SYMPOSIUM S

S: Thermoelectric Materials 2003-Research and Applications

December 1 - 3, 2003

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* Invited paper

SESSION S1: Low Dimensional Systems and Nanocomposites I
Chair: George Nolas
Monday Morning, December 1, 2003
Room 313 (Hynes)

10:30 AM *S1.1
Thermoelectric Power, Electrical Resistance, Magnetoresistance, And Optical Reflectivity Of Bismuth Nanowire Composites. Joseph P. Heremans, Delphi Research Labs, Shelby Township, Michigan.

The thermoelectric power of bismuth nanowires is theoretically calculated to be greatly enhanced, on the basis of the size-quantization of the electron wavefunction in nanowires with diameters below 50 nm, and this is expected to lead to the development of high figure of merit thermoelectric materials. We review here the experimental observation of such enhancement in composites containing nanowires with diameters down to 9 nm. When the wire diameter is further decreased, localization effect take over and limit the thermopower. The theory further predicts the appearance of an energy gap in bismuth nanowires with diameters below 50 nm. We observe such a gap both in the temperature dependence of the resistivity and in optical reflectivity measurements, with a dependence on nanowire diameter consistent with theory.

11:00 AM S1.2
Phonon Thermal Conductivity of Superlattice Nanowires for Thermoelectric Applications. Chris Dames and Gang Chen; Mechanical Engineering, MIT, Cambridge, Massachusetts.

An incoherent particle model has been developed to calculate the phonon thermal conductivity of nanowires and superlattice nanowires. It is argued that the surface roughness and geometric variations of most real nanowires prevent the formation of idealized confined dispersion relations. Instead the 3D bulk dispersion is used, thus capturing only the classical size effects. The implications for thermoelectric applications are discussed using a model Si/Ge superlattice nanowire: the room temperature thermal conductivity may be reduced below the alloy limit (7.0 W/mK) when the diameter is less than 15 nm and/or the segment length is less than 20 nm. Acknowledgement: This work was funded by the NSF (CTS0129088) and DOE (DE-FG02-02ER45977).

11:15 AM S1.3
Thermoelectric Transport Properties of Bismuth Sulfide Nanocomposites. Patrick L. Garrity, Ven B. Reddy and Kevin L. Stokes; Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana.

We present an experimental study of the thermoelectric transport properties of a conducting polymer/bismuth sulfide nanocomposite system. Successful growth of bismuth chalcogenides in nanorod form of 10-15 nm diameter has allowed the formation of a core-shell particle, which utilizes the bismuth compound as a quantum-confining core and the conducting polyaniline as the outer shell of 2-3 nm thickness. True three dimensional quantum confinement of the carriers within the bismuth compound is obtained through the higher polyaniline bandgap energy as well as complete nanorod surface coverage. A bulk form of the core-shell system has been fabricated through pressing and sintering techniques which has resulted in a unique nanocomposite of nanorod core particles within a polyaniline matrix. The heterogeneous composite is found to exhibit decreased thermal conductivity due to increased phonon scattering which is desirable in thermoelectric materials. Additionally, the electrical conductivity and Seebeck coefficient is found to be responsive to doping levels of the outer polyaniline shell. This provides a convenient mechanism to control thermopower levels and subsequently allow another degree of freedom to be added to thermoelectric engineering techniques. We conclude by summarizing our main results and discuss future work with bismuth telluride and bismuth antimony nanocomposites.

11:30 AM S1.4
Solvothermal Preparations of Nanocrystalline Bi_2Te_3 Powders and The Study on Their Characterizations. Xiaohua Ji, Xinbing Zhao, Yanhua Zhang and Bohui Lu; Department of Materials Science, Zhejiang University, Hangzhou, Zhejiang, China.

Bi_2Te_3 are best-known and technological important thermoelectric materials currently availiable near room temperature with highest figure of merit $ZT \geq 1$. In this paper, Bi_2Te_3 nanocrystals of 15~25nm were prepared via solvothermal processes in which pyridine, absolute ethanol and distilled water were used as reaction medium respectively. The products were characterized by XRD and TEM, and the grain sizes have also been calculated by Scherrer Equation. A possible formation mechanism has been proposed. The results showed that the reaction products' purity, crystallization degree and grain sizes were all increased with the increase of the dielectric constant and polarity of the solvent. A novel Bi_2Te_3nanowires with several tens nanometers diameter and up to more than ten microns lengths have been prepared when distilled water was used as reaction medium.

11:45 AM S1.5
The Low Temperature Synthesis of [(Bi2Te3)x(TiTe2)y] Superlattices using a Modulated Elemental Reactant Technique. Fred R. Harris, Robert Schneidmiller, Stacey D. Standridge and David C. Johnson; Chemistry, The University of Oregon, Eugene, Oregon.

A family of metastable [(Bi2Te3)x(TiTe2)y] superlattices (where x and y denote the number of layers of each of the two components) was prepared by annealing modulated elemental reactant precursors at temperatures below 280 C. Above 300 C, the metastable superlattices disproportionate into a mixture of Bi2Te3 and TiTe2. Through the design of the structure of the initial precursor, precise control of the superlattice unit cell composition is obtained. We propose a formation mechanism for these superlattices, and we discuss how the electrical properties correlate with changes in their nano-architecture.

SESSION S2: Devices I
Chair: Tim Hogan
Monday Afternoon, December 1, 2003
Room 313 (Hynes)

1:30 PM S2.1
Application of the Compatibility Factor to the Selection of Materials for Segmented and Cascaded Thermoelectric Generators. Jeff Snyder, [1]JPL, Pasadena, California; [2]California Institute of Technology, Pasadena, California.

Using the concept of thermoelectric compatibility efficient thermoelectric generators can be rationally designed by selecting or developing compatible, high efficiency materials. With four examples, compatible and incompatible systems are explained and materials proposed for targeted development. In the TAGS/SnTe generator, the SnTe is only marginally compatible with TAGS, and therefore produces little extra power. Alternative, compatible materials are suggested with improvements calculated. Materials for high temperature segmentation will be suggested or proposed for development. Cascaded generators avoid the compatibility problem with complicated wiring. The compatibility equations provide a simple derivation of the cascading ratio.

1:45 PM S2.2
Cooling Power Density of SiGe/Si Superlattice Micro Refrigerators. Gehong Zeng[1], Xiaofeng Fan[1], LaBounty Chris[1], Edward Croke[3], Yan Zhang[2], James Christofferson[2], Daryoosh Vashaee[2], Ali Shakouri[2] and John E. Bowers[1]; [1]Electrical and Computer Engineering, University of California, Santa Barbara, California; [2]Electrical Engineering, University of California, Santa Cruz, California; [3]HRL Laboratories, Malibu, California.

Experiments were carried out to determine the cooling power density of SiGe/Si superlattice microcoolers by integrating thin film metal resistor heaters on the cooling surface. By evaluating device's maximum cooling under different heat load conditions, the cooling power density was directly measured. Both micro thermocouple probes and the resistance of thin film heaters were used to get an accurate measurement of temperature on top of the device. Superlattice structures were used to enhance the device performance by reducing the thermal conductivity, and by providing selective emission of hot carriers through thermionic emission. Various device sizes were characterized. Maximum cooling and the cooling power density had a different dependence on the micro refrigerator size. Net cooling over 4.1 K below ambient and cooling power density of 598 W/cm2 for 40 x 40 um2 devices were measured at room temperature.

2:00 PM *S2.3
Superlattice Thin-film Thermoelectric Materials and Devices. Rama Venkatasubramanian, Brooks O'Quinn, Edward Siivola, Kip Coonley, Pratima Addepalli, Mary Napier, John Posthill and Tom Colpitts; Center for Thermoelectrics Research, Research Triangle Institute, RTP, North Carolina.

Thin-film nano-structured materials offer the potential to enhance the performance of thermoelectrics, offering new capabilities like small-footprint coolers for lasers and microprocessors to high-performance thermoelectric power sources in near-term and efficient refrigeration in long-term. Our recent focus has been to transition the enhanced figure-of-merit (ZT) in p-type Bi2Te3/Sb2Te3 and n-type Bi2Te3/Bi2Te3-xSex superlattices to performance at the module level with several device demonstrations. We have been able

to obtain a best ZT of ∼2 in a p-n couple, the fundamental cooling or power conversion unit in an operational module. In addition, we have been able to demonstrate p-n couple ZT of as much as 1.6 from heat-to-power efficiency data. The thermal interface resistances between the active device and the external heat source have been optimized. A power level of 38 mW per couple for a DT of about 107K, with 4-micron-thick element, was obtained. This translates to an active power density of ∼54 W/cm2 and a mini-module power density of ∼10.5 W/cm2. In short, power devices with thin-film superlattices are a real possibility. In the cooling arena, we have been able to obtain over 50K active cooling with thin-film modules, useable in several laser and microprocessor cooling needs. This is in spite of severe thermal management issues that had to be overcome noting that the "true" hot-side temperature, and hence the "true" DT, across the device are much higher. Characteristics unique to thin-film cooling modules such as sensitivity to atmosphere would be presented from a phenomenological point. The concept of High-Active-Flux, Low-Input-Output-Flux device, common to both power and cooling modules, to solve some of the fundamental issues in thin-film thermoelectric devices with experimental data on elements, numerical modeling, and device data will be presented. Some of the challenges that remain to addressed in the full development of this technology and thoughts on further progress in nanostructured materials will be presented.

2:30 PM S2.4
Influence of Doping Concentration and Ambient Temperature on the Cross-Plane Seebeck Coefficient of InGaAs/InAlAs superlattices. Yan Zhang[1], Rajeev Singh[1], Ali Shakouri[1], Gehong Zeng[2,1], Yae Okuno[2] and Yi-Jen Chiu[2]; [1]Electrical Engineering, UC Santa Cruz, Santa Cruz, California; [2]ECE, Univ. of California, Santa Barbara, Santa Barbara.

Seebeck coefficient is one of the key parameters to characterize the thermoelectric figure-of-merit (ZT). Its measurement perpendicular to thin film superlattice layers 1-3 micron thick is complicated due to the difficulty in measuring temperature accurately on both sides of the thin film. We have developed thin film heaters/sensors that could be integrated on top of superlattice devices ranging in size from 40 to 100 micron in diameter. By characterizing temperature distribution on top of the device for various device sizes and different superlattice thickness, we can obtain an accurate estimate for the cross-plane Seebeck coefficient. Measurements were performed on molecular beam epitaxy grown InGaAs/InAlAs superlattice structures lattice matched to InP substrate n+ doped with 0.5um InGaAs up to 1e19cm-3. Superlattice contained 25 periods of 5nm thick InGaAs n-doped with doping concentration varied from 2e18, 4e18, 8e18 to 3e19 cm-3 and 3nm thick undoped InAlAs. Devices with various sizes were fabricated using conventional lithography, dry etching and metallization techniques. It was interesting to note that contrary to the behavior in bulk material, Seebeck coefficient did not decrease monotonically with doping. This is attributed to large potential barriers between InAlAs and InGaAs layers (on the order of 500meV) and the formation of minibands in the structure. A preliminary theory of thermoelectric transport in superlattices in the regime of miniband formation has been developed and calculations are compared with experimental results. It is anticipated that this regime of transport could enhance the thermoelectric power factor (Seebeck coefficient square times electrical conductivity) beyond what can be achieved with bulk materials. This enhancement can be combined with the reduction of thermal conductivity in multi layer structures and improve the ZT of the material.

2:45 PM S2.5
Thermal Stability of p-type Bi_2Te_3/Sb_2Te_3 and n-type $Bi_2Te_3/Bi_2Te_{2-x}Se_x$ Thermoelectric Superlattice Thin-Film Devices. Kip D. Coonley, Brooks O'Quinn, Pratima Addepalli, Edward Siivola, Michael Puchan and Rama Venkatasubramanian; Center for Thermoelectrics Research, Research Triangle Institute, Research Triangle Park, North Carolina.

Thermolectric devices have been constructed using thin-film Bi_2Te_3/Sb_2Te_3 and $Bi_2Te_3/Bi_2Te_{2-x}Se_x$ superlattice thin-films. Since these devices are intended for use in systems that will operate at elevated temperatures over their lifetime as in many power conversion devices, the thermal stability of the thermoelectric couple's figure-of-merit is an important consideration. The ZT_e of p-type and n-type superlattice thin-film elements was evaluated at specific intervals during exposure to elevated temperatures of 150°C for up to 60 hrs. Results indicate that the figure-of-merit for p- and n-type superlattice films is not compromised over time when exposed to these operating temperatures. In fact, p-type superlattice thin-film ZT_e remains very constant while corresponding n-type ZT_e tends to remain constant or improve slightly over time when subjected to continuous exposure to elevated temperatures. Evaluation of these thin-films thermoelements is reported and implications of these results are considered for thin-film thermoelectric modules. In addition, we will report on performance of these devices after exposure to short cycles of much higher temperatures that are relevant in many opto-electronic packages.

SESSION S3: Oxides
Chair: Lidong Chen
Monday Afternoon, December 1, 2003
Room 313 (Hynes)

3:30 PM S3.1
Electronic Structure and Properties of Layered Cobaltate Thermoelectrics and Superconductors. David Joseph Singh, Center for Computational Materials Science, Naval Research Laboratory, Washington, District of Columbia.

Density functional calculations are used to elucidate the electronic structure and related properties of materials in the Na_xCoO_2 layered system, in the range $0.3 \leq x \leq 0.7$. These materials display remarkably high thermopowers for metals, and with modifications become useful thermoelectrics. Here it is found that density functional electronic structures are able to reproduce the experimentally measured thermopowers. However, at this level of theory, weak ferromagnetic instabilities are found. Comparison with experiment indicates that there are substantial spin fluctuations in these materials associated with proximity to a ferromagnetic critical point, which is approached with decreasing x. The recent observation of superconductivity in water intercalated samples may be a manifestation of these quantum fluctuations, in which case, the superconducting state would most likely have triplet pairing. In any case, these quantum fluctuations are key to stabilizing the high mass, high carrier density, paramagnetic ground state of the thermoelectric materials, which underlies their favorable thermoelectric properties.

3:45 PM S3.2
Thermoelectric Properties of Bi-substituted $Ca_3Co_4O_9$ Single Crystal. Masashi Mikami[1], Kanji Chong[2] and Ryoji Funahashi[3,1]; [1]CREST, Japan Science and Technology Corporation, Osaka, Japan; [2]Osaka Electric-Communication Univ., Osaka, Japan; [3]National Institute of Advanced Industrial Science and Technology, Osaka, Japan.

The recent discovery of large thermopower coexisting with low electric resistivity in Na_xCoO_2 and $Ca_3Co_4O_9$ has made layered-structural cobalt oxides recognized as promising candidates for thermoelectric materials. In these two-dimensional cobalt-containing oxides, it is proposed that the high thermoelectric performance is caused by unique structural and transport properties, such as a strong electron-electron correlation and a modulated structure. For $Ca_3Co_4O_9$ in particular, it is reported that the Bi-substitution for a part of Ca site enhances its thermoelectric properties in sintered polycrystalline material. In order to investigate accurately the origin of the superior thermoelectric properties in Bi-substituted $Ca_3Co_4O_9$, large single crystals are indispensable. Thus, we grew single crystals of Bi-substituted $Ca_3Co_4O_9$ by a solution method. The average size of the plate-like crystals was $3 \times 3 \times 0.05$ mm^3. The cationic ratio (Ca, Bi)/Co of the grown crystals measured by an energy dispersive X-ray spectrometer tended to exceed that of the starting ratio (Ca, Bi)/Co=3/4. For instance, the average cationic composition of the grown crystals was Ca:Bi:Co=3.3:0.3:4, while that of the starting material was Ca:Bi:Co=2.7:0.3:4. So, the crystallographic structure of the obtained crystals may correspond to the $Ca_2Co_2O_5$ phase rather than the $Ca_3Co_4O_9$ phase. Thermoelectric properties in the direction of ab-axis were measured at various temperature ranges. Seebeck coefficient of $Ca_{3.3}Bi_{0.3}Co_4O_{9+\delta}$ is positive and 130 μV/K at room temperature. The electrical resistivity is about 3 mΩcm at whole temperature region of 300-1080 K. The relation between the Bi content and thermoelectric properties will be presented.

4:00 PM *S3.3
Exploration of Thermoelectric Oxides and Development of Modules Consisting of the Oxide Devices. Ryoji Funahashi[1,2], Saori Urata[1], Masashi Mikami[2], Katsuhisa Mizuno[3], Takumi Kouuchi[3] and Kandi Chong[3]; [1]National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka, Japan; [2]CREST, Japan Science and Technology Corporation, Ikeda, Osaka, Japan; [3]Osaka Electro-Communication Univ., Neyagawa, Osaka, Japan.

In order to accelerate exploration of new thermoelectric materials, a high-throughput screening (HTS) technique has been developed. Using this technique, 1000 samples can be prepared and evaluated their Seebeck coefficient (S) at room temperature in a day. It is clarified that La-Ni-O and Nd-Ni-O systems show n-type thermoelectric properties. $LnNiO_3$ and Ln_2NiO_4 (Ln: La or Nd) are mainly formed in the samples possessing n-type property. Seebeck coefficient of $LnNiO_3$ and Ln_2NiO_4 is -20–40 μV/K at 973 K. While electrical

resistivity (ρ) of $LaNiO_3$ is as low as 5 mΩ cm, both $NdNiO_3$ and Nd_2NiO_4 show high resistivity of 20-50 mΩ cm at 973 K in air. Substitution of La with other cations seems to be effective to enhance power factor (S^2/ρ). Optimizing substituted cations and compositions has been tried by HTS. It is found out that Bi-substitution is effective to improve both Seebeck coefficient and resistivity of the $LaNiO_3$ system. At present the highest power factor is about 35 μW/m-K^2 for $La_{0.9}Bi_{0.1}NiO_3$ at 737 K. Thermoelectric devices are prepared using hot pressed p-type $Ca_{2.7}Bi_{0.3}Co_4O_9$ and n-type $La_{0.9}Bi_{0.1}NiO_3$ bulks. Thermal durability of the devices does not seem to be a problem. Power generation properties of the thermoelectric modules consisting of the oxide devices will be presented.

