermoelectric materials based on $NaCo_2O_4$, 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_2, will also be discussed as well as why this type of structure may well be critical to the development of the next generation 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 Na_xCoO_2 thin films.
Venimadhav Adyam[1], A. Soukiassian[2], D. A. Tenne[1], Qi Li[1], X. X. Xi[1,2], D. G. Schlom[2], R. Arroyave[2], Z. K. Liu[2], H. P. Sun[3], X. Pan[3], M. Lee[4] and N. P. Ong[4]; [1]Phyics, Pennsylvania State University, University Park, Pennsylvania; [2]Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania; [3]Department of Materials Science and Engineering, The University of Michigan, Ann Arbor, Michigan; [4]Physics Department, Princeton University, Princeton, New Jersey.

Layered cobaltate NaxCoO2 has attracted much attention recently due to its exceptional properties, one of which is its unusually high

thermoelectric power with low resistivity, and high carrier density. We have studied structural and transport properties of epitaxial Na_xCoO_2 thin films on (0001) sapphire substrate prepared by topotaxially converting an epitaxial Co_3O_4 film to Na_xCoO_2 with annealing in Na vapor generated from annealing either with sodium bicarbonate ($NaHCO_3$) or sodium acetate ($NaOOCCH_3$). The films are c-axis oriented and in-plane aligned with [10-10] Na_xCoO_2rotated by 30^o from [10-10] sapphire. Different Na vapor pressures during the annealing resulted in films with Na concentrations of x$\sim$0.68 and x$\sim$0.75, which showed distinct temperature dependent resistivity. The thermal power at room temperature for x=0.68 is $\sim$70 mV/K, which is similar to the single crystal samples of the same composition.

2:15 PM F2.3
Sr-doped $LaRuO_3$ as a Potential Thermoelectric Material.
J. He, B. Edwards, H. Zhang, D. Thompson and T. M. Tritt; Physics & Astronomy, Clemson University, Clemson, South Carolina.

The perovskite $La_{1-x}Sr_xRuO_3$ ($0.1 < x < 0.5$) polycrystalline samples have been prepared using solid state chemistry reaction. The phase constituent, compositional homogeneity and micro-morphology have first been checked by X-ray powder diffraction, Energy Disperse X-ray spectroscopy and scanning electron microscopy before being characterized with respect to the electrical resistivity, thermal conductivity and Seebeck coefficient between 10 and 300 K. Particularly, the compositional dependence of Seebeck coefficient of present compounds was studied in light of the comparison with the strongly correlated system Na_xCoO_4 and the relevant model proposed by W. Koshibae. Finally, the potential of using $La_{1-x}Sr_xRuO_3$ as a practical thermoelectric material is discussed.

3:30 PM F2.4
Synthesis and Thermoelectric Properties of $Na_xCo_2O_4$ Oxide Materials. Xiaofeng Tang[1], Ed Abbott[2], Joe K. Kolis[2], Kelvin Aaron[3] and Terry M. Tritt[3]; [1]Materials Science & Engineering, Clemson University, Clemson, South Carolina; [2]Chemistry, Clemson University, Clemson, South Carolina; [3]Physics & Astronomy, Clemson University, Clemson, South Carolina.

In 1997 Terasaki reported that $Na_xCo_2O_4$ 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, thermopower, thermal conductivity, heat capacity and magnetic susceptibility and moment of composition precisely controlled $Na_xCo_2O_4$ polycrystalline samples, which were prepared by a rapid-heat-up technique, were systematically studied and will be reported here. The anomalous decrease in resistivity around 500K revealed there could exist some unknown phase transition, although the thermopower continues to increase with elevating temperature. The thermal conductivity of single crystals $NaCo_2O_4$ grown via typical NaCl flux method was measured by our custom-designed steady state parallel thermal conductance (PTC) system and was found to be $\sim$5W/m-K. Along with the low in-plane resistivity $\rho\sim$0.30 mW-cm and high thermopower $\alpha\sim$100 mV/K, the power factor α^2/ρ and ZT of $NaCo_2O_4$crystal were found to have high values of $\sim 10^{-3}$ W/m-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 $Na_xCo_2O_4$ single crystals with sizes up to 6mm at low temperature of 550^oC. The as grown crystals were found to be Na-deficient and resistivity measurements revealed there exist two different types of crystals, one is metallic and another is semiconducting. Measurements on the compact pellet of crystals via hot press also revealed the semiconducting resistivity behavior, where energy gap E_g was found to be between 0.1 and 0.3eV.

3:45 PM F2.5
Fabrication of Na1-xCoO2 Thin Films for Thermoelectric Applications. Hanns-Ulrich Habermeier, Yoshiharu Krockenberger and Lan Yu; MPI-FKF, Stuttgart, Germany.

Terasaki et al. discovered 1999 unusual thermoelectric properties of Na1-xCoO2. Their uniqueness is based on the large Seebeck coefficients combined with low resistivity. The physics behind these properties might stem from the crystallographic anisotropy and the strong correlations of the electronic system.The application of this material, however, requires the availability af a reliable thin film technology able to controllably produce single phase epitaxial thin films. Krockenberger et. al. have recently accomplished the preparation of such films using pulsed laser deposition techniques combined with in-situ annealing procedures for the Na-concentration x $\sim$ 0,7. In this contribution we describe the further development of this technique in a two-stage process to expand the Na-concentration range for epitaxial single crystal-like thin films to $0.3 < x < 1$. The films are characterized by X-ray diffraction techniques, transport and magnetization measurements in addition to spectroscopic ellipsometry. Films deposited onto vicinal cut SrTiO3 substrates show highly anisotropic in-plane resistivities reflecting the layered structure of the material and the intrinsic anisotropy of resistivity parallel and perpendicular to the CoO2 sheets. Thermoelectric experiments have been performed using nanosecond pulsed laser irradiation as source for the temperature gradient and measuring the generated voltage in analogy to previous experiments yielding giant laser-induced voltages in YBCO deposited onto vicinal cut SrTiO3 substrates. The results for the thermoelectric signals for Na1-xCoO2 films are compared with those of YBCO and doped manganites and relevant device aspects will be discussed.

4:00 PM *F2.6
Giant Seebeck Effect Originating from 2DEG at the $TiO_2/SrTiO_3$ Heterointerface. Hiromichi Ohta[1,2,3], SungWng Kim[4], Kenji Nomura[3], Shingo Ohta[1], Takashi Nomura[1], Masahiro Hirano[3], Hideo Hosono[3,4] and Kunihito Koumoto[1,2]; [1]Graduate School of Engineering, Nagoya University, Nagoya, Japan; [2]CREST, JST, Kawaguchi, Japan; [3]ERATO-SORST, JST, Yokohama, Japan; [4]Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, Japan.

A high-density ($\sim 10^{21}$ cm^{-3}) two-dimensional electron gas (2DEG) that is confined within several atomic layers at the interface between two dielectric oxides, $TiO_2/SrTiO_3$ was found to be overcome a trade-off between the two material-based parameters, —S— and σ in ZT. According to an idea which was proposed by Hicks and Dresselhaus in 1993, confined carrier electrons within several atomic layer spaces should dramatically enhance —S— due to an increase in the density-of-states for conduction and/or valence band edge, while keeping the σ value almost unchanged. In order to realize several atomically confined 2DEG, we fabricated an interface composed of dielectric oxides, $TiO_2/SrTiO_3$, because the 2DEG at the interface should be confined to an extreme extent by means of the Debye shielding effect, since the dielectric constants of both TiO_2 ($\sim$100) and $SrTiO_3$ ($\sim$300) are very large. Epitaxial layers of TiO_2 was deposited on (100)-oriented $SrTiO_3$ single-crystal plates by pulsed laser deposition with the fourth-harmonic of an Nd:YAG laser with a polycrystalline TiO_2 target at 700^oC in an oxygen atmosphere. Optical absorption measurements of the $TiO_2/SrTiO_3$ revealed that the carrier electrons are produced in $SrTiO_3$ due to the O^{2-} vacancy formation during the TiO_2 deposition, and the electrons are confined at the interface in terms of band bending to form a high-density 2DEG. C-V measurements of the $TiO_2/SrTiO_3$ confirmed that a high-density 2DEG (ne $\sim 1.4 \times 10^{21}$ cm^{-3}) was successfully fabricated, which is localized in several molecular layers of Ti-O at the interface of $TiO_2/SrTiO_3$. The —S— values are as large as $\sim$1 mV·K-1, $\sim$7 times larger than that of the bulk, whereas the electron system maintains the rather high σ value of 1.4×10^3 S·cm^{-1}, leading to a ZT value of $\sim$5 at room temperature, which is substantially larger that of TE materials developed thus far. This finding provides a novel concept for TE materials design and expands broadly the range of possible choices for TE materials.

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

We discuss the theory and experiment of solid state energy conversion devices based upon the thermoelastic effect. It is a multilayer device with alternate layers having different thermoelastic properties. When the small device is forced to oscillate, dc heat will flow because of the nonlinear thermoelastic coupling of the different layers of material. The device can be used as a refrigerator, or as an energy conversion device. The model of this device is described, as well as the performance characteristics of several bench top models.

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 (Hynes)

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 nanoscale materials 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_2Te_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.*, CaB_6, SrB_6 and BaB_6nanowires) will be reported. The nanostructures were synthesized by pyrolysis of diborane (B_2H_6) over certain metal oxide powders (e.g., calcium oxide (CaO) for synthesis of CaB_6) at elevated temperature and low pressure. The experiments were performed in a home-built low pressure chemical vapor deposition (LPCVD) system. Nickel (Ni), Platinum (Pt) and Palladium (Pd) are effective catalytic materials for growth of aforementioned hexaboride TE nanostructures. The as-synthesized nanostructures were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy. Possible mechanisms for the growth of these novel boron-based TE nanostructures will be presented. Combined with other properties of boron-based materials (*e.g.*, low-density, superior mechanical properties, excellent thermal and chemical stability), these new TE nanostructures may find applications in the automotive industry and in high temperature micro- and nanoelectromechanical systems (MEMS and NEMS), electronics, and others.

F3.3
Nanoscale SiGe Thermoelectric Junctions. David T. Marx, Physics, Illinois State University, Normal, Illinois.

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

F3.4
Synthesis, Characterization, and Thermoelectric Properties of Chalcogenide Nanocrystalsand their Assemblies. Jeff Urban, Chris Murray, Dmitri Talapin and Elena Shevchenko; IBM/MSU, Yorktown Heights, New York.

Here we present the synthesis and characterization of individual nanocrystals and 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 can be controllably doped 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 AB13 superlattices. This will also serve to highlight recent work on the synthesis and thermoelectric properties of GeTe nanocrystals.

F3.5
(W)x(WSe2)y Superlattices - Materials Designed for Low Thermal Conductivity. Ngoc Thanh Nguyen[1], David C. Johnson[1], Catalin Chiritescu[2] and David G. Cahill[2]; [1]Chemistry, University of Oregon, Eugene, Oregon; [2]Materials Science, University of Illinois at Urbana-Champaign, Urbana-Champaign, Illinois.

One concept for producing extremely low thermal conductivity superlattices consists of combining two materials with different vibrational characteristics. We have prepared superlattices consisting of a variable number of layers of WSe2 and a 1.5 nanometer layer of W as building blocks. The superlattices were synthesized using modulated elemental reactant. Alternating thin layers of W and Se were deposited with a 1 to 2 ratio of W to Se and an appropriate thickness to yield an integral number of Se-W-Se layers of WSe2 followed by a layer of W to form the repeating unit of the superstructure. The evolution 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 microscope data.

F3.6
Electrochemically-Deposited Bi_2S_3 and $Pb_{3X}Bi_{2(1-X)}S_3$ Nanowires. Jana Sommerlatte[1,2], Woo Lee[1], Roland Scholz[1], Ulrich Goesele[1], Klaus Bente[2] and Kornelius Nielsch[1]; [1]Max Planck Institute of Microstructure Physics, Halle, Germany; [2]Institute of Mineralogy, University of Leipzig, Leipzig, Germany.

Thermoelectric nanowires have been predicted to have superior thermoelectric properties over bulk materials. Sulfosalts in general and especially bismuth sulfide and the Bi_2S_3-PbS compounds are semiconductors with a direct band gap transition. The band gap of the bulk Bi_2S_3-PbS alloys can be adjusted over a wide range from 0.41 up to 1.6 eV and exhibit a large variety of crystal structures. Due to the modular crystal structure $Pb_{3X}Bi_{2(1-X)}S_3$ tends to grow in a needle-like shape. Therefore these compound semiconductors are very suitable for the synthesis of crystallographically-oriented 1D nanostructures. In this paper we report on the synthesis of Bi_2S_3 and $Pb_{3X}Bi_{2(1-X)}S_3$ nanowires by electropdeposition in highly ordered alumina membranes with a monodisperse pore diameter of 50 nm. According to Baranski et al. [*J.Electrochem.Soc.* **127**, 766 (1980)] we have chosen DMSO as a nonaqueous solvent for the electrolyte. The deposition of Bi_2S_3 and $Pb_{3X}Bi_{2(1-X)}S_3$ took place under inert gas atmosphere at elevated temperatures (110°C). For the Bi_2S_3 deposition we have obtained nearly single-crystalline nanowires and a homogenous pore filling up to membrane thicknesses of 30 μm. The Bi_2S_3 nanowires exhibit the bismuthinite phase with a preferential orientation of the c axis parallel to the nanowire axis. In case of Bi_2S_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 $Pb_{3X}Bi_{2(1-X)}S_3$ nanowires which exhibit the cosalite $Pb_2Bi_2S_5$ or lillianite $Pb_3Bi_2S_6$ phase as the dominating crystal structure. We thank the German Ministry for Education and Research (BMBF, project number 03N8701) for financial support.

F3.7
Thermal Conductivity of (Bi2Te3)x(TiTe2)y Superlattices. Mary Smeller[1], David Johnson[1], David Cahill[2] and Catalin Chiritescu[2]; [1]Department of Chemistry, University of Oregon, Eugene, Oregon; [2]Department of Materials Science and Engineering, University of Illinois, Urbana Champaign, Urbana, Illinois.

A series of (Bi2Te3)x(TiTe2)y 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 (TDTR). A thermal conductivity of 0.230 W/mK was measured for a (Bi2Te3)4(TiTe2)3 superlattice, half as low as the value reported by Venkatasubramanian (J. Appl. Phys. 2001) for (Sb2Te3)x(Bi2Te3)y 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-Andra Borca-Tasciuc[1], Gang Chen[2] and Anatol Grozav[3]; [1]Rensselaer Polytechnic Institute, Troy, New York; [2]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [3]Institute of Applied Physics, Moldovan Academy of Sciences, Chishinau, 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 glass-coated melt spinning method. The fiber composites fabricated through this method consist of a Bi core, with a diameter that may range in different samples from a few hundreds of 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 6 μm diameter, free-standing Bi wire. Temperature dependent thermal conductivity and specific heat agree well with published data for bulk Bi. Preliminary results are presented for Bi wires of sub-micrometer diameter.

F3.9
Effects of Nanoporosity on Thermoelectric Properties: A One-Dimensional Model. Hohyun Lee and Gang Chen; MIT, Cambridge, Massachusetts.

Thermoelectrics is direct energy conversion between heat and electricity within a material. Its efficiency is denoted by 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)x(TiTe2)y Superlattices.
Benjamin Schmid, Clay Mortensen, Raimar Rostek and David C. Johnson; University of Oregon, Eugene, Oregon.

A series of (Sb2Te3)x(TiTe2)y superlattices with varying ratios of x and y was synthesized using the technique of modulated elemental reactants. This system parallels (Bi2Te3)x(Sb2Te3)y and PbTe/PbSeTe nanostructured materials, which have both been found to have enhanced figures of merit as a result of a reduced thermal conductivity. Superlattice structure and composition were determined by x-ray reflectivity, x-ray diffraction, electron probe microanalysis and Rietveld analysis. Thermal conductivity measurements were conducted to correlate superlattice period with properties.

F3.11
Thermoelectric Properties of Bi2Te3-Based Nanocomposites.
Qing Hao[1], Bed Poudel[2], Yi Ma[2], Dezhi Wang[2], Wenzhong Wang[2], Zhifeng Ren[2], Mildred S. Dresselhaus[3] and Gang Chen[1]; [1]Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Department of Physics, Boston College, Chestnut Hill, Massachusetts; [3]Department 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 much lower cost. The increased interfacial scattering 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)5(TiTe2)4 Superlattice Hot Pressed from Thin Films.
Sissi L Li[1], Mary M. Smeller[1], Maisha K. Kamunde[1], Clay D. Mortensen[1], Benjamin A. Schmid[1], David C. Johnson[1], Terry M. Tritt[2], Brad Edwards[2], Nobuyoshi Imaoka[3] and Isao Morimoto[3]; [1]Chemistry, University of Oregon, Eugene, Oregon; [2]Clemson University, Clemson, South Carolina; [3]Asahi Kasei, Fuji-City, Japan.

Using the modulated elemental reactant method, thin films of (Bi2Te3)5(TiTe2)4 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 523 K and 700MPa for 24 hours. The thermal and electrical properties of this bulk pellet are presented.

F3.13
Growth and Characterization of Bi_2Te_3 Nanostructures.
M. Craps, N. Gothard, R. Rao, T. M. Tritt and A. M. Rao; Physics & Astronomy, Clemson University, Clemson, South Carolina.

Bulk Bi_2Te_3 is one of the best known thermoelectric materials with a ZT $\sim$1 at room temperature. Theoretical studies have suggested that low-dimensional materials may exhibit ZT values that exceed 1. In this study, we used the pulsed laser deposition method to prepare Bi_2Te_3 nanostructures by ablating a rotating Bi_2Te_3 target in an inert atmosphere. Si substrates are pretreated with poly-l-lysine to form an adhesion layer for 10 nm colloidal Au particles which serve as catalyst seed particles for the growth of the nanostructures. Alternatively, we have also prepared Bi_2Te_3 nanostructures by subliming Bi_2Te_3 powder in the presence of gold coated substrates. Results from electron microscopy and vibrational spectroscopic studies will be presented.

F3.14
Preparation and Characterization of (TiTe2)x(Bi2Te3)y(TiTe2)x(Sb2Te3)z Superlattices.
Clay Mortensen, Benjamin Schmid, Raimar Rostek and David C. Johnson; Department of Chemistry, University of Oregon, Eugene, Oregon.

We explored TiTe2 as a diffusion diffusion barrier between Bi2Te3 and Sb2Te3 to limit interdiffusion of Sb and Bi. A series of (TiTe2)x(Bi2Te3)y(TiTe2)x(Sb2Te3)z 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)x(Sb2Te2)y 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)

8:00 AM *F4.1
QDSL Thermoelectric Materials.
T. C. Harman, R. E. Reeder, M. P. Walsh, B. E. LaForge, C. D. Hoyt, D. E. Mull, W. D. Goodhue and G. W. Turner; MIT, Lincoln Laboratory, Lexington, Massachusetts.

The development of nanostructed 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 PbSeTe/PbTe quantum-dot superlattice (QDSL) materials grown by molecular beam epitaxy, where we have now achieved ZT values of up to $\sim$1.1 at 300 K (Ref.1). While these values are not yet as high as thebest values that were previously obtained for more optimized n-type Pb-salt QDSL materials ($\sim$1.6 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 for Pb-salt-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 unicouple 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 unicouple devices, we have obtained a power density of $\sim$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 unicouple device measurements as well as the on-going development of fabrication techniques suitable for producing multicouple 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.
Joshua M. Zide[1], Gehong Zeng[2], Je-Hyeong Bahk[2], John E. Bowers[2], Woochul Kim[3], Arun Majumdar[3], Ali Shakouri[4] and Art C. Gossard[1]; [1]Materials, University of California, Santa Barbara, Santa Barbara, California; [2]Electrical and Computer Engineering, University of California, Santa Barbara, Santa Barbara, California; [3]Mechanical Engineering, University of California, Berkeley, Berkeley, California; [4]Electrical 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 nanocomposite made by incorporating semimetallic nanoparticles into semiconductors can have drastically different properties than the semiconductor itself, and these properties allow the material to be tailored for a wide range of applications, including thermoelectric power generation. The efficiency of a thermoelectric material is strongly dependent on the dimensionless figure of merit, $ZT=S^2\sigma T/\kappa$, where S is Seebeck coefficient, σ is electrical conductivity, and κ is thermal conductivity. ErAs is a rocksalt semimetal which forms into epitaxial nanometer-sized particles on a III-V semiconductor surface. Overgrowth is nucleated on the exposed semiconductor surface between the particles and is essentially defect-free. The properties of the resulting nanocomposite are dependent on the composition of the host semiconductor and on particle morphology, which can be

controlled during growth. We present experimental results on the incorporation of ErAs into various compositions of InGaAlAs (lattice matched to InP). The particles pin the Fermi level at an energy which is dependent on particle size and the composition of the semiconductor. For example, the Fermi level of InGaAs is pinned within the conduction band, increasing the free electron concentration and thus the electrical conductivity. In InAlAs, the Fermi level is pinned ∼400meV below the conduction band edge, and so the particles serve as a buried Schottky barrier. By carefully choosing the composition of the InGaAlAs, we can use the particles to increase the electron concentration (and the electrical conductivity) of the material while providing Schottky barriers around the particles to create a non-planar electron filtering (solid-state thermionic) system to improve the Seebeck coefficient. The thermoelectric power factor $S^2\sigma$ can be optimized at a given temperature by changing this barrier height. We also demonstrate further improvement in ZT by reducing the thermal conductivity of InGaAs by a factor of two to three through the incorporation of ErAs. This reduction is due to increased scattering of mid- to long- wavelength phonons and makes this system one of the only materials in which thermal conductivity is reduced below the so-called "alloy limit" without creating defects. This absence of defects allows us to reduce thermal conductivity without reducing electrical conductivity.

8:45 AM F4.3
Cross-Plane Seebeck Coefficient of InGaAs/InGaAlAs Superlattices with Embedded ErAs Nanoparticles in a Wide Temperature Range. Yan Zhang[1], Ali Shakouri[1], Gehong Zeng[2], Zhixi Bian[1], Josh Zide[3], Art Gossard[3], Woochul Kim[4], Suzann Sanger[4], Arun Majumdar[4], Rajeev Singh[1] and John Bowers[2]; [1]EE, UC Santa Cruz, Santa Cruz, California; [2]ECE, UCSB, Santa Barbara, California; [3]Materials Sci. & Eng., UCSB, Santa Barbara, California; [4]Mechanical Engineering, UCB, Berkeley, California.

Seebeck coefficient is one of the key parameters to evaluate the performance of thermoelectric coolers and power generators. However, it is very difficult to directly measure Seebeck coefficient perpendicular to thin film devices because of the difficulty of creating a temperature gradient and measuring accurately temperature and electrical potential on both sides of the thin film simultaneously. It has been shown that embedded ErAs nano-particles reduce the thermal conductivity of the bulk InGaAs substantially with a modest increase in the thermoelectric power factor (Seebeck coefficient square times electrical conductivity). In InGaAs/InGaAlAs superlattices with embedded ErAs nanoparticles, it is anticipated that the additional electron filtering can improve the thermoelectric power factor. A series of superlattice structures with various silicon co-dopings ranging from 2e18 to 1e19 cm-3 were grown using molecular beam epitaxy (MBE). Cross-plane Seebeck coefficient was characterized using thin film resistive heaters on top of the superlattice structure. This resistor acts both as a heat source and also as a thermometer once its resistance versus temperature was characterized. Since the superlattice is grown on InP substrate, the measured thermoelectric voltage has contributions from both the substrate and the superlattice. In order to extract the superlattice contribution, similar measurements were done on samples where the superlattice layer was etched off and only the substrate contribution was measured. The thermal conductivity of the 0.5 microns thin SiO2/SiN layer used to insulate the thin film resistor from the semiconductor surface has a non-negligible contribution compared to the total thermal resistance of the device. Thus independent 3w technique was used to measure the SiO2/SiN thermal conductivity in the whole temperature range. In this paper, we will describe in detail the test device and methodology we used to characterize the cross-plane Seebeck coefficient of in a temperature range of 100-600K.

9:00 AM F4.4
Transient Harman Measurement of the Cross-Plane ZT of InGaAs/InGaAlAs Superlattices with Embedded ErAs Nanoparticles. Rajeev Singh[1], Bian Zhixi[1], Daryoosh Vashaee[1], Ali Shakouri[1], Joshua Zide[2], Gehong Zeng[2,1], Hsu-Feng Chou[2], Art Gossard[2] and John Bowers[2]; [1]Electrical Engineering, University of California, Santa Cruz, Santa Cruz, California; [2]Electrical and Computer Engineering, University of California, Santa Barbara, Santa Barbara, California.

Transient Harman technique is used to characterize cross-plane ZT in InGaAs/InGaAlAs superlattice structures with embedded ErAs nanoparticles and with various concentrations of Si co-doping in the well regions. It has been shown that ErAs nanoparticles reduce the thermal conductivity of bulk InGaAs substantially and slightly increase the thermoelectric power factor Seebeck coefficient square times electrical conductivity). The InGaAs/InGaAlAs superlattice structure was designed to have a barrier height of ∼200meV. Calculations estimate that the power factor can be improved substantially in the cross-plane direction. ErAs nanoparticles provide free carriers inside the semiconductor matrix. Additional doping with Si increased the Fermi energy to just below the barrier height. Hall mobility and Seebeck measurements in the plane of the superlattice give a power factor similar to bulk ErAs:InGaAs. Direct measurements of the cross-plane thermoelectric properties (specifically the electrical conductivity) are challenging for thin-film superlattices. Transient Harman technique can directly measure cross-plane superlattice ZT. High-speed packaging is used to reduce signal ringing due to parasitics and achieve short time resolution (<1 micro seconds) in transient Seebeck voltage measurement. Direct ZT measurements are compared with independent measurements of cross-plane thermal conductivity and Seebeck coefficient.

9:15 AM F4.5
A Band Structure Phase Diagram Calculation of 2D BiSb Films. Ming Y. Tang[1] and Mildred S. Dresselhaus[1,2]; [1]Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; [2]Physics, 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, semimetallic BiSb alloys can be made semiconducting by using the low dimensionality quantum confinement concept. With these two previous concepts (size and alloy composition) in mind, it is valuable to further explore the dependence of the band alignment for different alloy concentrations and different confinement conditions for BiSb alloys. Following the study of the effect of the Sb 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 Sb concentration and the film thickness on the properties of BiSb alloy films. A band structure phase diagram is calculated, giving the details on the dependence of the relative band edge position on the film thickness and the Sb concentration. This phase diagram gives a first hand guideline for choosing the film thickness and the Sb concentration to better improve the thermoelectric performance of BiSb alloy films.

9:30 AM F4.6
Thermoelectric Transport Properties of Bi2Te3 Nanoparticle Films. Seong Yul Kim[1], Erin Dunbar[1], Daniel Tsang[1], Abhishek Jain[1], Arup Purkayastha[2], Ganapathiraman Ramanath[2] and Theodorian Borca-Tasciuc[1]; [1]Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York; [2]Materials 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 particles are grown with control over size and size distribution using a new room temperature synthesis method from microemulsions. 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 difference is linear and the Seebeck coefficient of the film can be extracted from the slope as S=-dV/dT. Electrical conductivity is determined using a two probe technique. A linear I-V characteristic is obtained for the films indicating ohmic behavior. Temperature dependent measurements are performed in the 80-300K temperature range. Thermoelectric measurements on films with particles sizes ranging between 3nm and 13nm are reported. The presentation will discuss the dependence of the power factor of the films on the nanoparticle size and film structure

9:45 AM F4.7
Bi2Te3: Structural Modulations in Epitaxially Grown Superlattices and Bulk Materials. Nicola Peranio[1], Oliver Eibl[1] and Joachim Nurnus[2]; [1]University of Tuebingen, Institute for Applied Physics, Tuebingen, Germany; [2]Fraunhofer Institut Physikalische Messtechnik, Freiburg, Germany.

Multiquantum well structures of Bi2Te3 are predicted to show an

enhancement of the thermoelectric figure of merit ZT [1]. Bi2Te3/Bi2(Te0.88Se0.12)3 superlattices (SL) with a layer thickness of 12 nm were epitaxially 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 Bi2Te3 and the reflections of the superstructure. The period length of the SL is 13.1+/-0.4nm. The SL is slightly bent with an amplitude of 30nm and a wave length of 400nm. Threading dislocations were found with a density greater than 2*10$\hat{9}$cm$\hat{(}$-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 (nns) parallel to the (1,0,10)-planes with a wave length of 10nm was found. This (nns) was also observed in n-type Bi2(Te,Se)3 and p-type (Bi,Sb)2Te3 bulk material and turns out to be of general character for Bi2Te3 materials. The (nns) did not show bending due to the superlattice and vice versa. Therefore, the structure is a superposition of the epitaxially grown superlattices (ans) and the structural modulations (nns). The structural modulation was analysed in n-type bulk material in detail. The (nns) consists of parallel dislocation lying on (1,0,10)-planes only a few nanometers apart with a high dislocation density of 10$\hat{1}$2cm$\hat{(}$-2). The Burgers vectors and the dislocation line directions were determined by stereomicroscopy. The investigations showed the presence of none, one or two (nns). Particularly the heat conductivity should be significantly decreased due to phonon scattering on the (nns) with its high dislocation density. For the phonons and the heat conductivity the (nns) could yield a reduced dimensionality and localization and anisotropic behaviour in the basal plane. Cubic AgPbmSbTe2+m bulk materials also showed a similar (nns) and an enhancement of the thermoelectric figure of merit ZT [4]. References: [1] Venkatasubramanian, R. et al., Nature, Vol. 413 (2001), pp. 597-602 [2] Lamprecht A. et. al., Proc 20th Int. Conf. on Thermoelectrics, Beijing, P.R.China (2001), pp. 335-339 [3] Peranio N. et. al., Proc 23th Int. Conf. on Thermoelectrics, Adelaide, Australia (2004), in press [4] Kuei-Fang Hsu, Science, Vol. 303 (2004), pp. 818-821

10:30 AM F4.8
Large Area Quantum Well Thermoelectric Generator. Harry Efstathiadis[1], Tianhua Yu[1], Frank Ramos[1], Pradeep Haldar[1], Saeid Ghamaty[2] and Norbert Elsner[2]; [1]College of Nanoscale Science and Engineering, University at Albany, Albany, New York; [2]Hi-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 supplies for both space and exterritorial 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 the concept, development, and testing in large area QW films of N-type SiC/Si mated with P-type B_4C/B_9C, 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 sputter deposition technique on n-type (100) silicon substrates. This deposition approach might be proven to be the most suitable for potentially manufacturing large area thermoelectric devices in a cost effective manner. These more basic studies are being carried out to better understand variables such as film thickness, deposition rate and other important parameters of these ∼10 nm films. The resulting multilayer stacks are being examined in terms of thin film uniformity, thickness, growth rate, composition, resistivity, and thermoelectric performance, by spectroscopic ellipsometry, Focused Ion Beam (FIB), Secondary Ion Mass Spectroscopy (SIMS), cross section Transmission Electron Microscopy (TEM), and electrical measurements. Issues, which could cause film stack degradation, such as interface layer formation, film delamination, and crack formation lowering the device performance will be presented and correlated to device efficiency.