4:30 PM S3.4
Thermoelectric Properties of Textured $InGaO_3(ZnO)_m$ Ceramics. Ryoji Asahi[1], Changtai Xia[1], Hisashi Kaga[1], Shingo Hirano[1,2] and Toshihiko Tani[1]; [1]Frontier Research Department, Toyota Central R&D Labs., Inc., Nagakute, Aichi, Japan; [2]Department of Materials Engineering, University of Tokyo, Tokyo, Japan.

Materials design and syntheses of the homologous compound $InGaO_3(ZnO)_m$ are presented for the thermoelectric application. First principles calculations of doping energies, thermopowers, and thermal conductivities were performed to understand and optimize the thermoelectric properties. Ceramic samples were synthesized by a solid-state reaction at 1423K for 12 hrs in air, followed by sintering at 1823K for 2hrs in air. Aluminum doping for a zinc site effectively enhanced an electrical conductivity and a power factor, as predicted by the calculations. A lower thermal conductivity, mainly due to a smaller elastic constant along the c axis, was obtained by an increase of m. The power factor and ZT at 1000K were evaluated to be $3.8x10^{-4}$ W/K^{2}m and ZT$\sim$0.16, respectively, for the randomly oriented ceramics with m=3. Since this compound features the layered structure along the c axis, we utilized a templated grain growth (TGG) technique to obtain highly textured ceramics. Platelet micro-crystals of $InGaO_3(ZnO)_m$ and $In_2O_3(ZnO)_m$, which can facilitate the TGG process, were synthesized by flux methods. The latter templates mixed with Ga_2O_3 powder, however, tended to form the spinel structure, Ga_2ZnO_4, during the reactive TGG process, resulting in the random orientation of $InGaO_3(ZnO)_m$. We report thermoelectric properties of the textured ceramics and compare with the random ones.

SESSION S4: Skutterudites
Chair: Terry Tritt
Tuesday Morning, December 2, 2003
Room 313 (Hynes)

8:30 AM S4.1
Effect of Ni in new skutterudite compounds $Ca_xCo_4Sb_{12}$. M Puyet[1], B Lenoir[1], A Dauscher[1], M Dehmas[2], J Hejtmanek[3], C Stiewe[4], E Muller[4] and H Scherrer[1]; [1]Laboratoire de Physique des Materiaux, UMR 7556, Ecole des Mines, Nancy, France; [2]Laboratoire de Science et Genie des Materiaux et de Metallurgie, UMR 7584, Ecole des Mines, Nancy, France; [3]Institute of Physics, Academy of Sciences of the Czech Republic, Praha, Czech Republic; [4]Institute of Materials Research, German Aerospace Center (DLR), Cologne, Germany.

During the last ten years, skutterudite materials have been widely studied due to their unique physical properties. Antimonide skutterudites received particular attention from an engineering point of view since these materials exhibit better thermoelectric performance than state of the art thermoelectric materials when working at elevated temperatures. One of the most interesting property is that their crystalline structure can be filled by guess atoms R. Actually, a phenomena of rattling can appear for these fillers and reduce substantially the lattice thermal conductivity. It was remarked in different issues that the rattling effect in $R_xCo_4Sb_{12}$ compounds coupled with a substitution of cobalt by nickel may improve the thermoelectric performance. In this communication, we present and discuss results concerning the influence on the transport properties of nickel substitution in a new class of skutterudite compounds, with the alkaline earth calcium as the filler atom. All the compounds were synthesized by traditional metallurgical technique. The Seebeck coefficient, the electrical resistivity and the thermal conductivity have been measured in a wide range of temperature. It is shown that similarly to the case of $Ba_xCo_4Sb_{12}$, the substitution of Ni on the Co sites has a beneficial effect.

8:45 AM S4.2
Synthesis and Thermoelectric Properties of CexFe4-y-zRuyCozSb12 Skutterudite Alloys. Thierry Caillat, Jeff Sakamoto and Liana Lara; Jet Propulsion Laboratory, Pasadena, California.

Advanced unicouples based on n-type CoSb3 and p-type Ce0.9Fe3.5Co0.5Sb12 are currently being developed at the Jet Propulsion Laboratory. These unicouples have the potential to achieve conversion efficiencies on the order of 15% when operated at a hot-side temperature of 975K and a cold-side temperature of 375K. They could be integrated in a variety of thermoelectric power generation devices including Advanced Radioisotope Power Systems for future NASA deep space missions. Current skutterudite materials being used are limited to a hot-side temperature operation of about 975K. Expanding this limit by using more refractory skutterudite materials capable of stable operation at temperatures >975K will potentially further increase the efficiency of the unicouples. A research effort is currently underway at JPL to develop skutterudite materials that could operate at temperatures up to 1275K. Among the candidate materials, CexFe4-yzRuyCozSb12 alloys are being investigated. Initial temperature stability tests indicate that CeRu4Sb12 is stable up to 1275K, about 200K higher than for his iron analog, CeFe4Sb12. The synthesis CexFe4-yzRuyCozSb12 alloys is reported in this paper. Seebeck coefficient. Electrical resistivity, and thermal conductivity measurement results are presented and discussed as well the potential use of these materials into future generations of advanced unicouples.

9:00 AM S4.3
Synthesis and thermoelectric properties of Ce(Ru2.67Rh1.33)Sb12. Geoff D Staneff[1], Paul D Asimow[2] and Thierry Caillat[3]; [1]Materials Science, California Institute of Technology, Pasadena, California; [2]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California; [3]Jet Propulsion Laboratory, Pasadena, California.

Exotic filled skutterudite compositions were explored to determine their suitability for thermoelectric applications. While skutterudite occurs naturally as (Co,Ni)As3-x this work was undertaken with a nominal composition of (Ru0.75Rh0.25)Sb3 after the theoretical work of Fonari and Singh (Appl Phys Lett, 1999). Study in this skutterudite system was undertaken to experimentally verify its potential in n-type thermoelectric applications. Both filled and unfilled examples from this system were synthesized and studied, with Cerium as the filling ion. Standard synthesis routes were quickly exhausted without much success, though as a result of our initial work the nominal composition was adjusted to Ru0.67Rh0.33 to reflect a naturally stable ratio in RuRh skutterudites. Due to this dominant composition electroneutrality was expected to be achieved at 0.89 cerium filling and fully filled materials were expected to be strongly n-type. Unfilled Ru2.67Rh1.33Sb12 was synthesized using a straightforward quench synthesis technique. The filled thermoelectric Ce(Ru2.67Rh1.33)Sb12 was synthesized using a combination of solid state reaction of elemental constituents and high pressure hot pressing. A 6-8 multi-anvil device was used to provide the synthesis conditions of 6 GPa and dwell temperatures of 650C and 350C. Due to decreasing stability of filled skutterudites with increasing synthesis pressure high pressure synthesis requires low temperature hot pressing. As a consequence of this the filled RuRh skutterudite is no longer stable phase at synthesis conditions of 12 GPa. The resulting material, a new fully filled skutterudite, exhibited p-type conductivity and an electrical resistance of 1.755mΩcm that decreases with increasing temperature. Thermal conductivity, Seebeck, and Hall coefficients were measured on phase pure samples. The crystal structure of these Rhodium-Ruthenium skutterudites were refined using Rietveld analysis of the X-Ray diffraction data. Particularities of the synthesis route, details of the thermoelectric properties, as well as implications for other filled skutterudite systems will be discussed.

9:15 AM S4.4
Phonons and Thermal Conductivity in Skutterudite Thermoelectrics. Chris Kendziora[1], G S Nolas[2], J L Feldman[1], D J Singh[1], D Mandrus[3] and B C Sales[3]; [1]Materials Sciences Division, Naval Research Laboratory, Washington, District of Columbia; [2]Department of Physics, University of South Florida, Tampa, Florida; [3]Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

In materials with low carrier concentration, low frequency lattice phonons can be the limiting factor toward reducing thermal conductivity. We study optical phonon vibrations and correlate them with thermal conductivity for empty and filled skutterudites designed for thermoelectric applications, where low thermal conduction is critical. Polarized Raman scattering spectra of crystallite and polycrystalline samples are compared with theoretical predictions and analyzed in comparison to the thermal conduction properties. Our emphasis is on the $CoSb_3$ skutterudite and its filled derivatives, including materials with Ge, Sn, and La in the cages. We observe a strong correlation between aspects of the phonon spectrum and low thermal conductivity. This presents optical spectroscopy as a characteristic screening tool for potential thermoelectrics and is a crucial step toward predicting lattice thermal conductivities.

9:30 AM S4.5
Spin dynamics of the skutterudites (Na,Ba,Ca)Fe_4Sb_{12} probed by thermal and electrical transport. Michael Baenitz, Narayani Senthilkumaran, Andreas Leithe-Jasper, John Mydosh, Frank Steglich and Yuri Grin; Max Planck Institute for Chemical physics of Solids, Dresden, Germany.

Spin fluctuations play a major role in determining the nature of electrical and heat transport in superconductors and itinerant ferromagnets, in both oxides as well as the intermetallics[1]. In this paper we would be presenting the results of our rigorous experimental search in trying to understand the nature of spin dynamics in the novel thermoeletric materials called the skutterudites[2]. We have probed the spin dynamics of the weak itinerant ferromagnet $NaFe_4Sb_{12}$[3] and the non-magnetic compounds (Ba,Ca)Fe_4Sb_{12} using electrical resistivity, specific heat, thermopower, and thermal conductivity in magnetic fields and Hall effect and estimate the spin fluctuation temperature. Further evidence comes from ^{23}Na NMR investigations[4]. The alkaline metals were chosen to facilitate understanding the magnetic properties attributed to iron in the antimony framework without the complicating influence of the f-electrons in the RE based skutterudites. From the electrical transport, these materials can be classified as bad metals ($k_F \cdot l \approx 1$) displaying an S-shape ρ(T) typical of spin fluctuating systems. The ratio of the effective paramagnetic moment μ_{eff} to the saturation moment μ_S is $\approx$ 6.5 which fits qualitatively into the Rhodes-Wohlfarth plot. This points towards an electronic state which is intermediate between a ferromagnetic insulator and a paramagnetic metal according to the Stoner model. The Sommerfeld coefficient γ is 145, 115, 135 mJ/mol-K^2 for the Na, Ba and the Ca samples respectively which is rather high for a non f electron system. At low temperatures, the Hall resistivity of all the samples shows the presence of an anomalous component giving evidence for the presence of spin fluctuations. For $NaFe_4Sb_{12}$, the charge carrier concentration at 5 K is 6×10^{-10} m^3/C corresponding roughly to 4 holes per formula unit which is comparable to that of $LaFe_4Sb_{12}$. 1. T. Moriya, Spin fluctuations in itinerant electron magnetism, Springer Verlag. 2. C. Uher, Semiconductors and Semimetals, **68**, 139, (2001). 3. A. Leithe-Jasper et al., (accepted). 4. A. Rabis et al., to be published in the proceedings of the ICM 2003. WITHDRAWN 9/9/03 on-line per confirmation notice REINSTATED ABSTRACT 10/8/03 PER AUTHOR'S REQUEST, Dr. Narayani Senthikumaran.

9:45 AM S4.6
Thermoelectric Properties of Filled Skutterudite $Y_xCe_{1-x}T_4P_{12}$(T=Fe, Ru or Os) ($0 \leq x \leq 0.3$). Ram Giri[1], C. Sekine[1], I. Sirontani[1], I. Inagawa[2], C. H. Lee[3] and A. Yamamoto[3]; [1]Department of Electrical and Electronic Engineering, Muroran Institute of Technology, Muroran, Hokkaido, Japan; [2]Eniwa Development Center, Kyoto Semiconductor Corporation, Eniwa, Hokkaido, Japan; [3]AIST Central 2, Tsukuba, Japan.

Filled skutterudite compounds $Y_xCe_{1-x}T_4P_{12}$ (T=Fe, Ru or Os) ($0 \leq x \leq 0.3$) have been prepared at high temperature and high pressure. The samples were characterized by x-ray diffractometry. Electrical resistivity, Seebeck coefficient and thermal conductivity were measured. Dramatic suppression in thermal conductivity (K), has been found in $CeFe_4P_{12}$ with 10% Y doping. Thermal conductivity of $Y_xCe_{1-x}T_4P_{12}$ (T=Fe, Ru or Os) gradually decreases with increase of Y concentration. Mixing more than one rattler (Y and ce), consequence of arising randomness, caused to decrease the significant values of thermal conductivity.

SESSION S5: Low Dimensional Systems and Nanocomposites II
Chair: Mary Anne White
Tuesday Morning, December 2, 2003
Room 313 (Hynes)

10:30 AM S5.1
Low thermal conductivity and related thermoelectric properties of Zn_4Sb_3 and $CoSb_3$ thin films. Kazuhiro Ito[1], Lanting Zhang[2,1], Katsuyuki Adachi[1] and Masaharu Yamaguchi[1]; [1]Materials Science and Engineering, Kyoto University, Kyoto, Japan; [2]Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai, China.

Thermal conductivity and other thermoelectric properties were investigated on β-Zn_4Sb_3 and $CoSb_3$ thin films. They are prepared by co-deposition of the specific sets of Zn, Sb and Co targets by RF magnetron sputtering. The as-deposited amorphous thin films were annealed for crystallization at temperatures 603 and 473 K, respectively for β-Zn_4Sb_3 and $CoSb_3$. Thermal conductivity measurement was performed based on an AC calorimetry method using a commercial thermal diffusivity meter (LaserPIT, Ulvac-Riko, Inc.). For this measurement, a thin film was deposited on one half of a piece of borosilicate glass of 30μm thick. Thermal diffusivities of the regions with and without film deposition were measured respectively and were used to calculate the in-plane thermal conductivity of the thin film. The Zn_4Sb_3 thin films investigated are Zn-rich with respect to the stoichiometric composition. Their thermal conductivity decreases with decreasing film thickness and the grain size of thin films strongly depends on their thickness. A nano-scale grain size in a $\sim$350nm thick film specimen gives arise to an almost 50% reduction in its thermal conductivity ($\sim$0.5W/mK). The temperature dependence of the measured thermal conductivity of the $\sim$350nm thick film specimen seems to be weak and the thermal conductivity of the thin film is seen to be significantly lower than those of the bulk specimens. Low electrical resistivity and high Seebeck coefficient can be achieved simultaneously in the film specimen with properly controlled thickness and microstructure. A ZT of 1.2 at $\sim$460K has been obtained for the $\sim$350nm thick Zn_4Sb_3 film specimen. In contrast, the thermal conductivity of a $\sim$325nm thick film $CoSb_3$ specimen is found to be about 1.1 W/mK at room temperature, which is almost one tenth smaller than that of the bulk specimen, although its power factor is much smaller than that of bulk specimens.

10:45 AM S5.2
Theoretical Prediction of Thermal Conductivity of Nano-composites. Ronggui Yang and Gang Chen; Mechanical Engineering Department, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Nanocomposites have tailed mechanical, electrical and optical properties. In one hand, many experiments have been tried to obtain high thermal conductivity material using carbon nanotube based nano-composites for thermal management of electronics, especially the thermal interface materials (TIM). In the other hand, the size effect due to the interface scattering between the nanoparticles and the host material, and the phonon rarefaction effect might be explored for lower thermal conductivity, which can be very useful for improving the performance of thermoelelectric devices. In this paper, we study theoretically the thermal conductivity of nanocomposites with nanorod (nano-fiber) embedded in the host semiconductor material. We predict the thermal conductivity dependence on the interface condition, the size of nano-fibers, the volume fraction, and the bulk properties of the constituent materials. Acknowledgments: This work is supported by NSF (CTS0129088).

11:00 AM *S5.3
Quantum Dot Superlattice Thermoelectric Unicouples for Conversion of Waste Heat to Electrical Power. Theodore C. Harman, W. D. Goodhue, R. E. Reeder, B. E. LaForge, M. P. Walsh, C. D. Hoyt, D. E. Mull and G. W. Turner; Group 83, MIT Lincoln Lab., Lexington, Massachusetts.

Alloying $PbSe_{0.98}Te_{0.02}$ with SnSe provides an important variable in controlling the band structure of $PbSe_{0.98}Te_{0.02}$ nanodots. The total bandgap offset energy between the alloy nanodots and the PbTe spacer layer has been increased from 40 meV for $PbSe_{0.98}Te_{0.02}$/PbTe quantum dot superlattice (QDSL) structures to over 150 meV for PbSnSeTe/PbTe QDSL structures grown by molecular beam epitaxy and investigated for applications in thermoelectrics [1]. This paper describes the growth and characteristics of n-type and p-type QDSL materials. The typical unicouple device consists of a substrate-free, bulk-like (typically 0.1 mm in thickness, 10 mm in width, and 5 mm in length) slab of nanostructured PbSnSeTe/PbTe as the n-type leg and a metal wire as the p-type leg. Results on arrays of unicouple TE devices will be presented. Projections of future thermoelectric performance expectations for PbSnSeTe based QDSL materials will be presented. [1] T.C. Harman, P.J. Taylor, M.P. Walsh, B.E. LaForge, Science, **297**(2002)2229. This work was sponsored by the Department of the Navy and the Defense Advanced Research Projects Agency (DARPA) under Air Force Contract no. F19628-00-C-0002. The opinions, interpretations, conclusions and recommendations are those of the authors and are not necessarily endorsed by the United States Government.