10:45 AM F4.9
Fabrication and Characterization of Si-Ge Nanocomposite for Thermoelectric Applications. Dezhi Wang[1], Wenzhong Wang[1], Shuo Chen[1], Zhifeng Ren[1], Hohyun Lee[2], Gang Chen[2], Ming Tang[3], Mildred Dresselhaus[3,4], Pawan Gogna[5], Jean-pierre Fleurial[5] and Bradley Klotz[6]; [1]Physics, Boston College, Chestnut Hill, Massachusetts; [2]Mechanical Engineering, MIT, Cambridge, Massachusetts; [3]Electrical Engineering, MIT, Cambridge, Massachusetts; [4]Physics, MIT, Cambridge, Massachusetts; [5]JPL, Pasadena, California; [6]Dynamic Science,In, Aberdeen Providing Ground, Maryland.

Low dimension is one of the most promising directions to search for high-ZT thermoelectric materials. It has been predicted by theory and proved by experiments that structures such as quantum well and superlattice can increase ZT by several times vs the corresponding bulk materials. However, it is very difficult to manufacture those low dimensional structures in large scale for bulk applications. To realize those principles, we have designed a new structure so called Si-Ge nanocomposite, nano Silicon 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 *F4.10
Thermoelectric and thermomagnetic transport in PbTe with nanoscale structures. Joseph P. Heremans, Delphi Research Labs, Shelby Township, Michigan.

The development of bulk materials with nanoscale inclusions would be very useful for many large-scale applications. Nanometer-scale inclusions in lead chalcogenides are known to improve the thermoelectric figure of merit through a combination of two factors, a strong decrease in lattice thermal conductivity and an increase in the Seebeck coefficient over that of bulk PbTe for a given carrier concentration. This talk is focused on experimental results obtained on two types of PbTe nanocomposites, namely samples prepared by sintering powders with nanometer-sized grains, and samples prepared with nanoprecipitates of metallic Pb. The results are analyzed using the method of four coefficients. At each measurement temperature there are four unknowns, the carrier concentration, the mobility, the carrier effective mass, and the energy dependence of the relaxation time, which is modeled by a power law $\tau \propto E^r$. In order to determine these four unknowns uniquely at each temperature, four measurements are taken: the electrical conductivity, and the Hall, Seebeck and transverse Nernst-Ettingshausen coefficients. This 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 bulk samples, and the figure of merit is decreased, but the situation in samples containing nanoprecipitates is more favorable. No decrease in lattice thermal conductivity is measured in binary PbTe with nanoprecipitates.

11:30 AM F4.11
***Abinitio* study of electronic structure of Defects in Narrow Band-Gap Semiconductor PbTe*.** Salameh Mohammad Ahmad[1], S. D. Mahanti[1] and M. G. Kanatzidis[2]; [1]Physics and Astronomy, Michigan State University, East Lansing, Michigan; [2]Department of Chemistry, Michigan State University, East Lansing, Michigan.

A novel class of quaternary compounds $AgPb_mSbTe_{2+m}$ denoted as LAST-m have attracted considerable attention during last two years because of their large thermoelectric figure of merit ZT at high temperatures[1]. *Abinitio* electronic structure calculations have shown that in these compounds replacement of Pb atoms by Ag and Sb 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 hence on ZT. Recently, $Na_{1-x}Pb_mSb_yTe_{m+2}$ materials have been found to exhibit p-type conduction over a wide temperature range and for $Na_{0.95}Pb_{20}SbTe_{22}$, 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 $MPb_{2n-1}Te_{2n}$ (n=16), where M is a defect which can be a Pb vacancy, a monovalent atom (alkali atoms, Cu), a divalent atom (type IIB Zn, Cd, Hg and type IVA Sn, Ge) and a trivalent atom (Ga, In, Tl). 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 suppress the DOS near the top of the valence band (good for n-type thermoelectric). Sn and Ge behave like Pb and do not modify the DOS near the band gap region. The trivalent atoms Ga, In, and Tl behave differently than Sb because their valence configurations are (ns^2,np^1) in contrast to np^3 for Sb. Whereas In gives rise to states in the gap region, for Ga and Tl the impurity induced states are resonant with the valance band. * Work supported by ONR-MURI. References [1] K. F. Hsu et al., Science 303, 818 (2004). [2] Daniel Bilc et al., Phys. Rev. Lett. 93, 146403 (2004). [3] Pierre F. P. Poudeu and Mercouri G. Kanatzidis (private comminication).

11:45 AM F4.12
Thermoelectric Properties of Hot-pressed Core-shell

Nanoparticles Having the Shell of InSb. Seiji Take[1], Kikuo Okuyama[2] and Yukio Yamaguchi[3]; [1]Japan Chemical Innovation Institute, Tokyo, Japan; [2]Department of Chemical Engineering, Hiroshima University, Hiroshima, Japan; [3]Department of Chemical System Engineering, The University of Tokyo, Tokyo, Japan.

Many studies have been reported about various particles which are dispersed in thermoelectric materials in order to improve the thermoelectric properties. But significant improvement has not been reported because dispersed particles cause reduction of electric conductivity as well as increasing of phonon scattering. Here, we propose hot-pressed core-shell nanoparticles. Each core is well dispersed in sintered shell in nano-scale, which is expected quantum confinement of the carriers. We fabricated the hot-pressed Pt/Au core-shell nanoparticles. The Pt/Au nanoparticles used had following sizes; the core (Pt) was about 2nm diameter, and the shell (Au) thickness was an average of 1nm. The value of figure-of-merit ZT measured was 2.6E-3 at 300K, which was bigger than both 1.1E-3 of bulk Pt and 1.5E-3 of bulk Au. It was confirmed that the hot-pressed Pt/Au was not alloying by means of XRD investigation. Seebeck coefficient (S) of Pt/Au, bulk Pt and bulk Au were 8.3, 1.9, 5.1μV/K, respectively. So, it was considered that significant improvement of S mainly caused 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 Poon
Tuesday Afternoon, November 29, 2005
Room 313 (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 (CVD) 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 Sengupta[1], Rao R. Revur[1], Troy Pyles[1], J. R. Schorr[1], Jennifer Nelson[2], Julie Anderson[2], James H. Adair[2] and Norbert Elsner[3]; [1]MetaMateria Partners, Columbus, Ohio; [2]Penn State University, University Park, Pennsylvania; [3]Hi- Z, San Diego, California.

Significant improvement in thermoelectric performance has been realized in low-dimension semiconductor systems. However, these gains have only been demonstrated in thin film systems. To become commercially viable, new lower cost processing routes are needed for preparing bulk materials that contain nanostructured, thermoelectrically active components. In this paper, an approach that maintains nanoscale features in a bulk material, which may lead to improvement in thermoelectric properties will be reviewed. In this approach, nanoparticles of PbTe were first synthesized. These PbTe nanoparticles were then coated with a thin film of PbSe. The resulting coated particles, as well as uncoated 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 Poudel[1], W. Z. Wang[1], D. Z. Wang[1], Y. Ma[1], Z. F. Ren[1], Q. Hao[2], H. Lee[2], G. Chen[2] and M. S. Dresselhaus[3]; [1]Physics, Boston College, Chestnut Hill, Massachusetts; [2]Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [3]Department 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 processed using P2C device 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 doped 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, B. 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 constituently based on good bulk thermoelectric materials. The challenge has been to achieve these higher performance values in a bulk material that may be easily transitioned into a device. Recently, we have accomplished high yield synthesis of PbTe-based nanostructures by a thermally driven vapor transport method. We have performed compaction techniques in order to yield a bulk pellet 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.

3:30 PM *F5.5
The Nanostructured Thermoelectric Materials AgPbmSbTe2+m (LAST-m). Mercouri G. Kanatzidis, Michigan State University, East Lansing, Michigan.

The family of chalcogenide lead-based compounds, AgPbmSbTem+2, 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 co-existing set well defined phases. Electron microscopic 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 PbSe/PbTe thin films. The impact of these nanostructural features on the thermoelectric properties of these materials is strong. We will discuss the dependence of charge and thermal transport properties of these materials on the composition and preparation conditions.

4:00 PM F5.6
Electronic Structure of $AgSbM_mTe_{m+2}$ (M=Pb, Sn) Compounds - Implications on Thermoelectric Properties*. Khang Hoang 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]. *Abinitio* electronic structure calculations can shed some light on the possibility of finding such resonant structures[2]. Recently, quaternary compounds $AgSbM_mTe_{m+2}$ (M=Pb, Sn) have emerged as materials for potential use in efficient thermoelectric power generation at high temperature[3,4]. These systems possess simple cubic NaCl structure on average. However, detailed information about the ordering of Ag and Sb ions is not available. Monte Carlo (MC) simulations on the systems using an ionic model show a variety of nanostructures associated with the ordering of Ag and Sb ions[5]. In order to investigate the relationship between the nanostructures of these quaternary compounds observed in MC simulations[5] and their electronic structure, we have carried out detailed calculations in several compounds: M=Pb (m=2,14) and M=Sn (m=1,2). These calculations were carried out in density-functional theory (generalized-gradient approximation for exchange-correlation) using

PAW method[6]. Results for a monolayer structure of M=Pb and m=14 (one layer of $AgSbTe_2$ sandwiched between 7 layers of Pb_2Te_2) show the existence of quasi-1D and quasi-2D band structures (in the layer) that give rise to a peak (width ∼0.25eV) 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 alternate layers of $AgSbTe_2$ and Pb_2Te_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 $AgSbSn_2Te_4$ we find extremely interesting structures in the neighborhood of the Fermi energy (FE). There are 3 peaks (width ∼0.25 eV) and the FE lies at the minimum between the 1st and the 2nd peak and the system is metallic (DOS at FE is ∼2 states/f.u., 1f.u.= $AgSbSn_2Te_4$). 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 thermopower) in a related compound $AgSbSnTe_3$[4]. * Supported by ONR-MURI. References [1] G. D. Mahan and J. O. Sofo, Proc. Natl. Acad. Sci. USA 93, 7436 (1996). [2] D. Bilc *etal.*, Phys. Rev. Lett. 93, 146403 (2004). [3] K.-F Hsu *etal.*, Science 303, 818 (2004). [4] J. Androulakis *etal.*(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, 17953 (1994).

4:15 PM F5.7
Thermoelectric Materials $AgPb_mSbTe_{2+m}$ (LAST-m) with High Figure of Merit. Structural Evidences Breaking the Myth of Solid Solutions. Eric Quarez[1], Kuei-Fang Hsu[1], Robert Pcionek[1], N. Frangis[2], E. K. Polychroniadis[2] and Mercouri Kanatzidis[1]; [1]Department of Chemistry, Michigan State University, East Lansing, 48824, Michigan; [2]Department of Physics, Aristotle University of Thessaloniki, Thessaloniki, GR-54124, Greece.

Recently, we described the family of chalcogenide lead-based compounds, $AgPb_mSbTe_{2+m}$, or LAST-m materials (LAST for Lead Antimony Silver Tellurium), several members of which exhibit large ZT values from ∼1.2 (LAST-10) to ∼2.2 (LAST-18) at 800 K. Preliminary electron microscopic examination of these samples revealed endotaxially dispersed quantum dots (i.e. regions 2 to 4 nm in size that are rich in Ag-Sb and are surrounded by a PbTe matrix). This is a significant observation and raises important new questions as to the possible impact of these nanostructural features on the thermoelectric properties. We present here structural studies to fully characterize the LAST materials on the atomic scale and probe the extent and nature of nanostructuring. $AgPb_mSbTe_{2+m}$ samples with different m value were prepared and characterized by powder/single crystal X-ray diffraction, electron diffraction and high resolution transmission electron microscopy. Powder diffraction patterns of different members (m = 0, 6, 12, 18, ∞) are consistent with pure phases crystallizing in the NaCl-structure-type (Fm-3m space group) and the proposition that the LAST family behaves as solid solutions between the PbTe and $AgSbTe_2$ compounds. However, electron diffraction and high resolution transmission electron microscopy studies suggest the LAST phases are inhomogeneous at the nanoscale with at least two coexisting sets of well-defined phases. Moreover, within each nanodomain we observe extensive long range ordering of Ag, Pb and Sb atoms. The long range ordering can be confirmed by single crystal X-ray diffraction studies. Indeed, data collections of five different single crystals were successfully refined in space groups of lower symmetry than Fm-3m including P4/mmm and R-3m. The results reported here dispel the decades long belief that the systems $(AgSbTe_2)_{1-x}(PbTe)_x$ are solid solutions.

4:30 PM F5.8
Nanostructuring and its Influence on the Thermoelectric Properties of the AgSbTe2-SnTe Quaternary System. Ioannis Androulakis[1], Robert Pcionek[1], Eric Quarez[1], Oleg Palchik[2], Ctirad Uher[2], Jonathan Dangelo[3], Tim Hogan[3] and Mercouri G. Kanatzidis[1]; [1]Chemistry, Michigan State University, East Lansing, Michigan; [2]Physics, University of Michigan, Ann Arbor, Michigan; [3]Electrical and Computer Engineering and Materials Science and Mechanics, Michigan State University, East Lansing, Michigan.

The structural and thermoelectric properties of the AgSbTe2-SnTe quaternary system have been studied. Powder x-ray diffraction indicates a cubic NaCl-type structure in contrast with the single crystal refinements, which point towards tetragonal symmetry. The apparent discrepancy was lifted by high-resolution electron microscopy imaging which revealed the system to be a nano-composite formed by thermodynamically driven compositional fluctuations rather than a solid solution as it was viewed in the past. As a result the thermal conductivity is retained at very low values, which is in accord with recent theories on thermal transport in heterogeneous systems. The charge transport properties of the system exhibit a rich physical behavior. This is highlighted in the Ag0.85SnSb1.15Te3 composition where a very high almost metallic carrier concentration (∼5×10$\hat{}$21 cm-3) was found to coexist with a large thermoelectric power response of the order of ∼160 μV/K at high temperatures as a result of a heavy hole effective mass that is almost six times that of the electron rest mass. Financial support from the Office of Naval Research (Contract No. N00014-02-1-0867 MURI program) is gratefully acknowledged.

4:45 PM F5.9
Effects of Antimony on the Thermoelectric Properties of the Cubic $Pb_{9.6}Sb_yTe_{10-x}Se_x$ Materials. Pierre Ferdinand Poudeu Poudeu[1], Jonathan D'Angelo[2], Adam Downey[2], Joseph Sootsman[1], Robert J. Pcionek[1], Zhenhua Zhou[3], Oleg Palchik[3], Timothy P. Hogan[2], Ctirad Uher[3] and Mercouri G. Kanatzidis[1]; [1]Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan; [2]Department of Electrical and Computer Engineering, Michigan State University, East Lansing, Michigan; [3]Department of Physics, University of Michigan, Ann Arbor, Michigan.

The effects of the variation of Sb and Se contents on the thermoelectric properties of $Pb_{9.6}Sb_yTe_{10-x}Se_x$ in the intermediate temperature range were investigated. The $Pb_{9.6}Sb_yTe_{10-x}Se_x$ family was derived from $Pb_{9.6}Sb_{0.3}Te_{10}$ (cubic, $Pm\text{-}3m$) 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 thermopower 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 temperature. Samples with composition $Pb_{9.6}Sb_{0.2}Te_{10-x}Se_x$ (y = 0.2) showed n-type conduction in the entire temperature range. The value of the thermopower decreases with increasing of Se content. For $Pb_{9.6}Sb_{0.2}Te_8Se_2$, a maximum figure of merit of ZT∼ 0.8 was obtained around 600 K. High resolution transmission electron microscopy of $Pb_{9.6}Sb_{0.2}Te_8Se_2$ 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 thermopower with only modest improvement of the electrical conductivity.

SESSION F6: Low Dimensional Structures III
(Nanowires) and New Materials
Chairs: Lidong Chen and Hiromichi 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 Linke[1] and Tammy E. Humphrey[2]; [1]Physics Department and Materials Science Institute, University of Oregon, Eugene, Oregon; [2]Department of Electrical Engineering, University of California Santa Cruz, Santa Cruz, California.