11:30 AM S5.4
Crystallographically-Oriented Electrochemically-Deposited Bismuth Nanowires. Oded Rabin[1], Gang Chen[2] and Mildred S Dresselhaus[3]; [1]Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [3]Physics, Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Nanowires of thermoelectric materials have been predicted to have superior thermoelectric characteristics over the bulk material. Both the quantization of the electronic density-of-states and the enhancement of surface scattering are expected to increase the value

of the Seebeck coefficient and decrease the value of the thermal conductivity in low-dimensional systems. In this paper, recent advances in the preparation of bismuth nanowires by electrochemical deposition into porous anodic alumina templates are presented. Previously, bismuth nanowires have been synthesized via electrochemical deposition, pressure injection of the melt, and vapor phase condensation in the pores of porous anodic alumina templates. While electrochemical deposition is advantageous for the preparation of large quantities of small diameter nanowires, in terms of their crystal quality nanowires obtained by this method thus far are inferior to samples made by other methods: they are polycrystalline and show no preferred crystallographic orientation along the main nanowire axis. These materials properties are highly relevant to the thermoelectric performance, particularly with anisotropic materials such as bismuth, since low effective carrier masses, long mean free paths and phase coherence lengths are desirable. We have found synthetic conditions that lead to improvements in the crystallinity and orientation of 200nm nanowire arrays. Comparison of the structural and transport properties of these samples to those of samples prepared by other methods will be functional for verifying and improving theoretical predictions over the influence of structural factors on thermoelectricity in nanowires. We gratefully acknowledge the support from DOE (DE-FG02-02ER45977) and ONR (contract N0014-02-1-0865).

11:45 AM S5.5
A Variational Solution of the Thermoelectric Transport Properties of Two-Component Nanocomposite Systems.
Patrick L. Garrity and Kevin L. Stokes; Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana.

The successful fabrication of a nanocomposite in bulk form consisting of an anisotropic assembly of nanoscale sized particles has required an increased understanding of the theoretical aspects of the thermoelectric transport properties. Our particular nanocomposite consists of nanorods that are within the quantum confined regime of one dimensional carrier transport. Upon fabrication of the bulk composite, these nanorods are embedded within a three dimensional conducting matrix that exhibits altered transport properties. We address the nanorod component by assuming a single parabolic band within the one dimension density of states to accommodate the single dimensional transport of the quantum confined carriers. Both elastic and inelastic scattering of electrons or holes is accommodated by solving the variational form of the Boltzmann transport equation. Inelastic interactions include the three dimensional bath of longitudal and transverse acoustic phonon deformation potential scattering with the one dimensional confined electrons of the quantum wells. An altered lattice thermal conductivity of both the confined and surrounding conducting matrix is calculated separately to account for umklapp and boundary scattering of the acoustic phonons which undergoes considerable interface scattering with the embedded nanorod system. Exact expressions for the bulk effective electrical resistivity, thermal conductivity, Seebeck coefficient and figure of merit are then obtained through the field decoupling tranformation, which is a special case of two component composites. Our method is easily generalized to any two component composite and is independent of the components geometry as well as applications of one, two or three dimensional transport regimes with or without quantum confinement. Application to the emerging field of nanocomposites is discussed and comparison to available experimental data is presented.

SESSION S6: Complex Bulk Materials and Measurements I
Chair: Kevin Stokes
Tuesday Afternoon, December 2, 2003
Room 313 (Hynes)

1:30 PM S6.1
Anisotropy in Thermoelectric Properties of $CsBi_4Te_6$.
Duck-Young Chung[1], S D Mahanti[2], Jeffrey Dyck[3], Citrad Uher[3] and Mercouri G Kanatzidis[1]; [1]Chemistry, Michigan State University, East Lansing, Michigan; [2]Physics and Astronomy, Michigan State University, East Lansing, Michigan; [3]Physics, University of Michigan, Ann Arbor, Michigan.

$CsBi_4Te_6$ has been reported as a promising thermoelectric material (ZT $\sim$ 0.8 at 225 K), which could efficiently function at low temperatures for cooling applications. The compound crystallizes in a needle-type morphology reflecting monoclinic unit cell parameters of a = 51.9205(8) $\AA$, b = 4.4025(1) $\AA$, c = 14.5118(3) $\AA$, β = 101.480(1)deg. The structure features NaCl-type $[Bi_4Te_6]$ slabs that are infinitely extended along the needle axis (b-axis) and Bi-Bi bonds interconnecting slabs along a-axis which build up layers separated by Cs atoms with high atomic displacement parameters. These morphology and structural characteristics imply highly anisotropic features in its thermoelectric properties. TE properties previously reported on $CsBi_4Te_6$ have been performed along the needle (b-) axis since effective charge transport is generally expected to be along the needle axis. Electronic structure calculations, however, indicate that the layers in which the charges are confined to move are almost perpendicular to the interconnected $[Bi_4Te_6]$ layers and this phenomenon is due to the presence of Bi-Bi bonds which is unique for the systems consisting of Bi/Te network. Also, a large ZT value of the hole-doped $CsBi_4Te_6$ reflects a large anisotropy in the carrier effective masses associated with the Bi-Bi bonds (a-axis) in the valence band. Therefore, investigation of anisotropy in physical and thermoelectric properties is necessary to fully understand this material. Here, TE properties of $CsBi_4Te_6$ measured along all primary directions will be discussed and compared with the prediction from band structure calculations.

1:45 PM S6.2
Electronic structure and thermoelectric properties of $A_xMo_3Sb_5Te_2$.
Navid Soheilnia and Holger Kleinke; Chemistry, University of Waterloo, Waterloo, Ontario, Canada.

The binary antimonide Mo_3Sb_7 is metallic, but its band structure exhibits a gap of *ca.* 0.9 eV located above the Fermi level. We proved that Mo_3Sb_7 can be chemically modified to become semiconducting by replacing 2 Sb atoms with 2 Te atoms (per formula unit) [1]. This material could be an attractive candidate for the thermoelectric energy conversion, as its thermal conductivity may be lowered by creating the *rattling* effect upon intercalation of small cations [2], and its band structure may be tailored, i.e. the band gap size modified. Simply put, the higher the Te content and the higher the cation amount, the smaller is the band gap, which can virtually reach any value below 0.5 eV [3]. Cations such as A = Mn, Fe, Co, Ni, Cu, and Mg can be added into the cubic void formed by Sb and Te atoms. Without any cell distortions, the A-Sb/Te distance would be 2.69 $\AA$, which may lead to a *rattling* effect depending on the size of the cation. E.g., the Ni-Sb contacts in $NiSb_2$ are as short as 2.44 $\AA$, while the Mg-Sb bonds in Mg_3Sb_2 are 2.82 $\AA$. Physical property measurements of Seebeck coefficients, electrical and thermal conductivity are in progress. E.g., thus far we have attained Seebeck coefficients of up to 200 μV/K. We will present both the experimental and the theoretical results of this ongoing study. [1] E. Dashjav, A. Szczepenowska, H. Kleinke, *J.Mater.Chem.* **12**, 345 - 349 (2002). [2] E. Dashjav, H. Kleinke, *Mat.Res.Soc.Symp.Proc.* **730**, 131 - 136 (2002). [3] N. Soheilnia, E. Dashjav, H. Kleinke, *Can.J.Chem.*, in press.

2:00 PM *S6.3
Thermoelectric Properties of Cubic $AgPb_nSbTe_{2+n}$.
Mercouri G Kanatzidis[1], Kuei-Fang Hsu[1], Junghwan Do[1], Tim P Hogan[2], Fu Guo[2] and Sim Loo[2]; [1]Chemistry, Michigan State University, East Lansing, Michigan; [2]Electrical and Computer Engineering, Michigan State University, East Lansing, Michigan.

Thermoelectric heat to electricity converters could play a key role in future energy conservation, management and utilization. More efficient thermoelectric materials need to be identified that are suitable for high temperature applications. The material system $AgPb_nSbTe_{2+n}$ has been synthesized and its properties determined. When 10 < n < 18 and when doped appropriately, certain members exhibit a high thermoelectric figure of merit at high temperature. At this temperature range the $AgPb_nSbTe_{2+n}$ surpass in performance other bulk thermoelectric materials. The new series of compositions $AgPb_nSbTe_{2+n}$ is a family of materials with cubic crystal structure. The various members of the series are designed to exhibit maximum mass fluctuation generated by Ag-Pb-Sb disorder and they also show interesting microscopic inhomogeneities that may be responsible for the observed high power factors of these materials. Several members were investigated extensively through doping and crystal processing variations. The maximum ZT is achieve at high temperatures (700-800 K) making these materials suitable for possible power generation applications. If time permits we will also present data for the corresponding selenides analogs.

2:30 PM S6.4
New Transport Measurement Systems for Characterization of Thermoelectric Materials.
Fu Guo[1], Junghwan Do[2], Mercouri G Kanatzidis[2] and Timothy P Hogan[1]; [1]Electrical and Computer Engineering Department, Michigan State University, East Lansing, Michigan; [2]Department of Chemistry, Michigan State University, East Lansing, Michigan.

With the emergence of promising new materials for thermoelectric applications, measurement systems are in great need for characterization of new thermoelectric materials in a timely and effective manner. This paper presents the design of a convenient room temperature electrical conductivity (σ) and thermoelectric power (S) measurement system. The design of this system enables rapid screening of sample materials while providing accurate measurement

of the transport properties, and has been useful for measuring electrical conductivity, sample uniformity, and contact resistance. A second measurement system presented in this paper is a computer-controlled drift measurement system with the vacuum chamber partially submerged in a liquid nitrogen flask. This drift system has the capability of simultaneous measurements of electrical conductivity, thermoelectric power, and thermal conductivity over a temperature range of 80-400K. Various reference materials, such as Ni, stainless steel, Mo, Bi2Te3, etc., were used to evaluate the above systems. The design and implementation of these measurement systems along with data from the reference materials, and new thermoelectric materials will be presented in this paper.

2:45 PM S6.5
Effect of K/Bi Ordering on the Electronic Structure of $K_2Bi_8Se_{13}$[†]. Daniel I Bilc[1], Paul Larson[2], S. D. Mahanti[1] and M. G. Kanatzidis[3]; [1]Physics and Astronomy, Michigan State University, East Lansing, Michigan; [2]Naval Research Laboratory, Washington, District of Columbia; [3]Chemistry, Michigan State University, East Lansing, Michigan.

$K_2Bi_8Se_{13}$ belongs to a class of complex Bi-Te-Se systems which show great potential for thermoelectric performance. This compound forms in two distinct phases α-$K_2Bi_8Se_{13}$ (triclinic with space group P-1) and β-$K_2Bi_8Se_{13}$ (monoclinic with space group P 2_1/m). In the β-phase, there are four sites with mixed K/Bi occupancy. To understand the electronic properties of these two different phases we have carried out electronic structure calculations within *abinitio* density functional theory (DFT) using full potential linearized augmented plane wave (LAPW) method. The generalized gradient approximation (GGA) was used to treat the exchange and correlation potential. Spin-orbit interaction (SOI) was incorporated using a second variational procedure. The α-phase is found to be a semiconductor with an indirect band gap of 0.47eV[3]. For the β-phase we have chosen two different ordered structures with extreme occupancies of K and Bi atoms at the "mixed sites". Both systems are semi-metals[3]. To incorporate the effect of mixed occupancy we have chosen a supercell with an alternative K/Bi occupancy at the "mixed sites". The system is found to be a semiconductor with an indirect gap of 0.38eV. We have shown that the mixed occupancy is crucial for the system to be a semiconductor because the Bi atoms at the "mixed sites" stabilize the Se-p orbitals of the nearest neighbor Se atoms by lowering their energy. We find a strong anisotropy in the effective mass near the conduction band minimum, with the smallest effective mass along the mixed K/Bi chains. This large anisotropy suggests that β-$K_2Bi_8Se_{13}$ can be an excellent n-type thermoelectric material . [†]Supported by the Office of Naval Research. 3. Daniel I Bilc *etal.*, MRS Proceedings Volume 691, G13.1.1 (2002)

SESSION S7: Novel Approaches I
Chair: Dave Johnson
Tuesday Afternoon, December 2, 2003
Room 313 (Hynes)

3:30 PM S7.1
Molecular Dynamics Study of Thermal Transport in Silicon Nanowires. Liu Yang and N. Mingo; NASA Ames Research Center, Moffett Field, California.

Nanowires are candidates for super thermoelectric materials due to their potentially enhanced thermopower and electric conductivity, and reduced thermal conductivity. In this work, we investigate the lattice thermal conductivity of Si nanowires and bulk Si through molecular dynamics simulations, using Kubo correlation method. In the temperature range from 100K to 1000K, the results show that the thermal conductivity of Si nanowires is one to two orders of magnitude smaller than the bulk, depending on the wire width and temperature. By obtaining the temporal autocorrelation functions for the wire and bulk, we found a striking change in correlation pattern and a shortening of correlation lifetime in nanowires compared to bulk. The physics behind the thermal conductivity change is derived from the correlations. The drastic reduction in thermal transport in nanowires is mainly attributed to phonon lifetime reduction due to the surface enhanced scattering, while interestingly the speed of sound modification is not playing any major role. The phonon mean free path in nanowires is suppressed to a length scale comparable to the wire width.

3:45 PM S7.2
Thermoelectric Properties of Si-Ge Nanocomposites. Tom Harris[1], J Liu[4], J Y Huang[4], Z F Ren[4], M S Dresselhaus[2,3], B Klotz[5] and R Dowding[5]; [1]Mechanical, MIT, Cambridge, Massachusetts; [2]Physics, MIT, Cambridge, Massachusetts; [3]Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; [4]Physics, Boston College, Chestnut Hill, Massachusetts; [5]Army Research Laboratory, Aberdeen Proving Ground, Maryland.

High figure of merit has been reported in superlattice structures in recent years mainly due to a large reduction in device thermal conductivity, while maintaining or even enhancing the power factor. These findings suggest the possibility of using nanocomposites to reduce a material's thermal conductivity and thereby increasing the thermoelectric figure of merit. The current work reports on the thermoelectric properties of various Si-Ge nanocomposites synthesized in a simple and straightforward process that allows one to exploit nanoscale physics while rapidly producing macroscale devices. Composite synthesis consisted of combining Si nanoparticles approximately 20 nm in diameter with micron-sized Ge particles in various atomic ratios via hot-pressing to form macroscale samples. Electrical conductivity, thermal conductivity, and Seebeck coefficient were measured near room temperature for each of the nanocomposite samples and compared with the values of SiGe bulk alloys. We demonstrate that a significant reduction in thermal conductivity can be achieved in such structures.

4:00 PM S7.3
Structure and Magnetic Properties of New Transition-Metal-Doped Germanium Clathrates. Yang Li, Weiping Gou, Ji Chi and Joseph H. Ross; Department of Physics, Texas A&M University, College Station, Texas.

We have investigated the formation of transition-metal doped Ba-Ge clathrates, and have found several materials which form with the chiral clathrate structure (which has also been called type IX). Fe-, Co- and Cr-doped clathrates form with the chiral clathrate type, substituting on the framework of the structure with nominal composition Ba_6Ge_{25}. We describe details of the synthesis of these materials. Attempts to form Ni and Cu clathrates in this structure yielded the type I clathrate as previously reported. X-ray diffraction and EDS and WDS measurements confirmed that the transition metals enter the clathrate lattice. For the chiral clathrates, structural refinement of the powder x-ray data showed large thermal parameters for Ba sites 2 and 3, similar to the behavior reported for Ba_6Ge_{25}. These are the sites in the open channels, and we examine the potential of these materials for thermoelectric applications. Fe-doped $Ba_6Ge_{25-x}Fe_x$ forms with $x = 3$, and very few vacancies, in accordance with a Zintl concept. Mossbauer spectroscopy indicates the Fe atoms to be distributed among several framework sites, while for type-I $Ba_8Cu_5Ge_{40}$, NMR measurements confirm the Cu to be located on the 6*c* crystallographic site. SQUID magnetometry shows the Fe clathrate to be magnetic, while the Co, Cr, Ni, and Cu clathrates are essentially nonmagnetic, however with dilute moments present, attributed to wrong-site atoms. The Fe-doped clathrate exhibits a complex magnetic behavior, with a mixture of ferromagnetic and spin-glass-like characteristics, and a long-range ordering transition at about 180 K. This work supported by the Robert A. Welch Foundation and the National Science Foundation.

4:15 PM S7.4
Progress in the Electrochemical Deposition of Superlatticed Thermoelectric Materials. Jennifer A. Herman, Nosang V. Myung, Chen-Kuo Huang, James R. Lim and Jean-Pierre Fleurial; Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

It has been predicted that the engineering of low dimensionality structures, such as superlattices and nanowires, has the potential to enhance the efficiency of thermoelectric devices. A process for the electrodeposition of Bi_2Te_3/Sb_2Te_3 superlatticed nanowires from a single aqueous electrolyte is currently under development at the Jet Propulsion Laboratory (JPL). Efforts are now focusing on using cyclic voltammetry to better understand the electrochemical deposition process for $Bi_xSb_{2-x}Te_3$. An overview of this investigation will be given with an emphasis on improving film quality and morphology, and enabling the electrochemical deposition of superlattices. Recent progress in improving electrochemical fabrication techniques for obtaining superlatticed thin films and nanowires will be discussed.

4:30 PM S7.5
Thermoelectric properties characterization of nanostructures based on the Harman method. Claudiu Liviu Hapenciuc[1], Theodorian Borca-Tasciuc[1], Fazeel J. Khan[1], Toh-Ming Lu[2] and Gwo-Ching Wang[2]; [1]MANE Dept., Rensselaer Polytechnic Institute, Troy, New York; [2]Physics, Rensselaer Polytechnic Institute, Troy, New York.