We recently showed theoretically how the bandstructure in thermionic (1) or thermoelectric (2) materials needs to be designed 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 implementation of our theoretical predictions using high-quality, heterostructured III-V nanowires, which will be used for proof-of-concept experiments. (1) T.E. Humphrey, R. Newbury, R.P. Taylor and H. Linke, Phys. Rev. Lett. 89, 116801 (2002). (2) T.E. Humphrey and H. Linke, Phys. Rev. Lett. 94, 096601 (2005).

8:30 AM F6.2
Thermoelectric Modeling of Si-Si1-xGex Ordered Nanowire Composites. Ming Y. Tang[1], Mildred S. Dresselhaus[1,3], Ronggui Yang[2] and Gang Chen[2]; [1]Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; [2]Mechanical Engineering, MIT, Cambridge, Massachusetts; [3]Physics, 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 interface 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-Si1-xGex ordered nanowires composite. The composite can be viewed as having the Si wires inside the Si1-xGex host matrix. Thus, core-shell Si/Si1-xGex nanowires can be considered as the building block of the composite. The effect of the wire diameter and the shell alloy composition on ZT will be presented. Experimental realization of this model will also be discussed.

8:45 AM F6.3
Synthesis of Bi2Se3 Nanowires Using a Hydrothermal Method. Yi Ma, 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, Cu Ka, Bruker AXS), a field emission scanning electron microscope (SEM, JEOL-6340F), and a field emission transmission electron microscope (TEM/HRTEM, JEOL-2010F) equipped with an energy-disperse X-ray spectrometer (EDS). XRD pattern clearly demonstrates that the majority of the as-prepared powders are of pure Bi2Se3 phase. The SAED and HRTEM studies indicate that the as-prepared Bi2Se3 nanowires are highly crystallized single crystals. Based on our experimental results, a possible growth mechanism is discussed.

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

Nanowire arrays of a good room temperature thermoelectric material, bismuth telluride, have been electrodeposited into porous alumina templates using pulsed-potentiostatic methods. The 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 have been assessed with scanning electron microscopy (SEM) and the orientation of the nanowires inside the templates has been determined using powder x-ray diffraction (XRD). AC resistance, DC resistance, ΔT and Seebeck coefficients have been measured, and ZT has been estimated. The arrays tested contain nanowires that are roughly 35 nm in diameter and 50 μm in length. Although not yet at small enough diameters for predicted quantum confinement, the bismuth telluride arrays have shown enhanced figures of merit compared to their bulk counterparts.

9:15 AM F6.5
Incorporation of Bismuth Antimony Nanowire Arrays into Thermoelectric Couples. Jennifer Keyani[1], J. W. Sharp[2] and Angelica M. Stacy[1]; [1]Chemistry, University of California, Berkeley, Berkeley, California; [2]Research 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 ($Bi_{1-x}Sb_x$), the best n-type, low temperature bulk TE material, will show enhanced ZT at nanowire diameters less than 50 nm. We have fabricated $Bi_{1-x}Sb_x$ 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 millimeter length scales. This has been accomplished within 40 nm diameter pores for alloy compositions of $0.07 < x < 0.30$. Metal contacts were electrodeposited on top of the nanowires, and the nanowire/alumina composite was then incorporated as one leg of a TE couple. The ZT of the device was extrapolated from ΔT, AC resistance, and DC voltage measurements.

9:30 AM F6.6
Thermoelectric Properties of Bi and $Bi_{1-x}Sb_x$ Nanowires. M. V. Vedernikov, 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 $Bi_{1-x}Sb_x$ nanowires. This mineral consists of thin tubes with internal diameter of about 5 nm and length up to 1 cm. The asbestos nanotubes were filled with melted Bi or Bi-Sb alloy under a 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 $Bi_{0.75}Sb_{0.25}$ nanowires is comparable with that of Bi nanowires. The possible explanation of unusual thermoelectric properties of these nanowires is presented.

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

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

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

Silicide formed with rhenium is of interest owing to potentials as a promising candidate material for thermoelectric applications. The silicide is a defect disilicide with the stoichiometry of $ReSi_{1.75}$ instead of $ReSi_2$. We have recently determined the crystal structure belongs to the monoclinic system with an ordered arrangement of Si vacancies in the parent $C11_b$ lattice. Binary $ReSi_{1.75}$ exhibits significantly anisotropic thermoelectric properties such that the value of Seebeck coefficient along $[100]_{C11b}$ is positive (230μV/K at 330K) while it is negative (-300μV/K at 600K) along $[001]_{C11b}$. This may result from the highly anisotropic electronic structure of $ReSi_{1.75}$. The dimensionless figure of merit (ZT) for binary $ReSi_{1.75}$ is as high as 0.7 at 1073 K when measured along [001] while the ZT value along [100] is moderate. We have made some efforts to improve the thermoelectric properties of $ReSi_{1.75}$ by alloying with 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 larger, the Si vacancy concentration decreases with the appearance of shear structure on (107). When the valence electron number is smaller, the Si vacancy concentration increases with the appearance of shear structure on (-109). In general, no significant improvement in thermoelectric properties is observed when the shear structures appear upon alloying. When Mo is alloyed, however, the adaptive (incommensurate) structure is formed as a result of simultaneous and random occurrence of (-109) and (107) shears in every unit cell. No significant increase in electrical resistivity occurs with this defect structure and significant improvement in thermoelectric properties is observed in Mo-bearing alloys, as exemplified by the high value of dimensionless figure of merit (ZT) of 0.85 at 800 °C when measured along [001]. On the other hand, when Al is added, thin defect layers containing a kind of shear structure are locally and sporadically formed at some of twin boundaries. In the defect layer, shear occurs mostly on (-109). The microstructure containing these thin defect layers is very effective in reducing thermal conductivity and thus increasing the ZT value to the level of 0.95 is achieved at 150 °C. Structure-property relationships of rhenium silicide will be fully discussed, in particular in the light of nano-scale defect structures.

11:00 AM F6.9
Highly Anisotropic Thermoelectric Properties of $ReSi_{1.75}$ Single Crystal. Min Wook Oh[1], Katsushi Tanaka[2], Haruyuki Inui[2], Myung-Hoon Oh[3] and Dang-Moon Wee[1]; [1]Dept. of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejon, South Korea; [2]Dept. of Materials Science and Engineering, Kyoto University, Kyoto, Japan; [3]Dept. 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 $C11_b$ lattice. Although the electrical transport properties of the silicides have been reported by several researchers, they are controversial with each other. Our recent measurements on the electrical transport properties of single crystals of $ReSi_{1.75}$ indicated that the value of electrical resistivity along [001] (the c-axis of the parent $C11_b$ structure) is higher than that along [100] (the a-axis of the parent $C11_b$ structure). Also, our findings reveal a semiconducting behavior in the temperature dependence of the electrical resistivity for both orientations. It is noteworthy that 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 orientation dependences of the sign of thermoelectric power (positive or negative) are unique, to the best of our knowledge. Of course, the anisotropic thermoelectric power mechanism is not yet well understood. The transport properties of electrons in semiconductors can be conveniently derived by solving the Boltzmann equation. Most theoretical works derive the coefficients related to electrical transport properties, such as the drift mobility and thermoelectric power under the assumption of parabolic and isotropic band structures. However, non-parabolic and anisotropic band structures are important for narrow band gap semiconductors such as $ReSi_{1.75}$. We have made some effort to calculate the electrical conductivity and thermoelectric power of $ReSi_{1.75}$ for various temperatures with the assumption of the non-parabolic and anisotropic band structures and to clarify the origin of the anisotropic thermoelectric power with the derived values. We found that the contribution of holes to the whole energy transportation along [001] induced by the Seebeck effect is negligible due to the large effective mass of holes along [001], which is mainly derived from the characteristic flat band feature of the band structures. In this picture, the negative thermoelectric power along [001] at high temperatures is well understood within the two-band conduction.

11:15 AM *F6.10
Thermoelectric Properties of Icosahedral Cluster Solids.
Kaoru Kimura[1,3,4], Junpei Tamura Okada[2], Hongki Kim[1], Takehito Hamamatsu[1], Tomohiro Nagata[3] and Kazuhiro Kirihara[4]; [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]Nanoarchitectonics 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 or environment of icosahedral cluster can cause metallic-covalent bonding conversion, which can cause that the electrical conductivity σ and the Seebeck coefficient S can be as high as those of metals and semiconductors, respectively. Five-fold symmetry of the icosahedral cluster does not match with the translational symmetry of a crystal, consequently makes lower thermal conductivity κ with complex structure. For these reasons, ICS are promising candidates for thermoelectric materials. Using MEM/Rietvelt method, we successfully obtained the clear image of the electron density distribution for α-AlReSi approximant crystal. The bond strength distributes widely from weak metallic to strong covalent bond, and the intra-cluster bonds are stronger than the inter-cluster ones. This means that α-AlReSi is located at the intermediate state of molecular, metallic- and covalent-bonded solids. Composition dependences of atomic density and quasi-lattice constant for AlPdRe icosahedral quasicrystals show the above situation is the same in the 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 Ru for Re. In β-rhombohedral 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, σ is increased very much, S is decreased even to negative value and κ 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 $Yb_{14}MnSb_{11}$.
Shawna R. Brown[1], Susan M. Kauzlarich[1], G. Jeff Snyder[2] and Franck Gascoin[2]; [1]Chemistry, University of California, Davis, Davis, California; [2]Materials and Device Technology, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

Thermoelectric research has seen a renewed interest in the past decade which has been spurred by the increased environmental, energy and aerospace challenges facing todays 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, $Yb_{14}MnSb_{11}$, have revealed a high figure of merit at elevated temperatures (900-1275 K). The Zn-doped analog, $Yb_{14}Mn_{1-x}Zn_xSb_{11}$ with x = 0.17, 0.33, 0.50, 0.67, and 0.83, has been synthesized with aims of evaluating the doping influence on the physical properties of the system, and also improving the figure of merit beyond that of $Yb_{14}MnSb_{11}$ by adding disorder and lowering the thermal conductivity. Recent microprobe, single crystal diffraction, DSC/TG, electrical resistivity, Seebeck and MPMS measurements on these doped crystals will be presented. The results obtained from these compounds will be compared to other promising thermoelectric materials.

SESSION F7: Thermionics and Photovoltaics
Chairs: Gerald Mahan and Ali Shakouri
Wednesday Afternoon, November 30, 2005
Room 313 (Hynes)

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

A brief overview of the research activities at the ONR MURI center on Thermionic Energy Conversion will be presented. The goal is to achieve direct thermal to electric energy conversion with >20% efficiency and >1W/cm2 power density at a hot side temperature of 300-650C. 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 vacuum 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.
Zhixi Bian and Ali Shakouri; Electrical Engineering Department, University of California Santa Cruz, Santa Cruz, California.

The performance of a thermoelectric material is determined by the figure of merit ZT, which is a function of the Seebeck coefficient, and the electrical and thermal conductivities. Heterostructure integrated thermionic energy converters are expected to offer larger thermoelectric power factor S by selective emission of hot electrons. 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 and the parasitic heat loss. The main 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 nonplanar heterostructure interface with roughness in order of electron mean free path. This is expected to have some combined benefits of increased effective interface area, and reduced total internal reflection for the electron trajectories arriving at the interface. Monte Carlo simulations of various geometries show that the carrier emission can be improved by 70% for nonplanar barrier compared to the planar counterpart. The second method is to use planar high barrier heterostructures with different effective masses for charge carriers in well and barrier regions. When an electron passes from a lower effective mass emitter and arrives at a barrier with higher effective mass, since both the lateral momentum and total energy are conserved, part of the lateral energy is coupled to the vertical direction and the electron gains momentum in the direction perpendicular to the interface to enter the barrier region. For high potential barriers, the improvement is about the same as the ratio of the effective masses of the two materials, which can be a factor of 5-10 for typical heterostructure material systems.

2:15 PM F7.3
Transport Formalism for Multibarrier Thermionic Devices.
Tammy Ellen Humphrey and Ali Shakouri; Electrical Engineering,

University of California Santa Cruz, Santa Cruz, California.

Solid-state power generators and refrigerators in which electron transport is primarily ballistic and those in which it is primarily diffusive both achieve reversibility in the same limit; when the transport of electrons is restricted to the energy where the occupation of states is 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. In practice, however, we 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 thermionic devices offer more freedom 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 thermionic 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 thermionic devices can be maintained in multibarrier devices designed to have a length longer than the electron mean-free path in order to reduce heat flow through the lattice. In a material with a periodicity on the order of an electron mean-free path, it is expected that most electrons move ballistically through the barrier regions where electron density 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 transport formalisms. We are approaching this problem by adapting techniques developed in mesoscopic physics to describe transport through conductors connected to a multiplicity of reservoirs with different temperatures and chemical potentials. 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 Rawat[1,2], HoGyoung Kim[3] and Timothy Sands[1,2]; [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 multilayers are predicted to exhibit optimal thermoelectric figures of merit (ZT) for Schottky barrier heights in the range of 4 to 5 times k_BT (ref. [1]). In addition to the Schottky barrier height, the thermoelectric performance of these multilayered structures depends on the cross-plane thermal conductivity of the multilayer, thus alloying and a high interface density are desirable. For applications involving moderate to high hot-side temperatures ($\sim$300-700 ^oC), the multilayers must be stable against corrosion, decomposition, and interdiffusion. The nitrides meet these criteria, and offer potential materials combinations for metal-semiconductor multilayers with tunable electronic and thermal transport properties. Nitrides such as TiN, ZrN, VN, and TaN are metals whereas GaN, InN, ScN and their alloys are semiconductors. In this presentation, we describe our efforts to evaluate the potential of metal/semiconductor nitride multilayers for direct thermal energy conversion. Prototype multilayers have been synthesized by reactive pulsed laser deposition in ammonia ambient at substrate temperatures ranging from 550-750 ^oC. TiN/GaN and VN/GaN multilayers with periods from 5 to 15 nm and individual layer thicknesses down to 0.5 nm have been grown on MgO and sapphire substrates. Analysis by transmission electron microscopy and x-ray diffraction shows that the interfaces are stable and pinhole-free, with no detectable interdiffusion. Except in the case of the very thinnest GaN layers ($\sim$ 1nm 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} rocksalt planes parallel to the basal planes of GaN. Schottky barrier height measurements by the I-V method yield barrier heights in the range of 400 to 500 meV, suggesting that replacement of GaN with (In,Ga)N alloys will permit tuning of the barrier height into the desired 150 to 350 meV range. In-plane electronic transport measurements at room temperature show a transition from semiconducting to metallic behavior as the TiN layer thickness increases from the sub-nm range to a few nm. For multilayers with 10 nm GaN layers, the value of $S^2\sigma T$ is maximized 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 multi-layers is in progress and will be presented at the meeting. Reference: [1] $Improved Thermoelectric Power Factor in Metal - Based Superlattices$,D. Vashaee and A. Shakouri, Phys. Rev. Lett. 92, 106103 (2004).

3:45 PM F7.5
Effect of Nanostructured Emitters on the Performance of Vacuum Thermionic Energy Conversion Devices.
Joshua Ryan Smith[1], Griff Bilbro[2] and Robert Nemanich[1]; [1]Physics, North Carolina State University, Raleigh, North Carolina; [2]Electrical and Computer Engineering, North Carolina State University, Raleigh, North Carolina.

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

4:00 PM F7.6
Electron and Phonon Transport in Nanostructured Carbons.
Dieter M. Gruen and Paola Bruno; Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

Carbon dimer, C_2, a nucleation and growth species in hydrogen-poor plasmas leads to high secondary nucleation rates (10^{10} cm^{-2} sec^{-1}) and results in ultrananocrystalline diamond (UNCD) films composed of 3-5 nm crystallites.(1) Such films can be made n- or p-type conducting (up to 500 S/cm) by the addition of nitrogen or boron to the synthesis gas.(2) Although single crystal diamond is highly thermally conducting, UNCD has a thermal conductivity of 0.02W/Kcm because of effective phonon scattering at the disordered grain boundaries.(3) Tight-binding density functional calculations show that UNCD has a plethora of electronic states throughout the band gap of diamond with a pronounced narrow peak in the DOS at the Fermi level.(4) Grain boundary conduction is enhanced by the presence of nitrogen which results in an increased fraction of pi-bonded carbon atoms bridging the grain boundaries. Enhancement of thermoelectric properties in low dimensional materials has been extensively discussed.(5,6) Preliminary measurements on UNCD indicate that ZT values near unity can be reached. Work currently under way is aimed at optimizing ZT values by using nanotube/UNCD composites. Such composites have already been synthesized but not characterized.(7) The presence of "graphitic" nanowires covalently bonded to thermally insulating UNCD crystallites can be expected to result in improved electrical conductivity and mobility. Measurements on simultaneously synthesized and self-assembled nanotube/UNCD composites will be presented. *This work was supported by the U. S. Department of Energy, BES-Materials Sciences under Contract W-31-100-ENG-38. References 1. D. M. Gruen, "Nanocrystalline Diamond Films", Ann. Rev. Mater. Sci. 29, 211-59, (1999). 2. O. A. Williams, S. Curat, J. E. Gerbi, D. M. Gruen, R. B. Jackman, "n-type Conductivity in Ultrananocrystalline Diamond Films", Appl. Phys. Lett., 85, 1, (2004). 3. L. Nanver, DIMES Technical University, Delft, The Netherlands, Private Communication. 4. P. Zapol, M. Sternberg, L. A. Curtiss, T. Frauenheim, D. M. Gruen, "Tight-Binding Molecular-Dynamics Simulation of Impurities in Ultrananocrystalline, Diamond Grain Boundaries", Physical Review B., 65, 0454, (2002). 5. Y. M. Lin and M. S. Dresselbaus "Thermoelectric Properties of Superlattice Nanowires" Phys. Rev. B, 68, 075304 (2003). 6. T. E. Humphrey and H. Linke "Reversible Thermoelectric Nanomaterials", Phys. Rev. Lett., 94, 096601 (2005). 7. D. M. Gruen, and J. W. Elam, "Nanotube-Diamond Composites", MRS Fall Meeting, Paper #Q2.3, (December 1-5, 2003).

4:15 PM F7.7
Thermionic Electron Emission from Nitrogen Doped Diamond Films and their Potential in Vacuum Thermionic Energy Conversion. Franz A. Koeck, Yingjie Tang and Robert J. Nemanich; Physics, NC State University, Raleigh, North Carolina.

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 thermionic emission spectra and current vs. temperature results that establish that electron emission from nitrogen doped diamond films is detectable above $\sim$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 (Hf), we measure a voltage and current indicating energy conversion. This research is supported by the ONR under the TEC-MURI project.

4:30 PM F7.8
A Theoretical and Comparison Approach for Bass Modeling and Lean Fabrication of In-Line Continuous Thin Film Processes for Photovoltaic Modules. Hershall Joseph Shelley, Mechanical Engineering, Colorado State University, Fort Collins, CO, Colorado.

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. The current world photovoltaic production 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 a 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 for future needs. A 2 MW CdTe prototype production system is been 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 will have six sub-factories. A 100x volume improvement 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 lamination 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 continous manufacturing processes 2). Develop Manufacturing process research for economically producing these solar photovoltaic cells. Use High Processing Speed: Deposition speed is up to 100 times faster than other photovoltaic technologies Integrated, all in line production processing Demonstrate Lean and high production manufacturing of CdTe modules.

4:45 PM F7.9
Properties of direct bandgap Sn_xGe_{1-x} thin films and Quantum Dots. Jordana Blacksberg, L. Douglas Bell and Shouleh Nikzad; Caltech Jet Propulsion Laboratory, Pasadena, California.

Sn_xGe_{1-x} epilayers and quantum dots (QDs) are of great interest as materials that can provide tunable direct band gaps, with the potential for achieving entirely group IV-based optoelectronic devices. These materials could be used in a wide range of applications such as thermophotovoltaics (TPV), emitters, and infrared detectors. For thermophotovoltaic applications, Sn_xGe_{1-x} thin films and Sn QDs in direct conversion cells offer a potentially high payoff in a new and inexpensive material system. This system would be fully tunable to varying source temperatures. For example the bandgap of Sn QDs (theoretically tunable from virtually 0 eV and upwards) could be used up to $\sim$0.67 eV where Ge would start absorbing. While Ge is a direct bandgap semiconductor, an indirect to direct transition has been observed with the addition of $\sim$10 % Sn in Ge. Quantum confinement effects have been observed for Sn with dimensions $<$ 30 nm. Because SnxGe1-x and Sn QDs are direct bandgap materials unlike both Si and Ge, a high infrared absorption cross section would make monolithic thin film TPV devices possible. While the potential applications are appealing, due to large lattice mismatch and strong surface segregation substantial challenges remain in growth and processing. We have developed a growth process for strained, defect-free epitaxial SnxGe1-x thin films with Sn concentrations up to 15% on Ge (100) using low temperature ($<$ 200 °C) Molecular Beam Epitaxy (MBE), and have demonstrated extended long wavelength absorption beyond the Ge band edge using FTIR and photomodulated reflectance spectroscopy. Sn quantum dots (QDs) are formed in these films by annealing at $\sim$ 750 °C. In order to successfully integrate Sn_xGe_{1-x} into optoelectronic systems, a high QD density, successful elimination of defects, and control over QD size and uniformity will be required. We will discuss several parameters that have been found to effect these properties, including Sn concentration, layer thickness, annealing temperature, and substrate patterning. We will also discuss compositional analysis of quantum dot structures by energy dispersive x-ray spectroscopy as well as Local Electrode Atom Probe (LEAP) nanoanalysis.

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

F8.1
Optical Properties of Thermoelectric Alkali Metal Chalcogenide Compounds $K_2Bi_{8-x}Sb_xSe_{13}$.
Euripides Hatzikraniotis[1], Theodora Kyratsi[2,3], T. Zorba[1], Konstantinos M. Paraskevopoulos[1] and Mercouri G. Kanatzidis[2]; [1]Physics, Aristotle University of Thessaloniki, Thessaloniki, Greece; [2]Chemistry, Michigan State University, East Lansing, Michigan; [3]Mechanical & Manufacturing Engineering, University of Cyprus, Nicosia, Cyprus.

Research on complex chalcogenide compounds has shown that alkali bismuth chalchogenides (A/Bi/Q A= alkali metal; Q= S, Se, Te) have many attractive features that make these compounds promising for thermoelectric investigations. Potassium members such as $K_2Bi_8Se_{13}$ have a low symmetry monoclinic structure. The structure framework consists of two different interconnected types of Bi/Se building blocks of NaCl(100)- and NaCl(111)-type. Interconnected blocks leave structural tunnels where K+ ions reside. The highly anisotropic structure results in a needle-like morphology along the b-crystallographic axis. Their complex crystal structure leads to a very low thermal conductivity. It is possible that in addition to the large, low symmetry unit cell the weakly bound K+ ions play an important role via the ôphonon glass-electron crystal≫ mechanism. In this work, the infrared reflectivity spectra of several alkali metal chalcogenides are reported for the first time. Optical investigations were conducted on crystalline and palletized samples, treated at different conditions. The results from the analysis of the spectra will be presented and discussed in detail.

F8.2
Thermoelectric Properties of $K_2Bi_8Se_{13-x}S_x$ Solid Solutions.
Theodora Kyratsi[1,2], Sangeeta Lal[3], Tim Hogan[3] and Mercouri G. Kanatzidis[1]; [1]Chemistry, Michigan State University, East lansing, Michigan; [2]Mechanical & Manufacturing Engineering, University of Cyprus, Nicosia, Cyprus; [3]Electrical and Computer Engineering, Michigan State University, East lansing, Michigan.

The solid solutions of β-$K_2Bi_8Se_{13}$ exhibit very low thermal conductivity and highly anisotropic electrical properties. They can posses high power factors and thus comprise an interesting series of materials for thermoelectric investigations. Up to now substitutions on the Bi and alkali metal sites have been studied in order to tune the thermoelectric properties. In this work we present the thermoelectric properties of the sulfur-substituted $K_2Bi_8Se_{13-x}S_x$ members with respect to Seebeck coefficient, the electrical and thermal conductivity as a function of temperature. Seebeck coefficient measurements showed the n-type character of all members while the electrical conductivity shows higher values compare to the other solid solution series of the same type. Hall effect measurements indicate a high

carrier concentration which is typical in the alkali bismuth chalcogenide group of compounds. The lattice thermal conductivity is strongly affected due to the Se/S disorder. The temperature dependence of the figure-of-merit ZT shows that these materials have potential for power generation applications.

F8.3
Thermoelectric Properties of Tl_2Te-Sb_2Te_3 Pseudo-Binary System. Keita Goto, Ken Kurosaki, Hiroaki Muta and Shinsuke Yamanaka; Division of Sustainable Energy and Environmental Engineering, Osaka University, Suita, Japan.

Polycrystalline-sintered samples of thallium compounds, $(Tl_2Te)_{100-x}(Sb_2Te_3)_x$ (x=0.2, 0.5, 1.0, 3.0), have been prepared by melting Tl_2Te and Sb_2Te_3 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 about 600 K. The electrical resistivities of all the 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 $2.4x10^{-4}$ $Wm^{-1}K^{-2}$ at 580 K obtained for x=3.0, $(Tl_2Te)_{97}(Sb_2Te_3)_3$, 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 Tl_2Te 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 Properies of LnPdX (Ln = lanthanide; X = Sb, Bi) Ternary Compounds.
Takeyuki Sekimoto, Ken Kurosaki, Hiroaki Muta and Shinsuke Yamanaka; Sustainable Energy and Environmental Engineering, Osaka University, Suita, Osaka, Japan.

Polycrystalline samples of LnPdX (Ln = lantanide; 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 were measured by a 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 vlues of the thermoelectric power of ErPdSb and ErPdBi are positive in the whole temperature region. On ErPdSb and ErPdBi, the activation energy estimated from the natural logarithm of the electrical resistibvity vs the inverse of temperature plot is 0.30 and 0.03 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 temperature is 4.7W/m K and 5.0W/m K, 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 $AgPb_mSbTe_{m+2}$ (m=4,6,8).
Joseph Sootsman[1], Mercouri Kanatzidis[1], Oleg Palchik[2] and Ctirad Uher[2]; [1]Department of Chemistry, Michigan State University, East Lansing, Michigan; [2]Department of Physics, University of Michigan, Ann Arbor, Michigan.

The thermoelectric properties of the $AgPb_mSbTe_{m+2}$ family of compounds with values of m=10-18 have shown high figure of merit. These materials posses 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 Homologous Family $CsPb_mBi_3Te_{5+m}$. Aurelie Gueguen, Eric Quarez 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 $CsBi_4Te_6$. Recently, our effort to produce new materials that resemble to $CsBi_4Te_6$ led to the discovery of the homologous series of materials $CsPb_mBi_3Te_{5+m}$. 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 $CsBi_4Te_6$. The $CsPb_mBi_3Te_{5+m}$ compounds show low thermal conductivity compared to that of Bi_2Te_3 and $CsBi_4Te_6$. Preparing analogs of such compounds can be a way to tune the thermoelectric properties. We are currently investigating the substitution of lead in $CsPb_mBi_3Te_{5+m}$ by other elements such as silver, potassium, sodium, barium, strontium and calcium. We will present the new compound $Cs_{0.74}K_{0.76}Bi_{3.5}Te_6$. Single crystal X-Ray diffraction study indicated that this compound is isostructural to $CsPbBi_3Te_6$ (m=1) with cell parameters a = 6.3810 (9) $\AA$, b = 28.3263 (41)$\AA$, c = 4.4134(6) $\AA$ in the Cmcm space group. By analogy with $CsPbBi_3Te_6$, the formula of $Cs_{0.74}K_{0.76}Bi_{3.5}Te_6$can be rewritten as $(Cs_{0.74}K_{0.26})(K_{0.5}Bi_{0.5})Bi_3Te_6$. Preliminary electrical conductivity and thermopower measurements indicate n-type behavior. Further experiments aimed at preparing other analogs in the homologous series will be presented.

F8.7
Synthesis, Structures, and Magnetic Properties New Ternary Europium and Ytterbium Pnictogen Chalcogenides.
Geng Bang Jin[1], Shane J. Crerar[2], Arthur Mar[2] and Thomas E. Albrecht-Schmitt[1]; [1]Chemistry and Biochemistry, Auburn University, Auburn, Alabama; [2]Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada.

In this poster we will present recent results from our group on the preparation, single crystal X-ray diffraction studies, and magnetic property measurements on several new europium and ytterbium pnictogen sulfides and selenides. In the europium/Pn (Pn = Sb, Bi)/S or Se system, we will demonstrate the propensity of these compounds for containing Eu in the divalent state, whereas Yb is trivalent in these compounds. These Eu compounds undergo antiferromagnetic ordering at low temperatures. Our work on the Yb/Sb/S 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 f-, with Os d-, 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[1], Jonathan D'Angelo[1], Michael A. Pajor[1], Adam D. Downey[1], Edward Timm[3], Harold Schock[3], Mercouri G. Kanatzidis[2] and Timothy P. Hogan[1]; [1]Electrical and Computer Engineering Department, Michigan State University, East Lansing, Michigan; [2]Chemistry Department, Michigan State University, East Lansing, Michigan; [3]Mechanical 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 these devices under various load and temperature gradients [2]. An introduction to the system will be presented, as well as results for devices made of the L-A-S-T materials.

F8.10
Investigation of Low Resistance Contacts to Pb-Sb-Ag-Te (LAST) Materials for Module Fabrication.
Jonathan James D'Angelo[1], Jarrod Short[1], Adam Downey[1], Michael Pajor[1], Edward Timm[3], Harold Schock[3], Mercouri Kanatzidis[2] and Timothy Hogan[1]; [1]Electrical and Computer Engineering, Michigan State University, East Lansing, Michigan; [2]Chemistry, Michigan State University, East Lansing, Michigan; [3]Mechanical 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 temperatures and through thermal cycling. Here we present 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 20μWcm2 have been measured for annealed antimony to n-type LAST samples. We present the procedures for fabricating low resistance contacts and the use of these procedures towards the fabrication of high efficiency thermoelectric generator modules.

F8.11
Development of thermoelectric generating modules and system. Toshinori Ota, Kouichi Fujita and Chieko Tokunaga; Ishikawajima-Harima Heavy Industries, Yokohama, Japan.

IHI is investigating application of thermoelectric conversion systems on the usage of radiant heat for industrial furnace.The thermoelectric module unites receive the heat originating from the insulator by means of radiation.In this work, we show the deverop a methode of receiving heat and materials for reciving radiation.Experimental results are included related to the mechanical characteristics,as well as a performance of module based on the heat transmission and thermoelectric conversion characterristic.The results from these experiments will be presented at the conference.

SESSION F9: Half Heuslers, Thallium Tellurides, and Skutterudites
Chairs: Thierry Caillat 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. Poon[1], S. Culp[1], N. Sorloaica[2] and Terry M. Tritt[2]; [1]Physics, University of Virginia, Charlottesville, Virginia; [2]Physics & Astronomy, Clemson University, Clemson, South Carolina.

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

8:15 AM F9.2
High-Performance of Half-Heusler MNiSn (M=Hf,Zr) Single-Phase Thermoelectric Alloys Fabricated using Optical Floating Zone Melting. Yoshisato Kimura[1], Tomoya Kuji[2], Akihisa Zama[2], Yasufumi Shibata[3] and Yoshinao Mishima[1]; [1]Materials Science and Engineering, Tokyo Institute of Technology, Yokohama, Japan; [2]Graduate student, Materials Science and Engineering, Tokyo Institute of Technology, Yokohama, Japan; [3]Higashifuji Technical Center, Toyota Motor Corporation, Susono, Japan.