This work investigates the influence of heat leakeage and thermal and electrical contact resistance on Harman method based characterization of nanostructures, and proposes strategies to alleviate these effects.The discussion is illustrated by experiments performed on two-dimensional (film-on-substrate) and one-dimensional (nanowire array) systems. Microfabrication techniques are used to instrument

the film samples with microscale electrodes and temperature sensors. The work also explores thermoelectric characterization of nanowires using an electrically conductive AFM tip.

4:45 PM S7.6
Structural analysis and thermoelectric properties of Type-I clathrate compounds in the Ba-Ge-Ga system.
Norihiko Liszt Okamoto, Takumi Nishii and Haruyuki Inui; Materials Science and Engineering, Kyoto University, Kyoto, Japan.

There has been great interest in Type-I clathrate compounds of a stoichiometric composition of M_8X_{46} (M=alkali or alkali earth metals, X=Si, Ga, Ge) because of their good thermoelectric properties. These clathrate compounds have been known to possess a cubic crystal structure belonging to the space group of Pm-3n with two kinds of cage structures consisting of X atoms; X_{24}-tetrakaidecahedron and X_{20}-dodecahedron. Recently, the binary type-I clathrate compound of the Ba-Ge system is reported to have a stoichiometric composition of Ba_8Ge_{43} with half the 6c sites for Ge being randomly occupied by vacancies. However, our recent transmission electron microscopy (TEM) observations have indicated that Ba_8Ge_{43} possesses a superlattice structure with the lattice constant twice large as that for other Type-I clathrate compounds due to an ordered arrangement of Ge vacancies at 6c sites. Our tentative assignment indicates that the space group is changed to Ia-3d. 6c sites of the space group of Pm-3n are converted to 24c and 24d sites of the space group of Ia-3d and either of these two sites is occupied by vacancies. Upon alloying with Ga, Ga atoms preferentially occupy these sites corresponding to 6c sites in the space group of Pm-3n for a small level of Ga additions and the electrical conduction mechanism changes from of semiconducting for binary to of metallic for Ga-bearing alloys. Therefore, the occupancy behavior for 6c sites may play an important role in controlling its transport properties. We will present the results of crystal structure and microstructure analysis by TEM as well as thermoelectric property measurements for Type-I clathrate compounds in the Ba-Ge-Ga system and discuss the occupancy behavior for 6c sites in relation to the observed thermoelectric properties.

SESSION S8: Poster Session: Thermoelectric Materials and Technology
Chairs: Joseph Heremans, Tim Hogan, Dave Johnson, George Nolas, Jeff Snyder and Jihui Yang
Tuesday Evening, December 2, 2003
8:00 PM
Exhibition Hall D (Hynes)

S8.1
A Step-like Structure of the Electrical Conductivity of the p-type $CdCr_{2-x}Ga_xSe_4$ Spinel Semiconductors.
Tadeusz Gron[1], Andrzej Krajewski[1], Ewa Malicka[2], Joachim Kusz[1] and Alicja Waskowska[3]; [1]Institute of Physics, University of Silesia, Katowice, Poland; [2]Institute of Chemistry, University of Silesia, Katowice, Poland; [3]Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw, Poland.

Single crystals of the $CdCr_{2-x}Ga_xSe_4$ system were grown by vapor transport in closed quartz ampoules with anhydrous chromium chloride, $CrCl_3$, as a transporting agent with selenides CdSe and Ga_2Se_3 as solid phases. Single crystals of octahedral shape with well-formed regular (111) faces had the edge lengths of 3 mm [1]. The magnetic studies revealed that in the composition range of $0 \leq x \leq 0.06$ the single crystals under study are ferromagnets [2]. The structure refinements of the $CdCr_{2-x}Ga_xSe_4$ spinel single crystals were done using a KM4 4-circle diffractometer and a SHELXL-93 computer program [3]. The composition has been confirmed by microprobe analysis with a Cameca Camebax electron microbeam operated at 20 kV (accelerating voltage), a beam current of $5x10^{-8}$ A and a counting time of 1000 ms. Standards used were GaAs for Ga. The electrical conductivity of the spinel single crystals under study has been measured in <001> direction using the four-point dc method and in the temperature range from 80 to 310 K. The thermoelectric measurements were carried out at room temperature. The above investigations showed that all compounds under study are p-type semiconductors. For the sample with x=0.015 a step-like structure of the electrical conductivity (SLS EC) has been discovered in the magnetic regions in which the short and long range magnetic interactions took place, respectively. A presence of a few per cent of the Ga ions in the octahedral sites makes easier a dissolution of the ferromagnetic clusters finally leads to a rapid increase of the electrical conductivity with temperature increasing giving so-called the step-like structure. The remaining single crystals with larger Ga concentration x showed a typical Arrhenius temperature dependence of the electrical conductivity similarly as it was reported for the pure $CdCr_2Se_4$ spinel [4]. It means that the non-magnetic gallium ions play a sensitive role in the electronic transport. For the first time the SLS EC phenomenon in the $Zn_{0.95}[Ga_{0.03}Cr_{1.93}]Se_4$ spinel was observed also for a small concentration of the Ga ions located in the octahedral sites of the unit cell [5]. The SLS EC phenomenon observed in the spinel single crystals above mentioned, could be attractive because of the intriguing physical properties of materials and possible the potential for technological applications. References [1] I. Okonska-Kozlowska, E. Malicka, R. Nagel, and H.D. Lutz, J.Alloys Compd. 292, 90 (1999). [2] I. Okonska-Kozlowska, E. Malicka, A. Waskowska, J. Heimann, and T. Mydlarz, J. Solid State Chem. 158, 34 (2001). [3] G.M. Sheldrick, "SHELXL-93, Program for the Refinement of Crystal Structures", University of Goettingen, 1993. [4] H.W. Lehmann, and M. Robbins, J.Appl.Phys. 37, 1389 (1966). [5] T. Gron, E. Malicka, I. Okonska-Kozlowska, and A. Waskowska, Ferrites: Proceedings of the Eight International Conference on Ferrites (The Japan Society of Powder and Powder Metallurgy, Kyoto and Tokyo, 2000), pp.211-213.

S8.2
Thermoelectric Properties of High Symmetry Quaternary System Ag-Pb-Sb-Te.
Junghwan Do[1], Mercouri G. Kanatzidis[1], Fu Guo[2], Sim Loo[2] and Tim Hogan[2]; [1]Department of Chemistry, Michigan State University, East Lansing, Michigan; [2]Department of Electrical and Computer Engineering, Michigan State University, East Lansing, Michigan.

The thermoelectric (TE) properties of high symmetry quarternary tellurides, $Ag_mPb_nSb_mTe_{2m+n}$ were investigated. These materials crystallize in the space group, Fm-3m and have the NaCl crystal structure type with Ag, Pb and Sb disordered on the Na^+ cationic sites. Such complex compositions and structures (from the combination of two cubic phases, $Ag_mSb_mTe_{2m}$ + Pb_nTe_n) may give rise to complex electronic band structures and to tunable thermoelectric properties. Materials with high symmetry crystal structures and disorder in the heavy element sublattice, Ag-Pb-Sb-Te could be attractive for TE investigations due to their likelihood to possess a high ZT. Heavy elements and disorder are expected to have low phonon frequencies and therefore low thermal conductivity. Also, the high symmetry structure with possible high degeneracy of band extrema (i.e. large number of valleys in conduction band or peaks in the valence band) often results in high power factor. The charge transport and thermal conductivity of these materials were examined as a function of m and n. A p-type $Ag_mSb_mTe_{2m}$ rich phase with high ZT value (high thermopower and low thermal conductivity) is especially emphasized in this report.

S8.3
Thermoelectric Properties of Quenched $YB_2Cu_3O_{7-d}$ Samples.
Julio E. Rodriguez, Alvaro Marino and Julian Lopez; Department of Physics, Universidad Nacional de Colombia, Bogota, Colombia.

We have performed a study of temperature dependence of thermal conductivity, k (T), Seebeck coefficient, S(T) and electrical resistivity, ρ(T) on oxygen deficient polycrystalline samples of $YBa_2Cu_3O_{7-d}$ ($0 \leq d \leq 1$). Measurements of S(T), ρ(T) and k(k) were carried out as a function of the oxygen content in the temperature range between 77K and 300K. The influence of oxygen content on the transport properties and the dimensionless merit figure, (ZT) was studied. With the reducing of oxygen content the Seebeck coefficient and the electrical resistivity show an systematic increase, while k(T) decreases. ZT(T) exhibit an enhancement up to comparable values to those of conventional semiconductors ($0.1 \leq ZT \leq 0.5$). This behavior suggests that the charge carrier density is decreasing while the oxygen level decreases and opens the possibility to use this kind of materials as active thermoelements.

S8.4
Seebeck Coefficient and Thermal Conductivity of YBCO Ceramics.
Julio E. Rodriguez and Alvaro Marino; Department of Physics, Universidad Nacional de Colombia, Bogota, Colombia.

Measurements of Seebeck coefficient, S(T) and thermal conductivity, k(T) on polycrystalline $YBa_2Cu_3O_{7-\delta}$ ceramics were carried out in the temperature range between 77K and 300K. The samples were prepared by solid-state reaction method and submitted to different annealing time process at 500°C. The Seebeck coefficient was found to be very sensitive to the oxygen content and its ordering in the Cu-O chains. S(T) data changes from values of 5 μV/K at 200K, to values higher by more than one order of magnitude. The thermal conductivity showed a decreasing with the annealing time and its values was between 1.0W/mK and 5W/mK. By using the Wiedemann-Franz (WF) model and electrical resistivity measurements it was possible to determine the relative electronic and phonon contributions to the total thermal conductivity.

S8.5
Effects of Sb-doping on electric transport properties of Co-based half-Heusler compound.
Yasuhiro Ono[1], Shingo

Inayama[1], Hideaki Adachi[2], Satoshi Yotsuhashi[2], Yuzuru Miyazaki[1] and Tsuyoshi Kajitani[1]; [1]Applied Physics, Tohoku University, Sendai, Miyagi, Japan; [2]Advanced Technology Research Laboratories, Matsushita Electric Industrial Co., Ltd., Seika, Souraku, Kyoto, Japan.

Electric transport properties of half-Heusler compound NbCoSn and lightly Sb-doped NbCoSn have been studied in the range from 80 K to 850 K. As-prepared samples exhibit metallic behavior of the electric resistivity ρ ($d\rho/dT$)0). The absolute value of Seebeck coefficient S is almost the same in these samples and monotonically increases with increasing temperature (S=-200 μV/K at 850 K). The electric resistivity appreciably increases during the annealing process at 1123 K for 6 days. Unusual increase in ρ at about 200 K and a local minimum around 400 K is observed for annealed NbCoSn. Small enhancement of S is also found in this sample. The Sb-doped samples are metallic over the wide temperature range. Relatively large power factor (S^2/ρ) is obtained for $NbCoSn_{0.98}Sb_{0.02}$ at 850 K (28×10^{-4} W/mK^2 for as-prepared sample and 20×10^{-4} W/mK^2 for annealed sample). The band structure is calculated based on the crystal structure determination of NbCoSn, indicating that NbCoSn is an indirect semiconductor with a band gap of approximately 1 eV. This result is contrary to the metallic behavior of ρ in the present samples. Since ionic radii of Nb and Co are similar, 0.78 $\AA$ for Nb^{5+} and 0.79 $\AA$ for Co^{2+}, intermixing of Nb and Co at their sites may close the band gap, i.e., semimetallic band structure. This assumption is supported by the marked annealing effect on ρ and much higher ρ value in the annealed samples than in metallic half Heusler compounds, TiCoSn and TiNiSb.

S8.6

Synthesis and Thermoelectric Properties of $AgBi_3S_5$. Jun Ho Kim[1], Fu Guo[2], Tim Hogan[2] and Mercouri 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.

Recent investigations of new perspective thermoelectric materials have been devoted to compounds based on alkali metal, bismuth, and chalcogens such as $CsBi_4Te_6$ and β-$K_2Bi_8Se_{13}$. In order to yield a high figure of merit (ZT) promising thermoelectric materials are fundamentally required to have high electrical conductivity, high thermopower, and low thermal conductivity. Herein, the study of thermoelectric materials has focused on the optimization of ZT by virtue of creating compounds with complex structure and composition that affect an increase in thermopower and a decrease in thermal conductivity. In comparison with alkali metal bismuth chalcogenides, the silver analogues yield lower band gap energies due to the more covalent bonding contribution in their structures that can lead to higher electrical conductivity. Among minerals of bismuth chalcogenides, the silver compounds exhibit a variety of structures and compositions such as $AgBiS_2$, $AgBi_6S_9$, $Ag_3Bi_7S_{12}$, and $AgBi_3S_5$, all of which require further studies of their physicochemical and charge transport properties. It is worth to understand and evaluate this interesting system from the thermoelectric point of view. One of these interesting compounds, $AgBi_3S_5$ (pavonite), is the focus of this report.

S8.7

Calculating Seebeck Coefficients for Arbitrary Temperature Gradients. Peter P. F. Radkowski[1] and Timothy D. Sands[2]; [1]Applied Science and Technology, University of California, Berkeley, California; [2]School of Materials Engineering and School of Electrical & Computer Engineering, Purdue University, West Lafayette, Indiana.

A novel computational scheme has been used to predict the electric potentials generated by arbitrary temperature gradients in semiconductor materials. Written in object-oriented code, the Discrete State Simulation (DSS) is a coupled cellular automata simulator that builds upon the objects and rules of quantum mechanics. The DSS represents global non-equilibrium processes as patterns that emerge through an ensemble of scattering events that are localized at vibronic nodes. By tracking the energy-momentum-position coordinates of the individual particles that define the vibronic state at a node, the DSS undercuts equilibrium concepts such as temperature. Consequently, the DSS can represent physical systems that are described by more than one temperature or that contain physical features that defy definitions of temperature. Using modified bootstrap sampling algorithms, the DSS depicted (1) shifts in distribution functions induced by external fields and temperature gradients, (2) field-dependent transitions from linear mobility to non-linear mobility, (3) saturation velocities, (4) non-exponential decay functions generated by multiple phonon scattering modes, and (5) charge separations and electric potentials generated by temperature gradients. Ensemble averages were sensitive to the structure of dispersion relations, to the energy of the system, and to quantum coupling strengths. Seebeck coefficients were sensitive to the features of the electronic and the vibrational band structures, and their associated coupling coefficients.

S8.8

Formation of Misfit Dislocations and the Thermoelectric Properties of PbTe/SnTe/PbTe Heterostructures. Elena Ivanovna Rogacheva[1], Olga Nashchekina[1], Svetlana Lyubchenko[1], Yegor Vekhov[1], Mildred S Dresselhaus[2] and Gene Dresselhaus[2]; [1]Theoretical & Experimental Physics, NTU "Kharkov Polytechnic Institute", Kharkov, Ukraine; [2]Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Theoretical predictions and subsequent experimental confirmations of the possibility of a significant enhancement in the thermoelectric figure of merit in the IV-VI based superlattices stimulate a substantial interest in studying IV-VI low-dimensional structures. The fulfillment of the theoretical predictions depends on structural and kinetic factors, which determine the degree to which a real structure corresponds to a model. The goal of the present work is to study the influence of the transition from a strained to a dislocation structure of the interface on the thermoelectric properties of PbTe/SnTe/PbTe heterostructures grown on KCl substrates by thermal evaporation in vacuum. The electron microscopy study of the growth mechanisms of PbTe and SnTe layers on one another was carried out. The dependences of the thermoelectric properties on the SnTe layer thickness d (0.5-6.0 nm) at a fixed thickness of PbTe layers were investigated. In the thickness dependences of the Seebeck coefficient, the Hall coefficient, electrical conductivity, and charge carrier mobility, anomalies at d $\sim$ 2.0-2.5 nm, corresponding to the transition from pseudomorphic growth to the formation of edge misfit dislocations at the interfaces, were detected. At d $\sim$ 2.5 nm, we also observed maximum values of the thermoelectric figure of merit. It is suggested that the observed effect is a general occurrance and should be taken into account when optimizing growth technologies and when considering the change in the properties of superlattices resulting from a change in the mechanism of growth and from varying the thicknesses of the constituent layers.

S8.9

Fabrication and Testing of Advanced Thermoelectric Unicouple for Power Generation Applications. Jeff S Sakamoto, Thierry Caillat, Jean Pierre Fleurial and Jeff Snyder; JPL, Pasadena, California.

High-efficiency, segmented thermoelectric unicouples employing advanced thermoelectric materials with superior thermoelectric figures of merit are currently under development at the Jet Propulsion Laboratory (JPL). These segmented unicouples include a combination of state-of-the-art thermoelectric materials based on Bi2Te3 and novel p-type Zn4Sb3, p-type CeFe4Sb12-based alloys and n-type CoSb3-based alloys developed at JPL. The maximum predicted thermal to electrical efficiency is about 14% for a hot-side temperature of 975K and a cold-side temperature of about 300K. The paper describes the challenges for fabricating the segmented legs and tested them under various conditions for thermal and electrical performance. Some testing results are presented and compared to model predictions. In addition, various techniques for fabricating unicouple are presented. The thermal and electrical testing procedure is briefly described and discussed.

S8.10

Transport properties of quasi-one-dimensional nanostructures. Marat Viktorovich Vedernikov, O. N. Uryupin, Yu. V. Ivanov and Yu. A. Kumzerov; Ioffe Physical-Technical Institute, St.Petersburg, 194021, Russian Federation.

Quasi-one-dimensional semiconductors (quantum wires) are perspective materials for thermoelectric applications. Unfortunately, it is difficult to produce sufficiently thin and long nanowires. Therefore, thermoelectric properties of short quantum wires (such as carbon nanotubes) or thick wires (bismuth injected into the pores of an anodized alumina template) are studied now. We produce nanowires using the natural mineral chrysotile asbestos. It consists of thin asbestos tubes. The internal diameter of the tubes depends on a mineral deposit and varies from 2 to 15 nm. The length can reach 1 cm. The pressure injection of melted semiconductor into asbestos tubes leads to a formation of long wire bundle. Temperature dependences of thermopower, electrical resistance, and voltage-current characteristics of such InSb and Bi wires were investigated experimentally. Experimental and theoretical features of results obtained are discussed.

S8.11

Synthesis And High Temperature Thermoelectric Properties Of Alkaline-Earth Metal Hexaborides MB_6 (M=Ca, Sr, Ba). Masatoshi Takeda, Yosuke Kurita, Keisuke Yokoyama and Takahiro Miura; Department of Mechanical Engineering, Nagaoka University of

Technology, Nagaoka, Japan.

Boron-rich semiconductors such as boron carbide are candidate materials for high-temperature thermoelectric (TE) conversion, because they exhibit relatively high performance as a p-type TE material at high temperatures. Despite a number of studies searching for n-type materials in boron-rich semiconductors by doping, only a few n-type ones but with insufficient TE performance were reported. We found that CaB_6 and SrB_6 are n-type materials with high TE performance; in particular, dimensionless figure-of-merit ZT of SrB_6 reached approximately 0.3 at 1073K [1, 2]. To discuss the possibilities of further improvement in their TE performance, we synthesized alkaline-earth metal hexaborides (CaB_6, SrB_6, BaB_6) and examined the relationship between carrier concentration and TE performance. The experiments (Hall coefficient, Seebeck coefficient, and electrical conductivity) revealed that the TE properties of the hexaborides depend only on carrier concentration, and optimum carrier concentration which gives maximum power factor was estimated to be approximately 2×10^{20} cm^{-3}. The results suggest that the substitution of metal atoms while maintaining the optimum carrier concentration will be effective to improve overall TE performance, namely figure-of-merit, because such substitution will reduce lattice thermal conductivity and not significantly affect electrical properties. We also fabricated a TE device using SrB_6 and boron carbide as n-type and p-type elements, respectively. To the best of our knowledge, this is the first demonstration of the TE device composed of only boron-rich solids. [1] Masatoshi Takeda *etal.*, Mat. Res. Soc. Symp. Proc. **691** (2002) 209. [2] Masatoshi Takeda *etal.*, Proc. 21st Int. Conf. Thermoelectrics (2002) 173.

S8.12
Abstract Withdrawn

S8.13
Thermoelectric QW Device. Saeid Ghamaty and Norbert Elsner; Hi-Z Technology, Inc., San Diego, California.

The electronic and thermal properties of bulk materials are altered when they are incorporated into quantum wells. Two-dimensional quantum wells have been synthesized by alternating layers of B4C and B9C in one system and alternating layers of Si and Si0.8Ge0.2 in another system. Such nanostructures are being investigated as candidate thermoelectric materials for high figures of merit (Z). The predicted enhancement is attributed to the confined motion of charge carriers and phonons in the two dimensions and separating them from the ion scattering centers. Sputtering techniques have been used to prepare these multilayer films with thickness >10 micrometer. Films have been deposited on single-crystal 5 micrometers thick silicon substrates. The Seebeck coefficient (S) and resistivity (R) properties of these films have been determined over a broad range of temperatures from 4.2K to l200K and were previously reported. The S2/R values for these P type B-C and N type SiGe films were more than a factor of 10 to 30 times higher than bulk P type B-C and N type SiGe. Hi-Z Technology, Inc., has recently measured power and efficiency demonstrating a QW couple conversion efficiency of 14%. These measurements were made recently on a small couple that combined a multilayer QW of P type B4C/B9C with a QW of N type Si/SiGe. This couple operated between 50 and 250 degree C and was fabricated on a 5 micrometers thick Si substrate with ∼11 micrometers QW film thickness. The 14% efficiency was calculated by dividing the power out of the couple by the power in. The 14% efficiency was obtained with no correction for any extraneous heat losses, such as through the Si substrate and the heater wires. The experimental set up also confirmed a known efficiency of ∼5.5% for Bi2Te3 bulk alloys, assuring the data accuracy. The experimental data point and the predicted values agree quite well. A confirmation that these QW materials exhibit a much higher figure of merit than bulk alloys is that the maximum efficiency was achieved at a ratio of load resistance to QW couple resistance of 3 yielding a ZT of 4.1 at T∼150 degree C. The Bi2Te3 bulk alloys meet their maximum efficiency at a resistance ratio of ∼1.2 when their ZT value is close to 1. In another separate experiment, the B4C/B9C film was used as a cooler creating a maximum temperature difference of ∼45 degree C. This temperature difference gives ZT∼3 for T∼25 degree C. For this experiment, the P-type B4C/B9C was joined to small Cu wire. The QW film was the same material and thickness as used in the couple mention above for the power generation.

S8.14
Thermoelectric Properties of NaxCo2O4 Ceramics. xiaofeng Tang[1], Terry M Tritt[2], Ed Abbott[3], Joseph Kolis[3] and Julius Barnes[4]; [1]Materials Science & Engineering, Clemson Univ., Clemson, South Carolina; [2]Physics and Astronomy, Clemson Univ., Clemson, South Carolina; [3]Chemistry, Clemson Univ., Clemson, South Carolina; [4]Physical Sciences, SC State University, Orangeburg, South Carolina.

Due to its large thermopower and low resistivity, the ceramic oxide, NaCo2O4, is a promising and attractive candidate for potential thermoelectric applications. This is especially interesting given that NaCo2O4, is a ceramic compound with high decomposition temperature and chemical stability in air and without toxic elements involved. A review of previous work on the ceramic oxide system will be presented. Electrical and thermal transport properties of NaxCo2O4 single crystal made by NaCl flux method have been previously measured and reported. A conventional mixed oxide method was used to prepare polycrystalline NaxCo2O4 samples. In order to reduce the loss of sodium during the heat treatment at high temperature, atmosphere sintering with specific crucible arrangement and using calcined NaxCo2O4 as atmosphere powder was employed in our study. The effects of microstructure, mainly grain size, and Na concentration, which are substantially influenced by the heating rate, sintering temperature and holding time on the thermoelectric properties, such as Seebeck coefficient, electrical and thermal conductivity were investigated and will be reported. As well, the influence of oxygen flow during calcine and sintering processing on the thermoelectric properties was studied.

S8.15
Transport Properties of $CoGe_{1.5}Se_{1.5}$. Randolph Ertenberg[1], Matt Beekman[1], Joshua Martin[1], G. Nolas[1] and J. Yang[2]; [1]Department of Physics, University of South Florida, Tampa, Florida; [2]Materials Processes Laboratory, GM R&D and Planning, Warren, Michigan.

Skutterudites have become of great interest for thermoelectric applications in the last ten years. To further the understanding of this material structure and optimize its thermoelectric properties, the synthesis and characterization of polycrystalline n and p-type CoGe1.5Se1.5 was undertaken. Structural, morphological, chemical, electrical, thermal and magnetic properties were measured. These data are compared to those of the binary skutterudite CoSb3. The results of this study show a very sensitive dependence of the physical properties of these materials on the stoichiometry. While the thermoelectric figure of merit is quite low in these materials, it is apparent that optimization via void filling will lead to much improved thermoelectric properties.

S8.16
Order-Disorder Transition in the Crystalline Cd6Yb Material. Nicoleta Zina Sorloaica[1], Amy Pope[1], Donny Winkler[1], Terry Tritt[1], Verle Keppens[2], David Mandrus[3] and Brian Sales[3]; [1]Physics, Clemson University, Clemson, South Carolina; [2]Physics, University of Mississippi, Oxford, Mississippi; [3]Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

We performed the electronic and thermal transport measurements of single-phase poly-crystalline Cd6Yb. The resistivity, thermopower, thermal conductivity and heat capacity have been measured between 10 K and 300 K. From the electrical transport data we observed evidence of some type of a phase change in Cd6Yb with distinct changes in the temperature dependence of the resistivity, thermopower, thermal conductivity and heat capacity around T 110K. In addition, the elastic properties using resonant ultrasound (RUS) techniques investigated over a similar temperature range indicate a large "resonance dip" at T equal to 110K. The cubic Cd6Yb crystal, which is a 1/1 cubic approximant of the recently discovered icosahedral Cd5.7Yb, undergoes a reversible order-disorder transition at about 110 K. This makes the system very interesting compared to the quasicrystal phase Cd5.7Yb.

S8.17
Electronic Structure Calculations for PrFe4P12 Filled Skutterudit Using Extended Huckel Tight-Binding Method. Donald H. Galvan, Fisico Quimica, Centro de Ciencias de la Materia Condensada-UNAM, Ensenada, Baja California Norte, Mexico.

To get insight into the electronic properties of PrFe4P12 filled skutterudite, band electronic structure calculations, Total and Projected Density of States (PDOS), and Mulliken Population Analysis were performed. The energy bands yield a semi metallic behavior with a direct gap (at gamma) of 0.02 eV. Total and Projected DOS provides information of the contribution from each orbital of each atom to the the total DOS. Mulliken Population analysis suggest ionic behavior for this filled skutterudite.

S8.18
Performance of Integrated Thin-Film Thermoelectrics in Cooling Hot-Spots on Microprocessors-Experimental Setup and Results. Jai K Cancheevaram[2,1], Randall Alley[1] and Rama Venkatasubramanian[1]; [1]Center for Thermoelectrics, Research Triangle Institute, RTP, North Carolina; [2]Electrical and Computer Engineering, North Carolina State University, Raleigh, North Carolina.

The increasing performance of microprocessors results in increased thermal design power and local power densities, commonly referred to as Hot-spots, which reach in excess of 200W/cm2 in approximately 16mm2 areas at a die-level. Thermal management using passive heat-spreaders in conjunction with heat-pipes or phase-changers, face limitations such as low through-thickness thermal conductivity, increased thermal resistance at interfaces, low values of wick-thermal conductivity in heat-pipes, low vapor pressure etc. Bulk Thermoelectrics offer low COP and state-of-the-art 200um-thick elements can only handle power densities of ~50W/cm2. In comparison, Thin-film thermoelectrics [TFT] have measured ZT values of ~2 at 300K, 15us response time and potential to pump heat flux of several hundred Watts/cm2. TFTs can ensure that junction temperatures do not exceed the rated 85C - 95C range at such hot spots, to guarantee device performance and reliability. We have performed tests by thermally stressing a Pentium Processor and identifying stable deltaT (~53C) across the Heat sink, which enabled more efficient Heat Transfer to the ambient, in the absence of forced-convection cooling. This extends the performance of air cooling, integrated with TFT, as a cost effective solution with minimal impact on system design. A secondary test setup was built for a 16mm2 TFT to be placed on the Hottest Spot (~9mm2) of the processor, identified by infrared images. The TEC was powered by a custom-built OPA548 Amplifier circuitry. A 240W Peltier module assembly, with liquid cooling for accurate calorimetric measure of the COP of the system was included. Initial characterization was performed, by simulating the processor load with an aluminum block encasing a 50W resistive load. We will present the effect of cooling on the direct performance of the processor with the standard SPEC CPU 2000 benchmarks. The ability of TFT for reliable processor over-clocking will also be discussed.

S8.19
Thermoelectric properties of perovskite type titanate.
Hiroaki Muta, Ken Kurosaki and Shinsuke Yamanaka; Nuclear engineering, Osaka university, Suita, Osaka, Japan.

The polycrystalline perovskite type titanate, La doped CaTiO3-SrTiO3-BaTiO3 solid solutions were prepared by the solid state reaction. The electrical conductivity, the Seebeck coefficient, and the thermal conductivity of the samples were measured from room temperature to 873 K. All the samples showed metallic n-type conduction. The electrical conductivity decreased with increasing temperature, according to about T-1.5. This behavior indicates that the carriers are scattered mainly by lattice in the temperature range. The Seebeck coefficient value increased with temperature almost linearly. In the SrTiO3-BaTiO3 solid solution, the electrical conductivity decreased and Seebeck coefficient slightly increased with the lattice parameter. The result indicates that the shorter Ti-Ti distance is desirable for the enhancement of the power factor. The highest thermal conductivity was seen in the La doped SrTiO3, and decreased by Ca and Ba substitution. The figure of merit had a peak around 400-600 K and the value was about 3.5E-4 K-1.

S8.20
Thermoelectric properties of β-BaCu2S2 related compounds.
Hironori Uneda, Hiroaki Muta, Ken Kurosaki and Shinsuke Yamanaka; Nuclear Engineering, Osaka University, 2-1, Yamadaoka, Suita, Japan.

Polycrystalline-sintered samples of β-BaCu2S2 based compounds have been synthesized by melting in sealed quartz ampoules. β phase is obtained by quenching from 973 K to room temperature. The crystal structure of the samples has been determined by a powder X-ray diffraction (XRD) method. The electrical resistivity and Seebeck coefficient of β-BaCu2S2 increase with increasing temperature. β-BaCu2S2 shows extremely low thermal conductivity, about 0.6 W/m/K at room temperature. The dimensionless figure of merit ZT of β-BaCu2S2 shows relatively high value, 0.37 at 800 K. The effect of element substitutions on ZT of β-BaCu2S2 has been studied. The temperature dependence of the electrical resistivity of β-BaCu2S2 changes to metallic behavior by substituting elements, indicating the generation of holes in the valence band.

S8.21
Characteristics of Plasma Shock Waves in Pulsed Laser Deposition Process. Li Zhihua and Zhang Duanming; Physical Department, Hua Zhong University of Science and Technology, Wuhan, HuBei , China.

We modify the Sedov theory to describe plasma shock waves generated in a pulsed laser ablating process. Under the reasonable asymptotic behavior and boundary conditions, the propagating rules in the global free space (including close areas and mid-far areas) of pulsed-laser-induced shock waves are established for the first time. In particular, the temporal behavior of energy causing the difference of the propagation characteristics between the practical plasma shock wave and the ideal shock wave in point explosion model is detailedly discussed. The theoretical results calculated with our model are in good agreement with the corresponding experimental data. In addition, some important free parameters which could not directly be obtained from other previous works are determined naturally on the basis of our model.

S8.22
Substitution effect on the thermoelectric properties of CoTiSn based Half-Heusler compounds. Yoshiyuki Kawaharada, Hiroaki Muta, Ken Kurosaki and Shinsuke Yamanaka; Nuclear Engineering, Osaka University, Suita, Osaka, Japan.

Half-Heusler compounds are known to be intermetallic compounds with relatively large Seebeck coefficients and semimetallic to semiconductor like transport properties. This makes them attractive for study as potential candidates for thermoelectric materials. In the present study, we focus on the substitution effect on the thermoelectric properties of CoTiSn based Half-Heusler compounds. The thermoelectric transport properties of the Half-Heusler compounds were measured in the temperature range between 300 K and 900 K. The high temperature electrical resistivity and thermoelectric power (TEP) were measured simultaneously by a standard four-probe d. c. method using ULVAC ZEM-1. The high temperature thermal diffusivity were measured by a laser flash method using ULVAC TC-7000 and the heat capacity were measured by a differential scanning calorimeter using ULVAC Triple DSC. The thermal conductivity was estimated from the density, thermal diffusivity, and heat capacity. The TEP and resistivity show strong substitution dependence. The substitution dependences of the thermoelectric properties were discussed by using the results of the first-principle electronic band calculation.

S8.23
Thermoelectric Properties of $NaZn_{13}$ type Intermetallic Compounds. Yasutaka Amagai[1], Atsushi Yamamoto[2], Chul-Ho Lee[2], Hiroyuki Takazawa[2], Teruo Noguchi[2], Haruhiko Obara[2], Tsutomu Iida[1] and Yoshifumi Takanashi[1]; [1]Materials Science, Tokyo University of Science, Noda, Japan; [2]Energy Electronics Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Good thermoelectric performance is usually found in a semiconducting material with extremely low thermal conductivity. Recently semiconducting clathrate compounds, i.e. $Sr_8Ga_{16}Ge_{30}$, have attracted a great attention due to their glass-like low thermal conductivity. The origin of the low thermal conductivity has been discussed in connection with their special crystal structure, periodic IV group element cages of large coordinated polyhedra with alkaline or rare earth metals residing inside. Intermetallic compounds such as $NaZn_{13}$, $BaCd_{11}$, and Th_2Zn_{17} proto-type are known to have a similar 'cage' crystal structure. This paper describes experimental results of syntheses and evaluations of polycrystalline samples of $SrZn_{13}$, $BaZn_{13}$, $LaZn_{13}$, and $LaCo_{13}$. Zinc based system such as $SrZn_{13}$, $BaZn_{13}$, and $LaZn_{13}$ were prepared on the route of reacting the metals at a molar ratio of 1:12 in an evacuated quartz tube above their melting points. The samples were ground thoroughly, then hot-pressed into pellets. The polycrystalline sample of $LaCo_{13}$ was prepared by arc-melting under argon atmosphere with subsequent annealing at 1273K for 1 week. The powder X-ray diffraction and energy dispersive X-ray spectroscopy (EDX) revealed that $BaZn_{13}$ and $LaCo_{13}$ samples were single phase, while the $SrZn_{13}$ and $LaZn_{13}$ samples contained small amount of the impurity phase of metal zinc. The electrical resistivity and the Seebeck coefficient measurements were performed from 323K to 673K for $SrZn_{13}$, $BaZn_{13}$, and $LaZn_{13}$, from 323K to 973K for $LaCo_{13}$. The thermal conductivity was determined at room temperature. Through the electrical resistivity and Seebeck coefficient measurements, $SrZn_{13}$, $BaZn_{13}$, $LaZn_{13}$, and $LaCo_{13}$ were found to be a good metallic conductor. Among them the Seebeck coefficient of $LaCo_{13}$ is relatively high as a metal, showing the maximum value of 30μV/K at 400K. The lattice components of the thermal conductivity calculated for $SrZn_{13}$, $BaZn_{13}$, $LaZn_{13}$, and $LaCo_{13}$ assuming Wiedemann-Frantz law were 11W/mK, 8.6W/mK, 7.5W/mK, and 9.0W/mK, respectively.