Thermoelectric materials allow us to directly convert waste heat to clean electric energy without sacrificing the environment. Half-Heusler type intermetallic compound is one of attractive candidate thermoelectric materials that are applicable at high temperatures up to around 1000 K. It is well known that Half-Heusler MNiSn (M=Hf,Zr,Ti) compounds exhibit n-type semi-conducting behavior and excellent thermoelectric properties, especially high Seebeck coefficient and low electrical resistivity. A drawback of relatively high thermal conductivity can be improved for instance by solid solution 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 MNiSn (M=Hf,Zr) single-phase alloys, or alloys having almost single-phase, to evaluate 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 (Hf_{1-x}, Zr_x)NiSn alloys, where x widely 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, (Hf_{1-x}, Zr_x)NiSn alloys grown by OFZ exhibit tremendously excellent power factor, i.e. electrical figure of merit, ranging around 3.0 up to 3.6 mW/mK^2, 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 μV/K and that ZrNiSn alloy shows electrical resistivity lower than 50 $\mu\Omega$m at room temperature. In a temperature range from 700 to 1000 K, (Hf_{1-x}, Zr_x)NiSn alloys exhibit about -200 μV/K of thermoelectric power and about 50 mW/mK^2 of electrical resistivity regardless of Hf and Zr concentrations ratio. Thermal conductivity of OFZ (Hf_{1-x}, Zr_x)NiSn alloys strongly depends on the Hf and Zr concentrations ratio. The solid solution effect on lowering thermal conductivity is maximized at ($Hf_{0.5}$, $Zr_{0.5}$)NiSn alloy. Thermal conductivity of ($Hf_{0.5}$, $Zr_{0.5}$)NiSn alloy is effectively lowered around 3 W/mK which is about a half of the values of HfNiSn and ZrNiSn alloys. Consequently, the dimensionless thermoelectric figure of merit, ZT, of ($Hf_{0.5}$, $Zr_{0.5}$)NiSn alloy reaches as high as 0.9. It should be emphasized that further improvement of thermoelectric performance is possible through optimization of carrier concentration by the addition or substitution of elements, since ZT=0.9 has been achieved based on simple Hf-Zr-Ni-Sn quaternary alloy composition.

8:30 AM F9.3
Substitution effect on the thermoelectric properties of ZrNiSn based half-Heusler compounds. Hiroaki Muta, Takanori Kanemitsu, Ken Kurosaki and Shinsuke 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 were reached 3 mW/mK^2 above 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 for one week in sealed tubes. 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 Heusler alloy, titanium-tin alloy and pure tin element from XRD analysis. All the samples showed n-type semiconducting behavior. Pure ZrNiSn had lowest electrical conductivity and largest Seebeck coefficient. The substituted samples generally had lower Seebeck coefficient 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 coefficient. The result indicates high SPS temperature is desirable for the thermoelectric material. The maximum power factor was obtained for partially titanium substituted sample. The value reached about 4 mW/mK^2 at 700-900 K. Titanium and palladium substitutions effectively reduced the thermal conductivity. 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 R. Drymiotis, Amy Pope, Nicoleta Sorloaica and Terry Tritt; Physics and Astronomy, Clemson University, Clemson, South Carolina.

Half-Heusler alloys are excellent candidates for high-temperature thermoelectrics. Although several members of these alloys have been investigated extensively, the work done has been mainly on polycrystalline samples. However because of the intricacies of the half-Heusler lattice, mainly the existence of an ordered vacancy, polycrystalline samples might not be the appropriate choice. For the sake of comparison, we have investigated the properties of several single crystalline half-Heusler alloys. In particular we find that single crystalline TiCoSb is metallic whereas polycrystalline TiCoSb exhibits semi-metallic or semiconducting transport behavior. Small additions of V on the Ti side 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 arcmelted 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. Shinsuke 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 their thermoelectric properties. 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 Bi_2Te_3 and TAGS materials indicate relatively low the thermal conductivities, around 1.5 W/m/K. However, the thermal conductivities of our thallium compounds are below 0.5 W/m/K. Especially those of silver thallium tellurides are around 0.25 W/m/K 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 Tl-X-Te (X=Pb, Sn, Ge) systems. Atsuko Kosuga, Ken Kurosaki, Hiroaki Muta and Shinsuke Yamanaka; Sustainable Energy and Environmental Engineering, Osaka University, Suita, Osaka, Japan.

We recently focused the attention on Tl compounds due to their low thermal conductivity. In this study, some compounds of Tl-X-Te (X=Pb, 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. Almost 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, < 1 [W/m/K]. It can be said that the compounds of Tl-X-Te (X=Pb, Sn, Ge) systems have a possible candidate as a good thermoelectric material.

9:30 AM F9.7
Thermoelectric Properties of Ag-Tl-Te Ternary System. Ken Kurosaki, Atsuko Kosuga, Ketia Goto, Hiroaki Muta and Shinsuke Yamanaka; Sustainable Energy and Environmental Engineering, Osaka University, Suita, Osaka, Japan.

We have studied the thermoelectric properties of thallium compounds as novel thermoelectric materials. Especially, we focus on the Ag-Tl-Te ternary system. In this paper, we repot on a high performance thermoelectric material whose chemical formula is Ag_9TlTe_5. We prepared a polycrystalline sample of the compound by melting the appropriate amounts of Ag_2Te and Tl_2Te ingots 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 $3.87\text{x}10^{-4}$ $Wm^{-1}K^{-2}$ at 700 K. Although its electrical performance is not very high, Ag_9TlTe_5 exhibits an excellent thermoelectric figure of merit because of its extremely low thermal conductivity (around 0.25 $Wm^{-1}K^{-1}$). Its highest ZT value is 1.23, obtained at 700 K. Ag_9TlTe_5 combines extremely low thermal conductivity and relatively low electrical resistivity, making it a very interesting high-performance thermoelectric material.

10:15 AM *F9.8
Filling Fraction Limit for Impurities in CoSb3: Physical Understanding and Insight for New Thermoelectric Materials. Xun Shi, Yan Xu, Wenqing Zhang and Lidong Chen; Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China.

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

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

Tao He, Jiazhong Chen, T. Calvarese, 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 $Ce_x(Ru_{4-y}Ir_y)Sb_{12}$ Filled Skutterudite Compounds. April D. Jewell and Thierry Caillat; Jet Propulsion Laboratory, Pasadena, California.

Radioisotope Thermoelectric Generators (RTGs) have proved to be reliable, long-lived sources of electrical power that have enabled the conduct of a number of important U.S. missions since 1961. Past RTGs have used two types of thermoelectric materials: PbTe/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 $Ce_yRu_{4-y}Ir_ySb_{12}$ filled skutterudites compounds. We have synthesized polycrystalline samples for $x \leq 1.5$ by a powder metallurgy technique. Dense samples have been hot-pressed from the pre-reacted powders and characterized by a variety of techniques including electron probe microanalysis, differential scanning calorimetry and thermogravimetic analysis. Seebeck coefficient, electrical resistivity, Hall coefficient, and thermal conductivity measurements have been conducted on the samples from room temperature to 1275K. Results show that the samples are phase stable up to 1275K. The results of the transport property measurements are presented and discussed.

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

We acquire electron energy loss spectra of the binary skutterudites CoP3, CoAs3, CoSb3 and NiP3, 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-Kroning 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. Refrences [1] H. Raether. Excitation of Plasmons and Interband Transitions by Electrons. Vol. 88 of Springer Tracts in Modern Physics. Berlin: Springer-Verlag (1980). [2] D. Pines. Collective energy losses in solids. Rev. Mod. Phys. 28, 184-199 (1956). [3] R. F. Egerton. Electron Energy Loss Spectroscopy in the Electron Microscope. New York: Plenum Press (1986).

11:30 AM F9.12
The Synthesis and Characterization of CoSn1.5Te1.5, CoGe1.5Se1.5, and Partially Filled CoGe1.5Se1.5.
Arwyn Smalley[1,2], Qiyin Lin[1], David C. Johnson[1], Joshua Martin[3] and George S. Nolas[3]; [1]Chemistry, University of Oregon, Eugene, Oregon; [2]Chemistry, Norwich University, Northfield, Vermont; [3]Physics, University of South Florida, Tampa, Florida.

We have synthesized the skutterudite-like compounds CoGe1.5Se1.5, and CoSn1.5Te1.5 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 F9.13
Abstract Withdrawn

SESSION F10: Clathrates and New Measurement Techniques
Chairs: Tim Hogan and David Johnson
Thursday Afternoon, December 1, 2005
Room 313 (Hynes)

1:30 PM F10.1
The Dynamics of the Caged Guests in Filled Germanium Clathrates. Raphael P. Hermann[1,2], Fernande Grandjean[1], Veerle Keppens[2], Werner Schweika[3], George S. Nolas[4], David G. Mandrus[5], Brian C. Sales[5], Hans M. Christen[5], Pierre Bonville[6] and Gary J. Long[7]; [1]Dept of Physics, Universite de Liege, Liege, Belgium; [2]Materials Science and Engineering, The University of Tennessee, Knoxville, Tennessee; [3]Institut fuer Festkoerperforschung, Forschungszentrum Juelich, Juelich, Germany; [4]Dept of Physics, University of South-Florida, Tampa, Florida; [5]Div Condensed Matter, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [6]Service de Physique de l'Etat Condense, Centre d'Etudes de Saclay, Gif sur Yvette, France; [7]Dept 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 NH_3. In the filled gallium-germanium clathrates $R_8Ga_{16}Ge_{30}$, 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 as Einstein oscillators. Such a "rattling" behavior provides an efficient mechanism in reducing the thermal conductivity. Such materials are promising candidates for thermoelectric applications, because they behave as an electron-crystal and a phonon-glass. Inelastic neutron scattering and nuclear elastic scattering measurements have yielded the phonon density of states in $R_8Ga_{16}Ge_{30}$. The obtained Einstein oscillator energies are in good agreement with those obtained by other techniques such as atomic displacement parameters,[1] heat capacity,[1] Raman scattering,[2] and resonant ultrasound spectroscopy measurements.[3] Neutron diffraction studies on $R_8Ga_{16}Ge_{30}$ 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. Ultrasound attenuation in $Sr_8Ga_{16}Ge_{30}$ clathrates indicated a high density of tunneling states below ∼1 K.[4] Because the off-centering of the Eu guests is larger than for the Sr guests, the Eu dynamics is likely to be governed by tunneling instead of thermally activated hopping, even at higher temperatures. The detection of such slow guest motion is challenging because the typical time and energy scales involved are ca. 4 ns and 1 μeV, respectively. We have studied the europium dynamics by europium-151 Mössbauer spectroscopy – a technique that presents the advantage of specifically probing the behavior of the europium guests and we have measured the radio-frequency absorption in $Eu_8Ga_{16}Ge_{30}$. Both results indicate that the europium atoms are tunneling with a frequency of ∼450 MHz. 1. Sales B.C., Chakoumakos 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, 7157 (2000). 3. Zerec I., Keppens V., McGuire M. A., Mandrus D., Sales B. C., and Thalmeier P., Phys. Rev. Lett. 92, 185502 (2004). 4. Keppens V., Sales B.C., Mandrus D., Chakoumakos B.C., Laermans C., Phil. Mag. Lett. 80, 907 (2002).

1:45 PM F10.2
Transport Properties of Type II Sodium-Silicon Clathrates.
Matt Beekman[1], Jan Gryko[2] and George S. Nolas[1]; [1]Department of Physics, University of South Florida, Tampa, Florida; [2]Department 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 Na_xSi_{136} clathrates, where x has been varied between the minimum value of 0 and maximum value of 24. Transport measurements are presented, and the prospects of these materials for thermoelectric applications will be discussed.

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

The clathrates Sr8Ga16Ge30 and Ba8Ga16Ge30 are promising materials for thermoelectric applications due to their low thermal conductivity, high electrical conductivity and relatively high thermopower. Formation of stoichiometric films of these complex materials has been challenging. Laser ablation of the composite targets of these materials produced films with stoichometries closer to the starting material. However, very low ablation thresholds (<1 J/cm2) for these materials require the ablation to be carried out at low uv laser fluences to avoid molten particulate ejection. Low laser fluence leads to low plasma temperatures and variations in stoichometry 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 uv ablation laser 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 L. Okamoto, Katsushi Tanaka and Haruyuki Inui; Department of Materials Science and Engineering, Kyoto University, Kyoto, Kyoto, Japan.

The very low thermal conductivity is one of characteristics of clathrate compounds, which is believed to result from rattling motion of guest atoms in the large polyhedral cages. The rattling motion is monitored as anomalously large atomic displacement parameters (ADPs) at guest atom sites in X-ray and/or neutron diffraction

measurements. When values of ADPs are considerably large, the split-site model is sometimes employed for structure analyses. Then, the anomalously large ADPs based on the single-site model can be interpreted as a sum of two kinds of thermal motion; one is thermal vibration around split sites (ADP_{split}) and the other is thermal jump among the split sites. Upon alloying with Ga, values of lattice thermal conductivity of both type-I and -III 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 ADP based on the single-site model does not predict how lattice thermal conductivity is reduced. Values of ADPs based on the split-site model (ADP_{split}) for both type-I and -III compounds decrease with the increase in the Ga content, indicating that the value of ADP_{split} does not predict the tendency for reduction of lattice thermal conductivity. On the other hand, the distance between split sites for both type-I and -III compounds increases with the increase in the Ga content. The fact the split distance inversely correlates with the value of lattice thermal conductivity indicates that thermal jump among the split sites is a key factor for reducing lattice thermal conductivity in clathrate compounds.

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

Intermetallic clathrate coumpounds, in particular type-I and -III clathrates, have attracted considerable interest as promising thermoelectric materials because of their low thermal conductivity and high electric conductivity. Type-I clathrate compounds, M_8X_{46} (M=alkali or alkali earth metals, X=Si, Ge), are composed of two kinds of cage structures designated X_{24}-tetrakaidecahedron 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 electrical resistivity is not much different from that of single phase compounds. Such low thermal conductivity in two-phase mixtures is discussed in terms of mismatch in rattling phonon modes between type-I and -III clathrate compounds. One of the two-phase mixtures of type-I and -III exhibits a thermoelectric figure of merit as high as unity.

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

This paper presents the first cross-plane thermoreflectance image of the temperature distribution in a thermoelectric element under bias. Using the technique of lock-in CCD thermoreflectance imaging [1], we can map the temperaure 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 offers a complete picture of the quasi-equilibrium transport within the device. The submicron resolution of the thermoreflectance image enables clear determination of localized heating due at interfaces - for example to due contact resistance - and thermal imedance 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 Peltier and Joule components of the heating are possible, and finite difference simulations of the devices are presented for comparison with experiment. In this way it is possible to simultaneously aquire information about the Seebeck coefficient, electrical conductivity, and thermal conductivity of the thermoelectric material. The measurements demonstrate the feasiblity of non-contact thermal measurements at the sub-micron scale. [1] D Lueerssen, J Hudgings, P Mayer, R J Ram, "Nanoscale Thermoreflectance With 10mK Temperature Resolution Using Stochastic Resonance ", Semitherm, 15-17 March 2005

3:30 PM F10.7
Application of transmission line theory for modeling of a thermoelectric module in multiple configurations for AC electrical measurements. Adam Darwin Downey[1], Timothy P. Hogan[1], Edward Timm[3], John Androulakis[2], Eric Quarez[2], Ferdinand Poudeu[2], Mercouri G. Kanatzidis[2] and Harold Schock[3]; [1]Electrical and Computer Engineering, Michigan State University, East Lansing, Michigan; [2]Chemistry Department, Michigan State University, East Lansing, Michigan; [3]Department 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 electrical circuits for both the thermal and electrical characteristics of the module. Measurements were taken over the frequency range of 1mHz to 500Hz using lock-in amplifiers. We present data showing the extraction of ZT from such measurements on commercially available modules. By knowing either the heat capacity of the module or the average module Seebeck coefficient, determination of the thermal conductance can also be achieved. This first model proposed here provides a simple equivalent circuit which can be analyzed using an electrical simulator such as SPICE. This model makes use of the magnitude and phase of the electrical impedance measured by the lock-in amplifiers at the input terminals of the module and includes fitting parameters of the total electrical resistance, thermal 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 all components of a 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 unicouples in either a standard or inline configuration, 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 Mavrokefalos[1], Jianhua Zhou[1], JaeHun Seol[1], Feng Zhou[1], Michael Thompson Pettes[1], Li Shi[1], Chuangui Jin[2] and Xiaoguang Li[2]; [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 $ZT=S\hat{2}\times\sigma\times T\div\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the temperature. It was found in our measurements that the thermoelectric properties of individual electro-deposited bismuth telluride nanowires are largely influenced by the crystal structure including crystalline quality, chemical composition and surface roughness of the nanowires. The thermoelectric properties and crystal structure were characterized on different nanowires so that the correlation between the crystal structure and thermoelectric properties could not be established. In this paper, we report the development of a nano-instrument that allows us to characterize and correlate the structure and properties of the same individual nanowires. The nano-instrument is based on an improved design of our microfabricated suspended device which were reported earlier [4]. The current design of the device consists of two suspended membranes each suspended by six 400-800 μm long SiNx 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 using 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

chemical composition can be correlated with the obtained thermoelectric properties. This method is used for structure and property characterizations of individual bismuth telluride, bismuth antimonite, and antimonite telluride nanowires synthesized using an electrochemical deposition method. References: [1] Y.-M. Lin, X. Sun and M. S. Dresselhaus, Phys. Rev. B 62, 4610 (2000) [2] N. Mingo, Appl. Phys. Lett. 84, 2652 (2004) [3] J. Zhou, C. Jin, J. Seol, X. Li, L. Shi, submitted to Appl. Phys. Lett. [4] L. Shi, D. Li, C. Yu, W. Jang, Z. Yao, P. Kim and A. Majumdar, J. Heat Transfer 125, 881-888 (2003)

4:00 PM F10.9
Thermoelectric Transport Measurements of Bi2Te3 Nanostructured Films using a Scanning Hot Probe Technique. Claudiu Liviu Hapenciuc[1], Arup Purkayastha[2], Ganapathiraman Ramanath[2] and Theodorian Borca-Tasciuc[1]; [1]Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York; [2]Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

A scanning hot probe technique was developed for thermoelectric transport measurements of films. In this method a resistively heated Wollaston wire 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 thermal resistance of the film. The Seebeck coefficient 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 nanostructures solutions on glass substrates. The work will present the effect of growth and annealing conditions on the thermoelectric properties of the films measured at room temperature.

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

In 1990 Williams and Wickramasinghe reported a Scanning Chemical Potential Microsocpy (SCPM) method for the mapping of the thermovoltage formed at the tip-sample gap of a scanning tunneling microscope (STM) [1]. To explain their results, Stovneng and Lipavsky [2] proposed a model based on Bardeen's formula for tunneling current and Tersoff and Hamann's approximations to predict the tunneling thermovoltage as $V=\pi\hat{2}*k\hat{2}/(6e)*[d/dE(\ln\rho t(0))+d/dE(\ln\rho s(x,y,0))+z/h(2m/\Phi)\div 5]$ (1) where subscripts t and s denote the tip and sample, respectively, e is the electron charge, ρ is the local electronic density of states, E is the electron energy, z is the tip-sample separation, m is electron mass, h is Planck's constant, and Φ 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. Lyeo 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 in SThEM. While the tip and the sample were kept at two different temperatures in the SCMP 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 in the sample. The temperature gradient in the sample leads to a thermovoltage proportional to the spatial average of the local thermopower (or Seebeck coefficient, S(x, y) inside the non-uniform temperature zone of the sample, i.e., $V\approx S(x,y)(Tc-Ts)$ (2) where Tc is temperature at the contact point, Ts 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 an investigation 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] Stovneng, J. A. and Lipavsky, P. Phys. Rev. B 42, 9214 (1990). [3] Lyeo, H. K. et al. Science 303, 816 (2004).

4:30 PM F10.11
Thermoelectric Power of Gd-Doped Cerium Oxides (GDC): Measurement on Porous Samples. Hyungtae Lim and Anil V. Virkar; Materials Science and Engineering, University of Utah, Salt Lake City, Utah.

Measurements of thermoelectric power have been reported on many inorganic materials. In oxides, composition changes occur during measurement when subjected to variations in temperature and/or oxygen partial pressure. If a composition gradient exists across sample, due to imposed temperature gradient, an electromotive force (EMF) arises, known as Soret effect. In recent years to minimize effects of composition gradients, a modified technique has been used in which the average temperature is maintained constant. The composition changes that occur when subjected to various temperatures and atmospheres require chemical diffusion of oxygen in or out of the sample. Over the typical temperature range, diffusion kinetics is usually very sluggish. Thus, equilibration of sample composition under imposed conditions rarely occurs during the course of a typical experiment. Thus, measurements made on dense oxide samples often do not correspond to equilibrium conditions, and thus are not representative of the true thermoelectric power. To obtain accurate values of thermoelectric power of oxides corresponding to imposed conditions, measurements in this work were performed on porous samples instead of dense samples. Time required for compositional equilibration, which requires diffusion, is proportional to the square of diffusion distance, and inversely proportional to the chemical diffusion coefficient of diffusing species. In dense samples, diffusion distance is half the thickness of the sample, typically 1 millimeter. 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 Gd0.1Ce0.9O(2-δ) (GDC10). Silver does not change composition when heated in air, since it does not oxidize and does not exhibit compositional changes. It was observed that both dense and porous samples equilibrated in about same time, and measured thermoelectric power was also about the same. It was also observed that over the temperature range, time required for equilibration in porous GDC10 was several minutes. By contrast, time required for equilibration in dense GDC10 was several hours. The thermoelectric power on dense GDC 10 did not agree well with those on porous GDC 10 below ~600oC. Also, at low temperatures, EMF in dense samples did not equilibrate. Based on this work, it is concluded that thermoelectric power measured on dense samples is unreliable, especially at low temperatures. It is proposed that thermoelectric power measurements on oxides should be done on porous samples and not on dense.

4:45 PM ORGANIZER COMMENTS

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

F11.1
Pulsed Laser Deposition of Thermoelectric Cobaltate Thin Films. Weidong Si[1], Sang-moon Park[3], Yufeng Hu[2], Qiang Li[2] and Eli Sutter[3]; [1]Physics, Brookhaven National Laboratory, Upton, New York; [2]Materials Science, Brookhaven National Laboratory, Upton, New York; [3]Center 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 Calcium cobaltates on various substrates, including polycrystalline and (0001) sapphire, (100) and (111)Silicone wafer, even glass, by pulsed laser deposition. We found they have very good thermoelectric properties from the transport and magnetic measurements. We also found Calcium cobaltate have well-aligned crystal structure even on glass by cross-section transmission electron microscopy. A self-assembly mechanism may interpret the result.

F11.2

Thermoelectric properties of cubic perovskite-type manganese oxides. Yasushi Imamura, Hiroaki Muta, Ken Kurosaki and Shinsuke Yamanaka; Division of Sustainable Energy and Environmental Engineering, Osaka University, Suita, Osaka, Japan.

Several perovskite-type oxides have been studied for high temperature thermoelectric material. In this study, thermoelectric properties of cubic perovskite-type $SrMnO_3$ were investigated. This compound takes on a hexagonal structure by the ordinal synthesis method in air. By sintering in Ar atmosphere above 1673 K, it takes on Cubic structure because of the oxygen deficient. Polycrystalline $Sr_{1-x}La_xMnO_{3-\delta}$ and $SrMn_{1-x}Nb_xO_{3-\delta}$ (x = 0, 0.05, 0.1) were synthesized by solid state reaction of two-step method. In first step, oxygen-deficient perovskite were obtained by sintering 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 of non-annealed and 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-mentioned values. 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 increased with 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 samples was higher than that of non-annealed samples 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 results indicate that oxygen deficient generated carriers and acted as scattering centers for electrons. As a result, the power factor increased by annealing. The thermal conductivity of non-annealed and annealed samples showed similar value, about 2.5 $Wm^{-1}K^{-1}$ above 500 K. As a result, the figure of merit for La-doped system increased by annealing. The value was about ten times higher than that for the non-annealed samples.

F11.3

Fabrication of Grain-Aligned Bulks and Thick Films of Misfit Layered Cobalt Oxides by a Magneto-Scientific Process. Shigeru Horii[1], Taichi Okamoto[1], Toshiaki Kumagai[1], Tetsuo Uchikoshi[2], Tohru Suzuki[2], Yoshio Sakka[2], Jun-ichi Shimoyama[1] and Kohji Kishio[1]; [1]Dept. Applied Chemistry, University of Tokyo, Tokyo, Japan; [2]NIMS, Tsukuba, Japan.

Misfit layered cobalt oxides, Ca3Co4Oy (Ca349) and Bi2Sr2Co2Oy (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 polycrystals from a 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 Ca349 phase possessing an easy axis for magnetization along the c-axis, we tried to prepare thick films with the size of sub millimeter in thickness using an electrophoretic deposition (EPD) method under high magnetic fields. Grain-oriented thick films have been successfully fabricated, and the c-axis directions of aligned Ca349 grains were able to be controlled independently of the surface of a substrate by control of angle between an electric field and an applied magnetic field. We additionally report the convert of the easy axis 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 grain-alignment.

F11.4

Power Factor of Sr Doped $LaCoO_3$. Kouta Iwasaki[1], Tsuyoshi Itoh[1], Masahito Yoshino[1], Tsuneo Matsui[1,2], Takanori Nagasaki[2] and Yuji Arita[2]; [1]Department of Materials, Physics and Energy Engineering, Nagoya University, Nagoya, Aichi, Japan; [2]EcoTopia Science Institute, Nagoya University, Nagoya, Aichi, Japan.

$LaCoO_3$ has perovskite structure consisting of corner-sharing CoO_6 octahedra. Sr-doped $LaCoO_3$, $(La_{0.95}Sr_{0.05})CoO_3$, has been reported to exhibit high power factor more than 1×10^{-3} $Wm^{-1}K^{-2}$ [1, 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 $(La_{1-x}Sr_x)CoO_3$ [$0\leq x\leq0.09$] were prepared by a solid state reaction in air, and the electrical conductivity, Seebeck coefficient and the power factor were investigated. La_2O_3 (4N), $SrCO_3$ (4N) and Co_3O_4 (3N5) powders were used as starting materials. These powders were weighed with the appropriate amounts (the metal ratio was La:Sr:Co=1-x:x: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 measured by the least square method of the plot of ΔT (temperature difference) -ΔV (thermal electromotive force), and the contribution of lead wires (Pt) was subtracted. The electrical conductivity (σ) of $(La_{1-x}Sr_x)CoO_3$ [$0\leq x\leq0.09$] 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 $0.01\leq x$, and decreased with increasing Sr content. On the other hand, Seebeck coefficient of $LaCoO_3$ was negative below 350 K. The power factor (σS^2) of $(La_{1-x}Sr_x)CoO_3$ showed the maximum value below 650 K, and tended to decrease with increasing temperature above 650 K. The highest value of the power factor was 3.1×10^{-4} $Wm^{-1}K^{-2}$ for x=0.08 at 300 K. [1] T. Ohtani et al., J. Appl. Phys., 94 (2003) 6579. [2] J. Androulakis et al., Appl. Phys. Lett., 84 (2004) 1099.

F11.5

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

Measurements of Seebeck coefficient, S(T) and electrical resistivity, ρ(T) on polycrystalline $La_{2-x}Sr_xCuO_{4+\delta}$ (LSCO) ($0\leq x\leq0.2$) samples are reported. The Seebeck coefficient is positive in whole the measuremed temperature range (between 77K and 300K) and decreases with Sr content. At room temperature S(T) changes from 800 μV/K for the samples with the lowest levels of Sr to 30 μV/K for the samples with the highest levels of Sr. The behavior of S(T) fit to the Heikes model which describes the behavior of Seebeck coefficient in systems where the correlated hopping is present. The electrical resistivity shows a linear behavior with the temperature and it took values from 10^{-2} to 10^{-3} Ωcm. From the S(T) and ρ(T) measurements the thermoelectric power factor, PF was obtained. The maximum values for PF were about 25 μW/K^{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 (SEM) respectively. The behavior of transport properties opens de possibility of consider this family of perovskites as a thermoelectric material that work below room temperature.

F11.6

Fabrication and Properties of Thermoelectric Generator with Half-Heusler Compounds. Shinya Sakurada[1], Naoki Shutoh[1], Shinsuke Hirono[2] and Masami Okamura[2]; [1]Corporate R&D Center, Toshiba Corporation, Kawasaki, Japan; [2]Development Dept., Toshiba Materials Co., Ltd., Yokohama, Japan.

Half-Heusler compounds with the cubic MgAgAs-type structure have been of interest due to their potential as thermoelectric materials. Previously, we have investigated the effect of Ti substitution on the thermoelectric properties of (Zr,Hf)NiSn and revealed that substitution of Ti for (Zr,Hf) sites significantly reduced the thermal conductivity k and increased the Seebeck coefficient a. Moreover, it was also found that Sb doping at Sn sites reduced the electrical resistivity r and enhanced the power factor correspondingly. The combination of the low k and the high power factor resulted in a high ZT value. A maximum ZT value of 1.5 was achieved at 700 K for (Ti,Zr,Hf)Ni(Sn,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 studies on p-type half-Heusler compounds, Xia et al. have investigated ZrCoSb-based compounds and obtained an a of +0.13 mV/K, a r of 1 to 2 m orm 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 (Ti,Zr,Hf)CoSb compounds with three kinds of p-type dopants, namely Er, Fe, and Sn at the (Ti,Zr,Hf), Co, and Sb sites, respectively. The thermoelectric measurements were conducted at 300-773 K. Undoped (Ti,Zr,Hf)CoSb shows n-type behavior at 300-773 K and r for this compound is about 100 m orm cm at 700K. In contrast, when the doping concentrations are 5 at.%, (Ti,Zr,Hf)Co(Sb,X) exhibits p-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 (Ti0.3Zr0.35Hf0.35)Co(Sb0.85Sn0.15), an a of +0.31 mV/K, a r of 2.8 m orm cm, and a k of 2.7 W/mK, corresponding to

a ZT = 0.9, are obtained at 700 K. On the other hand, the ZT values obtained for Er- and Fe-doped compounds are less than 0.2. Next, we fabricated a thermoelectric module using half-Heusler compounds. This module consists of a large number of bar-shaped p-type and n-type materials connected electrically in series and sandwiched by two plates of thermally conducting but electrically insulating ceramics to form a module. The size of this module is 40 mm x 40 mm x 5 mm. The (Ti,Zr,Hf)Co(Sb,Sn) and (Ti,Zr,Hf)Ni(Sn,Sb) compounds referred to above are respectively used for the p-type and the n-type materials. Heat is supplied to one surface of the module and is emitted at a lower temperature from the opposite surface. The module generates an output power of 20 W under the thermal conditions of Th = 823 K (temperature at the surface where heat is supplied) and dT = 445 K (temperature difference between the two surfaces).

F11.7
Effects of SPS Condition on Thermoelectric Properties of ZrNiSn Based Half-Heusler Compounds. Takanori Kanemitsu, Hiroaki Muta, Ken Kurosaki and Shinsuke Yamanaka; Division of Sustainable Energy and Enviromental Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka, Japan.