S8.24
Thermoelectric Properties of Hot-Pressed GaN and InN. Atsushi Yamamoto[1], Yasuo Iwamura[2,1] and Shigeo Yamaguchi[2,1]; [1]Energy Electronics Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan; [2]Department of Electrical, Electronic and Information Engineering, Kanagawa University, Yokohama, Kanagawa, Japan.

We made an attempt to obtain bulk III-nitride semiconductors such as InN, GaN and $In_xGa_{1-x}N$ alloy using hot-press method in order to determine the high temperature thermoelectric properties. In general,

bulk synthesis of III-nitride compounds requires high-pressure nitrogen to suppress decomposition of nitrides. In this study, we successfully obtained mechanically-good bulk sample by hot-pressing the nitride powder prepared by pyrolysis reaction of a complex salt. The hot-pressed samples were confirmed to be single phase by x-ray diffraction, and showed relative density of 50% for GaN and 70% for InN. The samples had good mechanical strength, which was enough to handle in subsequent electrical and thermal measurement. The hot-pressed nitride samples showed negative Seebeck coefficient at and above room temperature. The Seebeck coefficient and the resistivity were -10 microV/K and 1.8×10^{-6} ohm-m for InN, and -50 microV/K and 1.9×10^{-4} ohm-m for GaN at 300K, respectively. The room temperature thermal conductivities determined by laser flash method with porosity correction were 17W/mK for InN and 2.6W/mK for GaN. For InN the Seebeck coefficient and the resistivity increased monotonously with increasing temperature, which indicates that InN is metal or degenerated semiconductor. The maximum power factor and figure of merit of InN within the measured temperature range were 2 x 10^{-4} W/mK^2 and 1.5×10^{-5} K^{-1} at 650K, respectively.

S8.25

Thermoelectric Properties of Novel Boron-Rich Cluster Compounds. Takao Mori, Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Japan.

Boron-rich cluster compounds are attractive materials for their stability under high temperature and in unfriendly (e.g. acidic) environments. Magnetic properties of some new rare earth boron cluster compounds have recently attracted increasing interest, being magnetically dilute materials but displaying a various range of properties such as the short range magnetic transitions in REB_{50} and isostructural $REB_{44}Si_2$ compounds, long range order in $GdB_{18}Si_5$, and 2 dimensional spin glass behavior in the homologous series $REB_{17}CN$, $REB_{22}C_2N$, $REB_{28.5}C_4$ [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], because the B_{12} icosahedral cluster compounds generally exhibit low thermal conductivity [3], actually exhibiting glass-like conduction for the crystalline YB_{66} compound, for example. In this work, the thermoelectric properties of the recently discovered boron cluster compounds are investigated up to high temperatures reaching over 1000 K. Relatively large Seebeck coefficients are observed and the electrical conductivity increases rapidly as temperature is increased through variable range hopping, while the Seebeck coefficients do not show a significant decrease in value. Possibility of using or modifying these novel boron cluster compounds for high temperature thermoelectric application will be discussed. This work is supported in part by a PRESTO fund project from the Japan Science and Technology Corporation JST. [1] for example, T. Mori, A. Leithe-Jasper, Phys. Rev. B 66 (2002) 214419. [2] T. Nakayama, J. Shimizu, K. Kimura, J. Solid State Chem. 154 (2000) 13. [3] D. G. Cahill, H. E. Fischer, S. K. Watson, R. O. Pohl, G. A. Slack, Phys. Rev. B 40 (1989) 3254.

S8.26

Materials of the thermoelectric conversion unit system within radiation heat transfer and the analysis. Toshinori Ota and Junichi Ochiai; Research Laboratory, Ishikawajima-Harima Heavy Industries Co.,Ltd, Yokohama, kanagawa, Japan.

We promote development of the thermoelectric conversion system which salvages heat loss of about 700K-900K which heat loss salvage has not formerly had had almost performed it for the electric resistance heating industry furnace which possesses water-cooling jacket wall on amount efficiency. In order to perform amount efficiency thermoelectric conversion in the industry furnace inside where a heat transmission system is mainly radiation, development of the amount efficiency thermoelectric conversion module which functions under the compound heat conduction condition which united solid heat conduction within radiation heat transmission and thermoelectric module is not a thermoelectric conversion formula for former convection heat transmission on major and is necessary. For this reason, the module performance analytic result which turned character of several physical properties of thermo-element and thermal radiation receiver of the upper part of modules, heat transmission characteristic, conductive characteristic and thermoelectric conversion property into the foundation and the result which performed the foundation examination which was turned to industry furnace application are reported.

S8.27

Electronic Structure of $(AgSb)_xPb_{n-2x}Te_n$[‡]. Daniel I Bilc[1], S. D. Mahanti[1] and M. G. Kanatzidis[2]; [1]Physics and Astronomy, Michigan State University, East Lansing, Michigan; [2]Chemistry, Michigan State University, East Lansing, Michigan.

The complex chalcogenide systems $(AgSb)_xPb_{n-2x}Te_n$ are narrow band-gap semiconductors and are very good candidates for room and high temperature thermoelectric applications. These systems form in the rock-salt structure similar to the well known two component system PbTe (x=0). In all these systems Ag and Sb atoms occupy randomly Pb sites although there is some evidence of short-range order. Extensive electronic structure studies have been carried out in PbTe, whereas as far as we know there are no electronic structure calculations in the ternary (n=2x) and quaternary compounds. To gain some insights into the electronic structure of these systems, we first perform electronic structure calculations in PbTe and $AgSbTe_2$. These calculations were carried out within *abinitio* density functional theory (DFT) using full potential linearized augmented plane wave (LAPW) method. The generalized gradient approximation (GGA) was used to treat the exchange and correlation potential. Spin-orbit interaction (SOI) was incorporated using a second variational procedure. The details of the electronic structure and the effect of Ag and Sb disorder will be discussed. ‡Supported by the Office of Naval Research.

S8.28

Preparation and Thermoelectric Properties of Layered Cobaltites Textured by a Reactive Templated Grain Growth Method. Hiroshi Itahara[1], Changtai Xia[1], Jun Sugiyama[1], Yoshiki Seno[1], Ryoji Asahi[1], Toshihiko Tani[1] and Kunihito Koumoto[2]; [1]Toyota Central R&D Labs., Inc., Nagakute, Aichi, Japan; [2]Nagoya Univ., Graduate School of Engineering, Nagoya, Aichi, Japan.

Large anisotropy in thermoelectric properties of layered cobaltites leads to a problem how to synthesize aligned polycrystals for the use in actual thermoelectric devices. Here, we report the preparation and characterization of c-aligned $[Ca_2CoO_3]_{0.62}[CoO_2]$ (CCO) polycrystals by a reactive templated grain growth (RTGG) technique using β-$Co(OH)_2$ platelets with the developed {00l} plane as templates. The β-$Co(OH)_2$ platelets obtained by a precipitation method were mixed with $CaCO_3$ powder, then the mixture was tape cast to align the platelets parallel to the basal plane. The obtained tape was cut into a sheet with 50 mm width and 80 mm length, and about 50 sheets were stacked and pressed into a monolithic plate with $\sim$ 3 mm thickness. The plates were dewaxed at 873 K in air, and then sintered with uniaxial pressure at 1193 K in O_2. Both TG-DTA study and high-temperature XRD analysis suggested that the β-$Co(OH)_2$ phase transforms to a spinel Co_3O_4 phase below 873 K; then, the Co_3O_4 phase reacts with $CaCO_3$ at 1193 K to produce CCO grains with preserving the {00l} orientation. The c-aligned CCO obtained in the present work exhibited a high degree of orientation and an anisotropic conductivity; *i.e.*, Lotgering's factor > 0.99, and $\sigma_{ab} \sim 5.5\ \sigma_c$ at 1060 K. Hence, it was confirmed that our RTGG technique is effective and versatile for preparing the c-aligned thermoelectric cobaltites.

S8.29

Thermoelectric Properties of Copper and Indium Containing Oxides. Tao He, J.J. Krajewski and M.A. Subramanian; DuPont CR&D, Wilmington, Delaware.

In recent years, there has been an renewed interest in the field of thermoelectrics driven by the need for more efficient materials for refrigeration and power generation. With the help of theory predictions, many new and novel classes of materials have been identified as potential good thermoelectrics. Model calculations predict that the thermoelectric figure-of-merit ZT can be enhanced in superlattice quantum-well structures. Being natural superlattices, compounds with low-dimensional structures have been investigated actively as potential thermoelectric materials. In this paper, lead copper oxide and Sn-doped silver indium delafossite oxide with layered structure were synthesized and their thermoelectric properties were examined in the temperature range of 300 - 600 K. All compounds show semiconducting behavior. Lead copper oxide has p-type conduction while silver indium oxide exhibits n-type conduction. Both oxides have high Seebeck coefficients and low the thermal conductivity. The electrical resistivity need to be reduced further down, and higher ZT values are expected at elevated temperatures.

S8.30

Thermoelectric measurements of TiS2 type materials. Edward Ernst Abbott[1], Joseph W Kolis[1], Nathan D Lowhorn[2], Will Sams[2] and Terry M Tritt[2]; [1]Chemistry Department, Clemson University, Clemson, South Carolina; [2]Physics Department, Clemson University, Clemson, South Carolina.

TiS_2 belongs to a family of layered compounds we believe may have a possible future as thermoelectric materials. At room temperature the thermopower, α, of TiS_2 is n-type and has a magnitude of $\sim$200 μV/K. The electrical resistivity, ρ, is on the order of 1 mΩ-cm at room temperature and displays metallic-like behavior with dR/dT >

0 from 300 K to 10K. Thus, these compounds exhibit relatively large power factors, PF = α^2/ρ, with a PF ~30 μW/K^2 cm at T = 300 K. This power factor is comparable to the state-of-the-art Bi_2Te_3 type materials. Plate like crystals of TiS_2 can be grown by the iodine vapor transport method to sizes of over 1 cm. In this synthetic approach some dopants can be integrated into the parent compound, effectively providing a route for the tuning of electronic properties. We will present effects of elemental doping on the electronic properties in these materials.

S8.31
Crystallographic Features of Rhenium Disilicide.
Katsushi Tanaka[1], Haruyuki Inui[2], Takuya Ohba[3], Satoshi Tsutsui[4] and Masaichiro Mizumaki[4]; [1]Adv. Mater. Sci., Kagawa University, Takamatsu, Japan; [2]Mater. Sci. & Eng., Kyoto University, Kyoto, Japan; [3]Mater. Sci., Shimane University, Matsue, Japan; [4]Japan Synchrotron Radiation Research Institute, Sayo, Japan.

Rhenium disilicide is a narrow-gap semiconductor and has an excellent figure of merit at high temperature. The crystal structure of the disilicide was first assigned to be a body-centered tetragonal $C11_b$ structure. Recent report has assigned the structure as monoclinic and the stoichiometry of the disilicide has been $ReSi_{1.75}$ owing to the occupancy of half the Si site being 75%. However, our recent results have indicated that additional spots appear in the electron diffraction patterns of $ReSi_{1.75}$; indicating that vacancies in Si sites make an ordered arrangement in the underlying $C11_b$ structure and the crystal contains four differently oriented domains. The crystal structure is monoclinic whose unit cell consists of eight unit cells of $C11_b$ structure. We have performed powder and single crystal X-ray diffraction measurements with synchrotron radiation which makes possible to determine the structure factors of the weak additional reflections. The powder pattern and the single crystal data have been analyzed by the RIETAN-2000 and modified XTAL programs, respectively. The results show that both Re and Si atoms are shifted from its position that is expected from the $C11_b$ structure.

S8.32
Thermo Physical Property Measurements of $(Ca_{1-x}Sr_x)_3Co_4O_9$ Films Using an Improved Transient Grating Method. Yoshiaki Takata[1], Hajime Haneda[1], Yutaka Adachi[1], Yoshiki Wada[1], Takefumi Mitsuhashi[1], Kenji Itaka[2] and Hideomi Koinuma[2]; [1]Advanced Materials Laboratory, NIMS, Tsukuba, Ibaraki, Japan; [2]Tokyo Institute of Technology, Yokohama, Japan.

We propose a method of convenient measurements of thermo physical properties including thermal decay time constants (τ) and thermal diffusivity constants (D) for a thermoelectric material. A composition-spread method is utilized for fabricating a film whose doping concentration varies from 0 to 0.125 continuously. An improved transient grating method that is a new version including higher spatial resolution and much more precise fitting function compared with the past conventional method is employed for characterizing thermo physical properties of the film. A demonstration is given for our reference material, $(Ca_{1-x}Sr_x)_3Co_4O_9$.

S8.33
Investigation of the Properties of Electrochemically Deposited Semiconductor Materials for Thermoelectric Applications. Chen-Kuo Huang, J A Herman, N Myung, J R Lim and J-P Fleurial; Jet Propulsion Laboratory, Pasadena, California.

At JPL, it is our desire to fabricate thermoelectric micro-devices for power generation and cooling applications using an electrochemical deposition (ECD) technique. We believe that the performance of our current micro-device developed is limited by the properties of the ECD materials. Therefore, the objective of this study is to develop ECD methods for obtaining n-type Bi_2Te_3 and p-type $Bi_{2-x}Sb_xTe_3$ thermoelectric materials with near bulk properties, as well as optimizing morphology and transport properties. The substrates used for ECD are SiO_2/Si wafers with either 1μm Bi_2Te_3 or 1μm $Bi_{2-x}Sb_xTe_3$ sputtered on top. From our experimental observations, ECD at higher temperatures typically leads to higher deposition rates but also increases film porosity. In general, the ECD films change their morphology from porous to smooth when the ECD potentials change from very negative to less negative vs. saturated calomel electrode (SCE) reference. The films of Bi_2Te_3 and $Bi_{2-x}Sb_xTe_3$ were initially obtained under various deposition conditions. Seebeck coefficients and transport properties were then measured along the direction parallel to the substrates before and after annealing at 250°C for 2hrs. From the data obtained, ECD n-Bi_2Te_3 material can achieve a high Seebeck coefficient (-189 μV/K) when it is deposited at -200 mV vs. SCE. The in-plane resistivity, in-plane mobility, and carrier concentration are 3.0 mohm-cm , 31 cm^2 V^{-1} S^{-1}, and 6.79 x 10^{19} cm^{-3}, respectively. As for the p-type $Bi_{2-x}Sb_xTe_3$, it is possible to achieve a high Seebeck coefficient (+145 μV/K) when it is deposited at -110 mV vs. SCE. The in-plane resistivity, in-plane mobility, and carrier concentration are 5.9 mohm-cm, 42 cm^2 V^{-1} S^{-1}, and 2.5 x 10^{19} cm^{-3}, respectively. From the results of our preliminary study, we have found the best conditions for depositing high quality Bi_2Te_3 and $Bi_{2-x}Sb_xTe_3$ materials with thermoelectric properties comparable to those of their state-of-the-art bulk samples.

S8.34
Effect of High Valence Metal Doping on Thermoelectric Properties of [Ca2CoO3-δ]0.62CoO2. Kazuyuki Fujie[1], Shigeru Horii[1], Jun-ichi Shimoyama[1,2], Ichiro Matsubara[3], Woosuck Shin[3], Norimitsu Murayama[3], Kenji Otzschi[1] and Kohji Kishio[1]; [1]Department of Applied Chemistry, School of Engineering, University of Tokyo, Bunkyo-ku, Tokyo, Japan; [2]PRESTO, Japan Science and Technology Corporation (JST), Kawaguchi, Saitama, Japan; [3]National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka, Japan.

[Ca2CoO3-δ]0.62CoO2 (~ Ca3Co4O9; Ca349) has been attracted as an excellent thermoelectric material for power generation at high temperatures because its single crystal was reported to show a practical figure of merit (ZT) over 1 [1]. Recently, our group reported that the thermoelectric properties of Ca349 polycrystalline bulk were dramatically improved by combination of magnetic c-axis alignment and densification processes [2]. However, the Ca349 compound was found to show large oxygen nonstoichiometry ($0<\delta<0.14$) at high temperatures through the thermogravimetric measurements [3], resulting in oxygen content dependent thermoelectric properties [2]. On the other hand, it is theoretically predicted that Seebeck coefficients (S) of layered cobaltites can be enhanced by lowering mean valence of Co ions at the CoO2 layers [4]. Therefore, enhancement of Seebeck coefficient is expected by the doping of high valence metals to the Co site at the Ca2CoO3-δ layer. In the present study, we attempted to synthesize high valence metal-doped Ca349 compounds ([Ca2Co1-xMxO3-δ]0.62CoO2; M = Re, Mo, or Nb) and evaluated their thermoelectric properties and oxygen nonstoichiometries. Moreover, c-axis aligned and/or dense polycrystals of these compounds were prepared. The single-phase compounds could be obtained up to x = 0.133 for M = Re, Nb and x = 0.1 for M = Mo by the solid state reactions in air. These high valence metal doped Ca349 compounds exhibited dramatically suppressed oxygen nonstoichiometry. Moreover, Seebeck coefficients of these doped compounds were enhanced with doping levels, x. Electric resistivity (ρ) systematically increased with doping level as for conventionally sintered bulk samples, however, it was remarkably improved by applying intermediate cold pressing processes down to almost comparable values with that of non-doped Ca349. Consequently, excellent power factors (S^2/ρ) were also obtained for the high valence metal doped Ca349. Thermoelectric properties of these doped Ca349 at high temperatures, where oxygen composition is stable, will be compared with oxygen nonstoichiometric pure Ca349.
[1] Funahashi *etal.*, *Jpn. J. Appl. Phys.* **39**(2000) L1127. [2] Sano *etal.*, *Jpn. J. Appl. Phys.* **42** (2003) L198. [3] Shimoyama *etal.*, *Jpn. J. Appl. Phys.* **42** (2003) L194. [4] Koshibae *etal.*, *Phys. Rev. B* **62** (2000) 6869.