Recently, extensive studies have been carried out on ZrNiSn based half-Heusler compounds as a thermoelectric material due to the high power factor, high mechanical strength and non-toxicity. The thermoelectric properties are very sensitive to the preparing condition and the nonstoichiometry in the compounds. In this study the effects of sintering condition on thermoelectric properties were investigated. The samples of $Zr_{0.7}Ti_{0.3}NiSn$ and $Zr_{0.5}Ti_{0.5}NiSn$ were prepared by spark plasma sintering (SPS) technique at the temperature in the range of 1273-1473 after annealing at 1073 K for one week. The thermoelectric properties were measured from room temperature to about 1000 K. In addition the sound velocity of the samples was measured by ultrasonic pulse-echo method for evaluation of intrinsic lattice thermal conductivity of the samples. We found that the electrical conductivity drastically increased with increasing the sintering temperature. While the Seebeck coefficient was independent of the temperature, thus high power factor was obtained for the sample sintered at high temperature. The value for $Zr_{0.7}Ti_{0.3}NiSn$ sintered at 1473 K was larger than that of pure ZrNiSn, reached 4 mW/mK^2 above 800 K. There were no impurity peaks in XRD patterns, however, the peaks of half-Heusler phase were broad for the annealed sample. The peaks for the sample sintered at high temperature were sharper than those of the only-annealed sample. Thus SPS at high temperature appeared to be effective for preparation of homogeneous sample. The thermal conductivity of substituted samples was lower than that of the pure ZrNiSn. The value for $Zr_{0.5}Ti_{0.5}NiSn$ 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 $Zr_{0.7}Ti_{0.3}NiSn$ sintered at 1473 K was about 0.48 at 900 K.

F11.8
Thermoelectric Properties of $Bi_2Sr_1Co_2O_9$ Tellurium-Doped Single Crystalline Whiskers. X. Tang[1], K. Aaron[1], Terry M. Tritt[1], D. Bourne[2], J. Barnes[2] and J. Payne[2]; [1]Physics & Astronomy, Clemson University, Clemson, South Carolina; [2]Physical Sciences, South Carolina State University, Orangeburg, South Carolina.

Long single crystalline 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 148μV/K and 5mΩcm respectively at 325K. Thermopower was measured using a differential technique, while resistivity was measured by a standard four-probe method.

F11.9
Thermoelectric and Structural Properties of the Ba2Ho(Cu3-xCox)O7-z Solid Solution.
Winnie Kwai-Wah Wong-Ng[1], Yufeng Hu[3], Zhi Yang[1], Qing Huang[2], Qiang Li[3] and Martin Green[1]; [1]Ceramics Division, NIST, Gaithersburg, Maryland; [2]Reactor Division, NIST, Gaithersburg, Maryland; [3]Appled Science, BNL, Upton, New York.

The search of thermoelectric materials for power generation and for solid-state cooling have 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 Co in the layered perovskite, Ba2HoCu3O7-z. The polycrystalline Ba2Ho(Cu3-xCox)O7-z (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 Ba2Ho(Cu3-xCox)O7-z 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 Ba2Ho(Cu3-xCox)O7-z compositions, the x=0.4 member gives the highest ZT of 0.017 at 270K. Structural investigations using neutron diffraction showed that Co substitutes for Cu in two different sites in the Ba2HoCu3O7-z structure depending on the x value. Results of the structural/property study will be discussed.

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 Hirahara and Yoshihumi Takanashi; Department Of Materials and Sicence Technology, Tokyo University Of Sicence, noda, Japan.

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 power generators 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$\sim$0.3 to 0.8 can minimize the thermal conductivity due to the randam ordering of the constitutent 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 Si1-xGex, we applied a die-casting growth technique combined with an advanced version of the Bridgman method. The grown samples were coin-shaped Si1-xGex polycrystalline crystals with a diameter of 16 mm and a thickness of 2 mm. Using die-casting combined with Bridgman growth brought about Si1-xGex precipitation in a form completely different from that predicted by the Si-Ge phase diagram. By combining this growth with subsequent heat treatment of the precipitated sample, $Si_{1-x}Ge_x$ with x= 0.4 to 0.8 were obtained. For the concentration variation in $Si_{0.5}Ge_{0.5}$, the deviation of the obtained germanium content was within $\pm$ 3%. We describe the preparation of the crystals by the die-casting growth process, and effects of post-annealing heat treatment of the grown samples, in terms of changes in the compositional fraction. For the grown samples, thermoelectric properties such as Seebeck coefficient, electrical conductivity, and thermal conductivity were measured over a temperature range from room temperature to 873 K. We present the results of the calculated 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.
Mustafa Karaman, Hilmi Onder Ozbelge, Naime Asli Sezgi and Timur Dogu; Chemical Engineering, Middle East Technical University, Ankara, Turkey.

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 armours with its high impact 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 BCl3-CH4-H2 gas mixture, in an impinging-jet CVD reactor. The impingement on the substrate surface is important in minimizing the effect of mass transfer limitations on the reaction rates. The chemical analysis of the reactor outlet stream was done by FTIR and formation of BHCl2 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 BHCl2 formation reaction. Effect of substrate temperature and composition of reactor inlet stream on the rates, conversions and selectivities of these two reactions were analysed and the results showed a complex reaction mechanism. The purpose of this study is to find a reaction mechanism which is in best accord with the experimental results. The parameters of the model rate expressions that are derived from the proposed reaction mechanisms are found statistically using nonlinear regression procedure.

F11.12
Abstract Withdrawn

F11.13
Thermoelectric Properties of $Mg_2Si_{1-x}C_x$ Crystals Grown by the Vertical Bridgman Method. Masayasu Akasaka, Yoshinori Higuchi, Tutomu Iida, Kenichiro Makino and Yoshihumi Takanashi; Materials Science and Technology, Tokyo University of Science, Noda, Japan.

Magnesium silicide (Mg_2Si), 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 thermal-to-electric power generation is the abundance of its constituent elements in the earthfs crust and the nontoxicity of its processing by-products. When compared with other thermoelectric materials such as PbTe, $CoSb_3$ and ZnSb that work over the same operating temperature range as Mg_2Si, the expected figure of merit for Mg_2Si is likely to be slightly lower, but it is still believed to be adequate for realizing thermoelectric power generation. Due to its environmentally friendliness, Mg_2Si also provides safe handling and device operation for practical use. Although Mg_2Si is the only stoichiometric silicide in the Mg-Si phase diagram, the conditions for growing high-quality and pure single crystals are required to realize more efficient thermal-to-electric conversion. The Mg_2Si crystal growth was derived from a congruent melt that was initiated from the stoichiometric Mg_2Si powder. A conventional vertical Bridgman method was used for the growth. For Mg_2Si, the grown crystals were single-like crystal and showed n-type conductivity in undoped condition. Although the high reactivity of molten or vapor Mg at elevated growth temperatures resulted in sticking of the melt Mg_2Si 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 $Mg_2Si_{1-x}C_x$. An intentional carbon incorporation in the grown crystals formed $Mg_2Si_{1-x}C_x$ crystals, 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^{-5} W/cmK^2 at 373 K when the composition x$\sim$0.03. We present the effects of carbon incorporation into Mg_2Si in terms of the thermoelectric properties by measuring the Seebeck coefficient, electrical conductivity, and the thermal conductivity.

F11.14
Thermal Conductivity of Novel Rare Earth Boron-Rich Cluster Compounds. Takao 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 new rare earth boron cluster compounds have recently attracted increasing interest, being magnetically dilute, insulating/semiconducting materials but displaying a wide range of properties with relatively strong magnetic coupling [1]. Interestingly, it has been indicated that the B_{12} 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 previously been investigated as possible thermoelectric materials [2] and we have recently shown that the rare earth boride $REB_{44}Si_2$ appears to be a promising system at high temperatures [3]. Boron cluster compounds have generally exhibited low thermal conductivity [4], actually exhibiting glass-like conduction for the crystalline YB_{66} 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. $REB_{44}Si_2$ has a similar low thermal conductivity to the YB_{66} system with $\kappa = 0.027$ W/cm/K at room temperature. A certain type of transition metal doping has been shown to increase the thermal conductivity in YB_{66}, while carbon doping actually decreases κ in YB_{66}. Effects on the other thermoelectric properties will also be discussed. This work was supported in part by PRESTO from the Japan Science and Technology Agency. [1] for example, T. Mori and A. Leithe-Jasper, Phys. Rev. B **66** 214419 (2002), T. Mori and H. Mamiya, Phys. Rev. B **68**, 214422 (2003), T. Mori, J. Appl. Phys. **95**, 7204 (2004). [2] H. Werheit, R. Schmechel, V. Fueffel, and T. Lundstrom, J. Alloys Comp. **262 – 263**, 372 (1997), T. Nakayama, J. Shimizu, K. Kimura, J. Solid State Chem. **154** 13 (2000). [3] T. Mori, J. Appl. Phys. **97**, 093703 (2005). [3] D. G. Cahill, H. E. Fischer, S. K. Watson, R. O. Pohl, G. A. Slack, Phys. Rev. B **40** 3254 (1989).

F11.15
Effect of Rare-Earth Cation Doping on Enhancement of the Thermoelectric Power of Zinc Oxide. Kiyoshi Fuda[1] and Shigeaki Sugiyama[2]; [1]Akita University, Akita, Japan; [2]Akita Pref. Ind. Tech. 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 1000 K, further evolution 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 solution 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 as a function of temperature ranging from 100 °C to 800 °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 commonly found 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 one ranging from -360 to ?400μVK^{-1} in the temperature range observed, the lowest ones for Pr-doped one ranging from -250 to -310 μVK^{-1}, whereas those for Al-doped one ranging from 80 to 140 μVK^{-1}. It should also be pointed out that the power factor at 100 °C for Pr-doped ZnO was twice or more as much as that for Al-doped one. From the results it seemed that rare earth doping is effective for enhancement of thermoelectric power of ZnO.

SESSION F12: Devices
Chair: Jihui Yang
Friday Morning, December 2, 2005
Room 313 (Hynes)

8:00 AM *F12.1
Development Progress Status of High Efficiency Thermoelectric Materials and Unicouples for Power Generation Applications. Thierry Caillat, Jeff Sakamoto, Jong-Ah Paik, April Jewell, Bijiang Cheng, Chen-Kuo Huang and Jean-Pierre Fleurial; Jet Propulsion Laboratory, Pasadena, California.

Radioisotope Thermoelectric Generators (RTGs) have proved to be reliable, long-lived sources of electrical power that have enabled the conduct of a number of important U.S. missions since 1961. Past RTGs have used two types of thermoelectric materials: PbTe/TAGs and SiGe. Reducing mass and improving the efficiency of state of practice 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 for state-of the art PbTe/TAGS and SiGe materials. 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 $\sim$ 14% has been demonstrated for a skutterudite/Bi2Te3 unicouple operating at a hot-side temperature of 975K and a cold-side temperature of 300K. 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 1275K. Refractory skutterudites such as CeyRu4-xIrxSb12 and CoxIr1-xSb3 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.

8:30 AM F12.2
Aerogels for Thermoelectric Power Systems. Jong-Ah Paik, Steven M. Jones, Jean-Pierre Fleurial, Thierry Caillat and Jeffrey S. Sakamoto; Jet Propulsion Laboratory, Catania, Italy.

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 process using acetonitrile as a main solvent and gels were 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 processing, which enables the ability to tailor 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 >100mg/cc). Data indicate 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 decreased to $\sim$ 2 % with 700 oC in vacuum. Altogether, 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 aerogel, free of cracks and offer improved sublimation suppression in practically all thermoelectric technologies used for power generation.

8:45 AM F12.3
High Efficiency Thermoelectric Power Conversion.
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 300?K and 900?K will have a conversion efficiency of approximately 17%. Effort is continuing to confirm 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[1], Adam D. Downey[1], Jarrod L. Short[1], Jonathan J. D'Angelo[1], Ed Timm[2], Kimberly A. Sarbo[2], Eric Quarez[4], John Androulakis[4], Pierre F. P. Poudeu[4], Harold J. Schock[2], Tom Shih[3] and Mercouri G. Kanatzidis[4]; [1]Electrical and Computer Engineering Department, Michigan State University, East Lansing, Michigan; [2]Mechanical Engineering Department, Michigan State University, East Lansing, Michigan; [3]Department of Aerospace Engineering, Iowa State University, Ames, Iowa; [4]Chemistry Department, Michigan State University, East Lansing, Michigan.

High efficiency thermoelectric modules are of great interest for power generation applications where 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 devices, and constant feedback from characterization. Pb-Sb-Ag-Te compounds are among the best known materials for this temperature range. Modeling of these materials and possible cascaded structures shows efficiencies of 14% can be achieved for low resistance contacts. Using antimony we have achieved contact resistivities less than 20 $\mu\Omega\cdot cm_2$. 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[1,2], Toshiyuki Mihara[1,2], Manabu Hirai[1,2] and Naoki Nabeshima[3]; [1]National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka, Japan; [2]CREST, Japan Science and Technology Agency, Kawaguchi, Saitama, Japan; [3]Osaka Electro-Communication University, Neyagawa, Osaka, Japan.

Thermoelectric generation systems can convert heat energy directly into electrical energy irrespective of source size. The requirements placed on thermoelectric materials, however, are not easily satisfied. Not only must they possess high conversion efficiency, but must also be composed of non-toxic and abundantly available elements having high chemical stability in air even at high temperature. $Ca_3Co_4O_9$ (Co-349) with a layered structure is a good p-type thermoelectric compound at high temperature in air. Moreover recently, perovskite $LaNiO_3$ (Ni-113) has been reported to show negative Seebeck coefficient (S) and low resistivity (ρ) 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_o) of the unicouples reaches 100mV at a hot-side temperature (T_H) of 1073K and a temperature difference (ΔT) of 500K in air. Internal resistance (R_I) can be suppressed to 14mΩ at T_H of 1073K in air and decreases with increasing temperature. Maximum output power (P_{max}) increases with T_H and reaches 177mW at T_H of 1073K (ΔT = 500K). This value corresponds to a volume power density of 961mW/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 oxide thermoelectric unicouples. It weighs 19.8 g and its dimensions are 53 mm long, 32 mm wide, and 5.0 mm thick. The hot-pressed thermoelectric oxide bulk materials used were connected with an Ag paste and Ag electrodes. The module's V_O 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[1], Je-Hyeong Bahk[1], John E. Bowers[1], Joshua Zide[2], Arthur Gossard[2], Yan Zhang[3] and Ali Shakouri[3]; [1]Department of Electrical and Computer Engineering, University of California, Santa Barbara, California; [2]Materials Department, University of California, Santa Barbara, California; [3]Electrical Engineering Department, University of California, Santa Cruz, California.

InGaAs with embedded ErAs nanoparticles is a promising material for thermoelectric applications. The incorporation of erbium arsenide metallic nanoparticles into the semiconductor can provide both charge carriers and create scattering centers for phonons. Electron filtering by heterostructure barriers can also enhance the Seebeck coefficient by selective emission of hot electrons. The thin film power generators consist of 200 n-p couples of ErAs/InGaAs superlattices elements, which were grown on InP substrate using molecular beam epitaxy. The elements are 5 μm thick and 200 μm x 200 μm large in size. There are a total of 400 thermoelectrical elements that are packaged within 650 μm thick AlN plates via flip-chip bonding. The output powers over 0.5 milliwatts were measured at 25K temperature difference across the whole device package. Simulations show that the output power density can reach up to 1W/cme 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 Kucherov[1], Peter Hagelstein[2], Victor Sevastyanenko[1], Harold Brown[1], Sivaraman Guruswamy[3] and Deepak Thimmegowda[2]; [1]ENECO, Inc., Salt Lake City, Utah; [2]MIT, Cambridge, Massachusetts; [3]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 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