S8.35
Hall Effect Measurements on New Thermoelectric Materials.
Jarrod Short[1], Sim Loo[1], Sangeeta Lal[1], Theodora Kyratsi[2], Kuei Fang Hsu[2], Mercouri Kanatzidis[2] and Tim Hogan[1]; [1]Electrical and Computer Engineering Department, Michigan State University, East Lansing, Michigan; [2]Chemistry Department, Michigan State University, East Lansing, Michigan.

In the field of thermoelectrics, the figure of merit of new materials is based on the electrical conductivity, thermoelectric power, and thermal conductivity of the sample, however additional insight is gained through knowledge of the carrier concentrations and mobility in the materials. The figure of merit is commonly related to the material properties through the B factor which is directly dependent on the mobility of the carriers as well as the effective mass. To gain additional insight on the new materials of interest for thermoelectric applications, a Hall Effect system has been developed for measuring the temperature dependent carrier concentrations and mobilities. In this paper, the measurement system will be described, and recent results for several new materials will be presented.

S8.36
Synthesis and Polyaniline-Coating of Bismuth Chalcogenides.
Ven B Reddy[1], Patrick L Garrity[2,1] and Kevin L Stokes[2]; [1]Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana; [2]Department of Chemistry, University of New Orleans, New Orleans, Louisiana.

¡p>¡style="text-align: justify">Our interest in the synthesis of bismuth chalcogenides stems from their possible enhanced thermoelectric properties in nanophase. One of the authors earlier

reported an efficient high-temperature synthesis of bismuth sulfide nanobeads [Kevin Stokes et al. 2002. Mat. Res. Soc. Symp. Proc. 730, V5.5]. We have simplified the high-temperature synthesis of bismuth sulfide nanophase as follows: A solution of thioacetamide in phenyl ether and a small amount of diethylene glycol at about 60 ^oC was added to a solution of bismuth oleate in phenyl ether and excess oleic acid at 250 ^oC under argon. The latter solution was prepared by reacting bismuth triacetate with molar excess oleic acid in phenyl ether at 140 ^oC for 30 min under argon. Five minutes after the addition of thioacetamide solution to bismuth oleate, the mixture was rapidly cooled to room temperature using a water-bath. Bi₂S₃ particles were precipitated by centrifugation and washed with ethanol and acetone. Synthesis of highly crystalline bismuth telluride nanoscale needles involved the reaction of bismuth trioleate in phenyl ether and excess oleaic acid with trioctylphosphine telluride at 60 ^oC for 3-5 min., followed by rapid cooling to room temperature in a water-bath. Bi₂Te₃ nanoneedles were separated by centrifugation and washed with ethanol and acetone. Longer reaction times adversely affect the monodispersity of nanorod populations and give a large proportion of larger particles.
¡style="text-align: justify">Polyaniline coating of nanophase bismuth sulfide and its telluride was achieved by heating a mixture of chalcogenide and polyaniline in toluene at 110 ^oC for 8-12 h, with intermittent sonication. Sonication is necessary for those compounds that do not give homogeneous suspension. It is not required when the nanomaterial gives transparent homogeneous solution. Following the completion of coating, excess polymer and the displaced capping ligand were removed by repeat washings with acetone or THF.

S8.37

Electronic Structure and Effective Mass Anisotropy of $(Bi_2Te_3)_m(Sb_2Te_3)_n$ Multilayers*. Hong Li, Daniel Bilc and S. D. Mahanti; Physics and Astronomy, Michigan State University, East Lansing, Michigan.

Venkatsubramanian et al. [1] have reported room temperature thermoelectric figure of merit (ZT) vlaues of $\sim\sim$ 2.4 in p-type $(Bi_2Te_3)_m(Sb_2Te_3)_n$ multilayers.In these systems, dominant charge transport takes place normal to the Bi(Sb)/Te layers (cross-plane direction) whereas in the bulk systems it is confined to these layers. Surprisingly the cross-plane and in-plane mobilities are comparable for systems with several (m,n) values. To find out the effect of multilayer structure on the band gap and the origin of mobility anisotropy between cross-plane and in-plane directions, we have carried out ab initio gradient corrected density functional calculations of the electronic structure for bulk Bi_2Te_3, Sb_2Te_3 and multilayer systems with (m,n) values (1,1) and (1,2). The global lattice structures of all the 4 systems are first optimized and then the atomic positions are relaxed while keeping the volumes and the c/a ratios fixed. Effective masses in different directions, direct and indirect band gaps obtained after global optimizations and local relaxations are compared with each other. The indirect gaps for the (1,1) and (1,2) multilayers are respectively 0.06 eV and 0.08 eV, while the ones for the bulk Bi_2Te_3 and Sb_2Te_3 are 0.14 eV and 0.12 eV, indicating a band gap decrease in the multylayer systems compared to the bulk systems. Cross-plane effective masses are found to be comparable to the average in-plane values, in agreement with mobility measurements. [1] R. Venkatsubramanian et al., Nature 413, 597 (2001) * Work partially supported by ONR/DARPA

S8.38

Thermoelectric Properties of Semiconducting Intermetallic Compounds : $FeGa_3$ and $RuGa_3$. Yasutaka Amagai[1], Atsushi Yamamoto[2], Chul-Ho Lee[2], Hiroyuki Takazawa[2], Teruo Noguchi[2], Haruhiko Obara[2], Tsutomu Iida[1] and Yoshifumi Takanashi[1]; [1]Materials Science, Tokyo University of Science, Noda, Japan; [2]Energy Electronics Instiute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Gap formation in $FeGa_3$ and $RuGa_3$ is thought to arise from the hybridization of a narrow band of d electrons (Fe and Ru) with a broad p band (Ga)$FeGa^{1)}$. This hybridization gives the valence and conduction bands of $FeGa_3$ and $RuGa_3$ a strong d character, and lead to sharp structures close to the band edges. It is well known that a narrow peak in the density of states at few k_BT from the Fermi energy can be beneficial for thermoelectric performance. The best to our knowledge, the Seebeck coefficient and the thermal conductivity of these compounds have never been reported. In this paper we present the thermoelectric properties of $FeGa_3$ and $RuGa_3$ above room temperature for the first time. Polycrystalline samples of $FeGa_3$ and $RuGa_3$ were successfully prepared by reacting the metals in an evacuated quartz tube. X-ray powder diffraction showed single phase patterns of $FeGa_3$ and $RuGa_3$. The polycrystalline materials were grounded thoroughly and hot-pressed into pellets to measure the transport properties. The electrical resistivity, the Seebeck coefficient and the thermal conductivity were determined from 320K to 973K. For both $FeGa_3$ and $RuGa_3$, the resistivity showed semiconducting nature, which were of the order of 10^{-3}ohm-m at 320K and decreased by about two orders of magnitude at elevated temperature. These compounds possess relatively large Seebeck coefficient. For $FeGa_3$, the value of Seebeck coefficient was negative from 320K to 973K, while that of $RuGa_3$ changed its sign from negative to positive at 440K. The maximum value of the power factor was 9 x 10^{-5} W /mK^2 for $FeGa_3$ at 320K and 4 x 10^{-4} W/mK^2 for $RuGa_3$ at 973K. 1) U.Haussermann *etal.*, J.Solid State Chem. 164, 94 (2002)

S8.39

Thermal Conductivity and Thermoelectric Properties of III-nitride and III-oxynitride Films. Ryohei Izaki[1], Yasuo Iwamura[1,2], Shigeo Yamaguchi[1,2] and Atsushi Yamamoto[2]; [1]Electrical, Electronic and Information Engineering, Kagawa University, Yokohama, Japan; [2]2Energy Electronics Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

From the viewpoints of environmental and energy-saving issues, there has recently been a great increase in the research and development of thermoelectric power generation systems. However, since no binary compounds better than Bi_2Te_3 and PbTe have been found for room-temperature applications and since Te is scarce, volatile, and toxic element, the application of Bi_2Te_3 and PbTe has been limited in commercial use. In terms of the reduction in the environmental stress, we have focused on the properties of III-nitrides and III-oxynitrides and have recently studied their thermoelectric properties. The samples studied here were III-nitride and III-oxynitride alloy films such as $Al_{1-x}In_xN$ and $Al_{1-x}In_xO_sN_t$ prepared by the reactive radio-frequency sputtering method. They were grown on SiO_2 glass substrates at 100 °C using N_2 and Ar gases. First, the in-plane thermal diffusivity D of the self-standing films (10μm) was measured using an ac calorimetric method in the temperature range of 300-673K. The results have shown that at an intermediate temperature the thermal diffusivity has a minimum value of 3.14x10^{-6} m^2/s for AlN, 7.65x10^{-7} m^2/s for InN, 7.53x10^{-7} m^2/s for $Al_{0.57}In_{0.43}N$, and 7.03x10^{-7} m^2/s for $Al_{0.28}In_{0.72}N$. Furthermore, we measured the temperature dependence of specific heat c of our samples by the differential scanning calorimetry (DSC) method. In addition to the values of D and c, we measured the mass density of the samples, the thermal conductivity was determined to estimate the figure of merit ZT. Using these data, we estimated ZT to be 0.1 for $Al_{0.28}In_{0.72}N$ at 873K. Although, at this stage, ZT is at most 0.1, the thermoelectric figure of merit of nitride films has not been reported. This study will be a standard for the development of a thermoelectric device using nitride films.

S8.40

Thermoelectric Properties and Microstructure of Nano-structured ZnO-based Materials Fabricated by Spark Plasma Sintering. Kyoung Hun Kim[1], Yong Jae Kwon[2], Chang Sung Lim[3] and Kwang Bo Shim[1,2]; [1]Ceramic Engneering, Hanyang University, Seoul, South Korea; [2]Dept. of Nano-Tech., Hanyang University, Seoul, South Korea; [3]Institute of Advanced Materials, Hanseo University, Seosan, South Korea.

The nano-structured ZnO-based thermoelectric materials were fabricated by a spark plasma sintering (SPS) process. Three batch compositions, pure and M-doped ZnO(M=Al or Ni), were prepared from the nano-sized powders which were synthesized by a polymerized complex method. The SPS process was performed in the temperature range of 850 - 900°C under an applied pressure of 40MPa for 5 minutes in vacuum atmosphere. The Seebeck coefficient, electrical and thermal conductivity of the specimens were measured with the variation of the temperature. SEM and TEM observation showed that nano sized pure and M-doped ZnO powders with the range of 20$\sim$30nm were successfully synthesized. PL and XRD analysis confirmed that Al and Ni were in-situly doped in ZnO structure. The M-doped specimens showed higher electrical conductivity than pure ZnO and showed metallic conduction behavior. In case of Ni-doped ZnO, the electrical conductivity increased with increasing the amount of doping, but in case of Al-doped ZnO, the electrical conductivity reduced with increasing the amount of doping because $ZnAl_2O_4$ which has poor electrical conductivity and acts as an electron conduction scattering center was formed in grain boundary. The thermal conductivity of M-doped specimens remarkably reduced because lattice defects which are originated form doping and oxygen vacancies and nano sized secondary phases in grain boundaries reduced thermal conductivity by the phonon scattering, which is very useful for improving the thermoelectric properties of the specimens

S8.41

Thermoelectric modeling of Si-Ge core-shell nanowires.

Ming Yeung Tang[1], Chris Dames[3], Mildred S. Dresselhaus[1,2], Gang Chen[3] and Zhifeng Ren[4]; [1]Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts; [3]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [4]Physics, Boston College, Chestnut Hill, Massachusetts.

Theoretical studies have been carried out to better understand the transport properties of Si-Ge core-shell nanowires. These nanowires consist of Si as the core material with an epitaxial layer of Ge. The diameter of the nanowire in the model is 30nm. A decrease in thermal conductivity is shown theoretically for this configuration due to the increase in interface phonon scattering. No significant reduction in either electrical conductivity or Seebeck coefficient is expected for these nanowires, and hence, ZT of this system increases. Experimental realization of this model will be discussed. This work is funded by NASA contract.

SESSION S9: Complex Bulk Materials and Measurements II
Chair: Thierry Caillat
Wednesday Morning, December 3, 2003
Room 313 (Hynes)

8:30 AM S9.1
Thermoelectric properties of thallium ternary compounds.
Ken Kurosaki, Hironori Uneda, Hiroaki Muta and Shinsuke Yamanaka; Nuclear Engineering, Osaka University, Suita, Osaka, Japan.

Polycrystalline samples of thallium ternary compounds, Tl9BiTe6, TlBiTe2, TlSbTe2, and AgTlTe have been prepared by melting in sealed quartz ampoules followed by hot pressing. The thermoelectric properties have been measured in the temperature range from room temperature to about 700 K. The electrical resistivity and Seebeck coefficient have been measured simultaneously using ULVAC ZEM-1 under a helium atmosphere. The thermal conductivity has been evaluated from the thermal diffusivity, heat capacity, and density. The thermal diffusivity has been measured by a laser flash method in vacuum. The thermophysical properties such as the melting point and elastic moduli of the compounds have also measured, and the relationships between the properties have been studied. Tl9BiTe6 and TlSbTe2 show excellent thermoelectric performance. The values of the thermoelectric figure of merit ZT of the compounds bear comparison with those of state-of-the-art thermoelectric materials. The maximum values of the ZT are 0.86 at 590 K for Tl9BiTe6 and 0.87 at 715 K for TlSbTe2.

8:45 AM S9.2
Thermoelectric Properties of $K_2Bi_{8-x}Sb_xSe_{13}$Solid Solutions.
Theodora Kyratsi[1], Duck-Young Chung[1], Jeffrey S Dyck[2], Wei Chen[2], Ctirad Uher[2], Evripides Hatzikraniotis[3], Konstantinos M Paraskevopoulos[3] and Mercouri G Kanatzidis[1]; [1]Chemistry, Michigan State University, East Lansing, Michigan; [2]Physics, University of Michigan, Ann Arbor, Michigan; [3]Physics, Aristotle University of Thessaloniki, Thessaloniki, 54124, Greece.

Solid solutions of the type β- $K_2Bi_{8-x}Sb_xSe_{13}$ ($0 < x \leq 8$) is an interesting series for thermoelectric investigations mainly due to their low thermal conductivity and highly anisotropic electric properties. In this work, the Seebeck coefficient, the electrical and thermal conductivity as a function of temperature and composition will be presented for members spanning the whole range of x. The sign and the temperature dependence of the Seebeck coefficient show a transition from n-type to p-type character with increasing incorporation of Sb in the lattice. The Bi/Sb disorder affects the lattice thermal conductivity where the Umklapp peak is suppressed. The thermoelectric performance is estimated up to high temperatures where the potential for applications of these materials appears to be.

9:00 AM *S9.3
Microstructure Design Approach to Thermoelectric Materials. Lidong Chen, Xun Shi, Xiangyang Huang and Jun Jiang; State Key Lab of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 200050, China.

Thermoelectric performance of polycrystalline materials is greatly influenced by their microstructures including grain sizes, grain boundaries, grain orientations in anisotropic compounds, dispersion states of the secondary phase in composites, etc. The material microstructures are sensitive to the preparation processes and the starting materials. These make the understanding of the microstructure influence on thermoelectric transport properties very complicated. In present study, we synthesized half Heusler-based and skutterudite-based composites using C60, amorphous Si3N4, and γ-Al2O3 particles as the dispersion phases; and Bi2Te3-based sintered materials with textured structures. For ZrNiSn-based half-Heuslers or CoSb3-based skutterudites, when dispersion particles are randomly and discretely dispersed in the matrix, ZT values are not enhanced because of power factor reduction even though thermal conductivity is also reduced. When the dispersion particles are dispersed homogeneously on the grain boundaries coating the matrix grains, an enhancement in ZT values is obtained due to a greater reduction of lattice thermal conductivity and an increase of thermopower in spite of somewhat decrease of electrical conductivity. In these samples, the carrier scattering mechanisms are much different than those of the matrix materials. This is considered to be due to the special grain boundary structures. The Bi2Te3-based sintered materials with preferred orientations have successfully been fabricated through a spark plasma sintering (SPS) technique by controlling the particle sizes of the starting powders and the sintering process. The obtained textured Bi2Te3-based materials show high mechanical strength and significant anisotropy in thermoelectric transport properties. Thermoelectric performance perpendicular to the pressing direction (with c-axis preferred orientation) is comparable to that of single crystal materials in the same crystallographic orientation. Details of the microstructure effect on thermoelectric transport properties will be reported in this paper.

9:30 AM S9.4
High Temperature Measurement System Design for Thermoelectric Materials in Power Generation Application.
Sim Y. Loo[1], Jarrod L. Short[1], Kuei-Fang Hsu[2], Mercouri 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.

Recent interest in thermoelectric materials for power generation applications has initiated the development of a measurement system for materials characterization in the 80K to 800K temperature range in our laboratory. This system has been specifically designed for measuring thermoelectric power, and electrical conductivity as needed for determining the power factor of the measured samples. This is a single sample measurement system based on a continuous flow cryostat. Significant effort has gone into the computer controlled data acquisition and PID controlled temperature stabilization. Investigations of the influence of temperature stability on the measured data will be presented along with important aspects of the system design, development, and testing. Data collected on reference materials, and new thermoelectric materials of interest will be presented.

9:45 AM S9.5
Effects of Alloying Elements on Thermoelectric Properties of ReSi1.75. Min Wook Oh, Jiajun Gu, Kosuke Kuwabara and Haruyuki Inui; Materials Science and Engineering, Kyoto University, Kyoto, Japan.

Binary rhenium disilicide is of interest owing to potentials as a promising candidate material for thermoelectric applications. The stoichiometry of the silicide is determined to be ReSi1.75 instead of ReSi2 and the crystal structure belongs to the monoclinic system with an ordered arrangement of Si vacancies in the parent C11b lattice. Binary ReSi1.75 exhibits significantly anisotropic thermoelectric properties such that the value of Seebeck coefficient along [100]C11b is positive (230μV/K at 330 K) while it is negative (-300μV/K at 600 K) along [001]C11b. This may result from the highly anisotropic electronic structure of ReSi1.75. The dimensionless figure of merit (ZT) for binary ReSi1.75 is as high as 0.7 at 1073 K when measured along [001] while the ZT value along [100] is moderate (0.15 at 900 K). We have tried to improve the thermoelectric properties of ReSi1.75 by alloying with Al, Ge, Mo and some other transition-metals. Al and Ge substitution for Si in ReSi1.75 improve the ZT value along [100] in the whole temperature range (323-1073 K). The temperature dependence of electrical resistivity measured along [100] indicates that the conduction mechanism changes from of semiconducting to of metallic upon alloying with Al and the value of electrical resistivity at room temperature for Al-added alloys is significantly reduced by two orders of magnitude when compared to the binary counterpart. Ge substitution for Si in ReSi1.75 reduce the value of electrical resistivity along [100] in the whole temperature range by an order of magnitude. Mo substitution for Re in ReSi1.75 considerably improve the ZT value along [001] in the whole temperature range. Improvement of thermoelectric properties along [001] and [100] occurs in different ways depending on alloying element. Nice ZT values can be achieved for both orientations when alloyed with Ge. This indicates that both p- and n-type legs can be fabricated from a single crystal avoiding contact loss of conversion efficiency. The effects of microstructural

changes caused by alloying with these ternary elements on the thermoelectric properties will also be presented.

SESSION S10: Novel Approaches II
Chair: Jihui Yang
Wednesday Morning, December 3, 2003
Room 313 (Hynes)

10:30 AM *S10.1
Antimony Telluride Under Pressure. Gerald Dennis Mahan, Physics, Penn State University, University Park, Pennsylvania.

John Baddings group has reported large increases under pressure in the figure of merit of commercial bismuth-antimony single crystal alloys[1]. Since the major component of the alloy is antimony telluride, we have sought an explanation of this phenomena by performing electronic structure calculations of antimony telluride under pressure [2,3]. These calculations provide a transport density of states, which is used to calculate the pressure and temperature dependence of the electrical resistivity and Seebeck coefficient. We find antimony telluride is an indirect gap material, and the indirect gap closes under uniaxial pressure of P=2.0 GPa. At T=300 K both the electrical conductivity and Seebeck increase under pressure as the band gap closes, in agreement with the experimental findings. The calculations also show that the band gap does not close, and not much happens, when hydrostatic pressure is used instead of uniaxial pressure. This result also agrees with the experiments. 1) D.A. Polvani, J.F. Meng, N.V.C. Shekar, J. Sharp, and J.V. Badding, Chemistry of Materials, 13 (6), 2068-2071 (2001) 2) M. Bartkowiak and G.D. Mahan, 18th Int. Conf. On Thermoelectrics (1999), (IEEE Cat. No, 99TH8407) pg 713 3) T. Thonhauser, T.J. Scheidemantel, J.O. Sofo, J.V. Badding and G.D. Mahan (submitted to Phys. Rev. B)

11:00 AM S10.2
Measurement Techniques for Thermoelectric Materials and Modules. Timothy P Hogan, Sim Loo, Fu Guo and Jarrod Short; Electrical and Computer Engineering Department, Michigan State University, East Lansing, Michigan.

Thermoelectrics is a multidiscipline area of study, rich in condensed matter physics, chemistry, engineering, and material science. The figure of merit used for evaluating individual materials consists of three interdependent material properties (S, σ, κ). The measurement of these properties should be taken on the same sample for all three measurements, preferably simultaneously. Each of these measurements requires close attention to potential sources of losses for accurate analysis of the materials and testing of theoretical models. For example, relatively simple scanning measurement techniques can be used to gain insight into accurate geometry measurements and influences of contact dimensions. In addition, the field of thermoelectrics spans a wide temperature range, from cryogenic temperatures to $>$ 1000 øC. This requires systems capable of large temperature variations, and/or multiple measurement systems for various ranges of interest. Additional measurements, such as Hall effect, help to gain further insight into the material properties and their optimization. The number and importance of measurements is further extended as the development of devices from these new materials is initiated, where studies of contact resistance and overall device performance must be evaluated. For mechanical robustness of fabricated modules, properties such as the coefficient of thermal expansion, and grain size for the new materials are of interest. Models for device behavior are useful in evaluating the measured results and further extracting material and device properties. In this paper, we review many of the measurement techniques used in evaluating bulk thermoelectric materials and devices, along with some of the models used in conjunction with these measurements.

11:15 AM S10.3
The Effect of Annealing on the Structural, Electrical, and Magnetic Properties of Metastable Skutterudites. Arwyn L. Smalley, Brandon Howe and David C Johnson; Chemistry, University of Oregon, Eugene, Oregon.

We report the low temperature synthesis (between 150 and 400 °C) of metastable skutterudite samples, with compositions of either CexCo4Sb12 (x=0-1), or MSb3 (M=Ru, Fe, and Ni). Samples were synthesized using an ultra-thin (10-15 $\AA$) layer, modulated elemental reactant technique. The formation of the metastable MSb3 compounds is highly dependent on composition, and they decompose into the thermodynamically stable products on annealing to higher temperatures (~600 °C). Rietveld refinement was used to study the effect of annealing on structural changes (such as lattice contraction) in the samples. In addition, we have studied the temperature dependence of the electrical and magnetic properties of these samples.

11:30 AM *S10.4
New Directions for Low Dimensional Thermoelectricity. Mildred S. Dresselhaus[1,2], Yu-Ming Lin[2], Marcie R. Black[2], Oded Rabin[3] and Gene Dresselhaus[4]; [1]Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; [3]Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; [4]Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Low dimensionality provides opportunities to modify the properties of bulk materials dramatically and to control materials properties independently in a manner that is not possible for bulk materials. The special characteristics of low dimensional materials to enhance thermoelectric performance have already been demonstrated in quantum wells, quantum wires, and quantum dots. Several recent advances are presented in this talk, including new opportunities opened up by nanowire superlattices for use in thermoelectric devices, a new demonstration of the semimetal-semiconductor transition in 1D systems, a new method for determination of the carrier density in nanowire arrays, the demonstration of dominant changes in the optical properties of bismuth nanowires relative to bulk bismuth, and the observation of new magneto-transport phenomena in bismuth antidot arrays.

SESSION S11: Devices II
Chair: Ryoji Funahashi
Wednesday Afternoon, December 3, 2003
Room 313 (Hynes)

1:30 PM S11.1
Approaches to Thermal Isolation with Thin Film Superlattice Thermoelectric Materials. Pratima Addepalli and Rama Venkatasubramanian; RTI International, Research Triangle Park, North Carolina.

Thermoelectric heat pumps are produced by assembling thermoelectric materials between two heat exchangers-one for the cold side and one for the hot side. The efficiency of the thermoelectric heat pump decreases with increasing temperature differential between the hot and cold side. Subdividing the overall assembly of thermoelectric elements into thermally isolated sub-assemblies [1] for improved efficiency has been considered for bulk materials [2]. We present the unique aspects of integrating the thermal isolation with thin film devices with specific reference to ZT $>$ 1. Previous studies have changed the aspect ratio (l/a) to manipulate resistance and thermal conductivity of the module for increased COP. These can be easily implemented in thin film devices employing microelectronic fabrication. However, we discuss the use of variation of Seebeck coefficient, given that hetero-structures will allow independent control of thermal conductivity, electrical conductivity and Seebeck coefficient. Implementation and thermal modeling of thermal isolation using polymeric dielectrics, zeolites and aerogels as physical barriers will be discussed. Additionally, changes in the heat exchanger design are also considered. Effect of fins geometry and design on the hot side (or the cold side) to remove varying amounts of heat to create sub-assemblies of modules with changing temperature differential will be presented. Effect of COP using two different fluids on the hot side and the cold side to extract heat off non-uniformly is considered. References: 1.Fenton, J.W., Lee, J.S., Buist, R.J., Counter-flow Thermoelectric Heat Pump with Discrete Sections, U.S. Patent No. 4,065,936 (Jan. 3, 1978) 2.Bell, L.E., Use of Thermal Isolation to Improve Thermoelectric System Operating Efficiency, Proceedings of International Thermoelectric Conference, 2002, 477-487. 3.Venkatasubramanian, R, Siivola, E., Colpitts, T., and O'Quinn, B. Thin-film Thermoelectric Devices with High Room-temperature Figures of Merit, Nature, 413, 2001, 597-602.

1:45 PM S11.2
Vacuum Thermionic Emission From Nanostructured Carbon Materials. Franz Alexander Koeck[1], Jacob M Garguilo[1], Yunyu Wang[1], Robert J Nemanich[1], Sanju Gupta[2], B R Weiner[3] and G Morell[4]; [1]Physics, NC State University, Raleigh, North Carolina; [2]Physics, University of Puerto Rico, San Juan, Puerto Rico; [3]Chemistry, University of Puerto Rico, San Juan, Puerto Rico; [4]Physical Sciences, University of Puerto Rico, San Juan, Puerto Rico.

Direct energy conversion by means of vacuum thermionic emission provides the basis for power systems that work efficiently without any moving parts, thus increasing lifetime and reliability. Electron emission measurements at various temperatures and electric fields in a vacuum environment are suitable for characterization of the emitter material. We have analyzed thermionic and field emission from carbon nanotube (CNT) and sulfur doped nanocrystalline diamond films by means of emission current measurements as well as imaging of the

electron emission by real time microscopic acquisition methods. Sulfur doped nanocrystalline and CNT films exhibit a strong temperature dependence in the emission at temperatures considerably lower than 1000°C with emission originating from singular sites. These materials are presented as the electron emitter for thermionic energy converters. Extensive studies on electron emission from nanostructured carbon, i.e. CNT and nanocrystalline diamond films have shown that these materials exhibit electron emission from emission sites with a reported size smaller than 10nm and an emission site density in the order of 105cm-2. Although the exact origin of this emission behavior is still unknown it is evident that electronic and topographic field enhancement are in part responsible for the observed emission behavior. High field enhancement exhibiting surface regions correspond to an increase in the local electric field which causes electrons to be removed from these surface areas in a highly efficient way. This effect could play an important role in a new generation of thermionic energy converters by eliminating space charge effects that occur at flat surface emitters in addition to manufacturing advantages by increasing the micron spaced emitter-anode distance. This research is supported by the ONR.

2:00 PM S11.3
SiGeC Cantilever Micro Cooler. Gehong Zeng[1], Edward Croke[3], Yan Zhang[2], James Christofferson[2], Ali Shakouri[2] and John E. Bowers[1]; [1]University of California, Santa Barbara, California; [2]University of California, Santa Cruz, California; [3]HRL Laboratories, Malibu, California.

Fabrication and characterization of SiGeC-based cantilever micro cooler is described. Silicon on insulator (SOI) was used as the substrate, and two layers of 3 um thick p-SiGe0.07C0.0075 and 1.14 um thick n-SiGe0.07C0.0075 were directly grown on the SOI using molecular beam epitaxy. All layers were lattice matched to the silicon substrate. Subsequently a unicouple micro cooler was fabricated using conventional integrated circuit processing and the cantilever structure was formed by removing the backside silicon layer of SOI substrate using deep reactive ion etching. Devices with different sizes were fabricated and characterized. By etching the top n-doped layer in one of the legs and by depositing metal electrode at the junction between the two legs, a unicouple cooler was fabricated without a need for regrowth. This could simplify substantially large scale integration and array fabrication of these devices. In these micro refrigerators, heat is transferred laterally from the junction between legs to the two contacts. Cooling by 1.2K at room temperature has been measured. Calculations show that heat conduction through the 0.2 micron thick silicon buffer layer on top of the SOI substrate is the main limitation to the device cooling performance.

2:15 PM S11.4
Experimental characterization and modeling of InP-based micro coolers R. Singh, D. Vashaee, Y. Zhang, M. Negassi, A. Shakouri, UCSC Y. Okuno, Y-J. Chiu, Gehong Zeng, John Bowers UCSB. Rajeev Singh, Daryoosh Vashaee, Yan Zhang, Million Negassi, Ali Shakouri, Y Okuno, Y-J Chiu, Gehong Zeng and John Bowers; Electrical Engineering, University of California, Santa Cruz, Santa Cruz, California.

In this paper we present experimental and theoretical characterization of InP-based heterostructure integrated thermionic coolers. In particular, we characterize the effect of doping on overall device performance. Several thin-film cooler devices have been fabricated and analyzed. They contain a one-micron thick superlattice structure composed of 25 periods of InGaAs wells and InGaAsP barriers (bandgap ~1.3 microns) with a thickness of 10 and 30nm, respectively. All the layers are lattice-matched to the InP substrate. Highly doped InGaAs layers are used on the top and bottom of the superlattice for contacting purposes. N-type doping in the InGaAs quantum wells was varied from 1.5*10$\hat{1}$8 to 8*10$\hat{1}$8cm-3, while the quaternary barrier layer was undoped. Device cooling performance was measured at room-temperature. Device current vs. voltage relation was characterized in a wide temperature range from 10K to room-temperature. Detailed models of electron transport in superlattice structures were used to simulate device characteristics and performance. Experimental results show that low-temperature electron transport is a strong function of well layer doping and that device maximum cooling decreases as doping increases. Theoretical models for both I-V curves and maximum cooling agree well with experimental results. The findings indicate that low-temperature electron transport is useful to characterize potential barriers and energy filtering in heterostructure thermionic coolers.

2:30 PM S11.5
System Constraints on Materials for Thermoelectric/ Thermionic Power Generation. Peter Mayer and Rajeev Ram; Research Laboratory of Electronics, MIT, Cambridge, Massachusetts.

The traditional metric quantifying a material's effectiveness in a thermoelectric (TE) generator is the thermoelectric figure of merit Z, and the most common measures of TE generator system performance are the efficiency and the generated power density. It is known that ideally the Z of the material and the temperatures of the hot and cold sides of the generator determine the maximum efficiency, and the output power density can be set by simply scaling the geometry of the TE material. As a result, considerable effort has been spent in the thermoelectric community trying to improve the Z of TE materials. However, when the entire thermoelectric generating system is considered, the simple figure of merit is no longer sufficient to characterize the generator efficiency, and the power density can no longer be scaled independently with the geometry. Calculations and measurements are presented here showing that when non-idealities such as imperfect heat-sinking and temperature dependent contact resistance and heat transfer coefficients are included in the system model, improving the lumped figure of merit Z is *not* generally the best approach to improving overall generator performance. Rather, we argue that the effects of changing each material parameter making up Z should be examined separately to best understand how to improve the generator. The changes from the ideal model are particularly apparent for thin devices with large power fluxes, for which ideal constant temperature boundary conditions are unphysical. An example is the weak dependence of generated power density with Seebeck coefficient and electrical conductivity for thin film ($<250\ \mu$m) TE elements. Because the heat transfer through the film is limited by its heat sink, the thermal conductivity of the TE device becomes the dominant factor in setting both efficiency and power density, in sharp contrast with the results of the ideal analysis.

2:45 PM S11.6
High-Temperature PbTe Thin Films for Use in Cascade Thermoelectric Power Generation. John B. Posthill, Paul D. Crocco, Tom S. Colpitts and Rama Venkatasubramanian; RTI International, Research Triangle Park, North Carolina.

PbTe-based materials have the potential to be used as a higher temperature stage of a cascade thermoelectric module that uses the significantly more efficient Bi2Te3/Sb2Te3 superlattice OMCVD films downstream at lower temperature. For a small weight penalty at the module level, an increase in overall module efficiency can be achieved in addition to now being able to use a higher temperature heat source – both characteristics can enable significantly lower overall system weight savings. PbTe, PbSe, and PbTe/PbSe multilayer and superlattice (SL) films were grown by evaporation on different substrates at 250C. All films were intrinsically n-type. Typical thermal conductivity values, as measured by the 3w technique, were found to vary from 4 W/m-K for PbSe films, to 2 W/m-K for PbTe films. Thermal conductivity of 50/50 PbTe/PbSe SL films varied with a minima observed at a SL periodicity of ~ 6nm when grown on vicinal GaAs (100) 2 degs. off-axis (k = 1.2 W/m-K). The lowest value for thermal conductivity observed in PbTe/PbSe films grown on vicinal GaAs (100) 15 degs. off is k = 1.1 W/m-K. XRD results showed the PbTe and PbSe grown on vicinal GaAs (100) 2 degs. off-axis were 200-oriented poly, while such films grown on vicinal GaAs (100)) 15 degs. off-axis were randomly oriented poly. A superlattice (or multilayer) effect on thermal conductivity in non-single crystal PbTe-based evaporated films is therefore demonstrated and will be contrasted with films grown on BaF2 (111).