SYMPOSIUM G
Thermoelectric Materials 2001–Research and Applications
November 26 – 29, 2001

Chairs

George S. Nolas
Dept of Physics
Univ of South Florida
Tampa, FL 33620-5700
813-974-2233

David C. Johnson
Dept of Chemistry
Univ of Oregon
Eugene, OR 97403
541-346-3422

David G. Mandrus
Oak Ridge Natl Laboratory
MS 6056, Bldg 3150
Oak Ridge, TN 37831-6056
865-574-6282

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*Invited paper
10:45 AM • GL1
OVERVIEW OF VARIOUS STRATEGIES FOR THE DEVELOPMENT OF NEW BULK MATERIALS FOR THERMOELECTRIC APPLICATIONS. Terry M. Trud, Dept of Physics and Astronomy, Clemson University, Clemson, SC.
Recently, there has been renewed interest in thermoelectric material research. There are a number of different systems of potential thermoelectric materials that are under investigation by various researchers; these efforts are aimed at minimizing lattice thermal conductivity while other efforts focus on materials that exhibit large power factors. An overview of the requirements and strategies for the investigation and optimization of a new system of materials for potential thermoelectric applications will be discussed. There are a number of new bulk materials under investigation in our laboratories at Clemson University in conjunction with our many collaborators. These include transition metal pentoxide/fluorides (e.g., HfF₃), quaternary materials (e.g., AlₓPdᵧMₜ₈ₓ and Crₓ₋ₓVₓ), halide sulfur alloys (e.g., TiₙSb₁₋ₓSbₓ), skutterudites (e.g., Co₉Fe₄Sb₁₃), and chalcopyrites (e.g., SrGa₂Ge₄Sb₁₃). Each of these systems is distinctly different yet each exhibits some prospect as a potential thermoelectric material. Results will be presented and discussed on each system of materials.

11:15 AM • GL2
ELECTRONIC BAND STRUCTURE CALCULATIONS FOR THE IDENTIFICATION AND OPTIMIZATION OF NOVEL THERMOELECTRIC MATERIALS. David J. Singh, Naval Research Laboratory, Center for Computational Materials Science, Washington, DC.
The use of density functional electronic structure calculations for identifying potential thermoelectric materials and guiding their optimization is discussed. The basic theoretical tools including band structure calculations and kinetic transport theory are briefly overviewed and features of relevance to thermoelectric performance are discussed. Features of band structures that are favorable to thermoelectricity are presented and illustrated using various examples. These include skutterudites and other novel materials like NixCoO2.

11:45 AM • GL3
THERMODYNAMIC CALCULATIONS IN NEW THERMOELECTRIC MATERIALS. J.C. Terecze, M.C. Record, Laboratoire de Physique-Chimie de la Matière Condensée, Université de Montpellier 2, Sciences et Techniques du Langueudoc, Montpellier, FRANCE; S.G. Fries, ACCESS e.V., RWTH Aachen, Innestrasse, GERMANY.
Performance enhancement of thermoelectric modules can be obtained by a good knowledge of the material properties involved in their fabrication. For this, thermodynamic calculations of the material. Improvement of the figure of merit in thermoelectric materials depends on multiple factors [crystallographic structure, electronic structure, phonon scattering, doping level, microstructure i.e. size and shape of grains, grain boundaries]. Making these optimized materials require at least more than three elements being thermoelectric materials typically multicomponent systems. The processes involved during the fabrication of the T.E. component lead to other problems: solidification processes entails segregations in single phases and, depending on the composition of the melt, eutectic precipitations. b. Pressure dependence of the materials compositions (in tellurides and selenides as well) entails point defects leading to imperfect electronic properties. c. Hot pressing processes entails elements diffusion in the grains and at the boundaries leading to non-equilibrium material with properties changing with time and temperature. Based on the CALPHAD approach, we present an overview of computational approach of the phase equilibria in multicomponent systems used in thermoelectric materials. The CALPHAD approach uses Gibbs energy description in order to calculate phase equilibrium as an add to optimize performance, design and tailor materials. The main objective of this method is to constitute available materials database lying on experimental assessed results, ab initio calculations and thermodynamic models of solutions and compounds. These descriptions are taken into account in the calculations presently performed by using software packages. As a result these multicomponent databases can be used to determine the chemical compositions of materials, calculate equilibrium, add to the understanding solidification and the remaining microstructure obtained by hot pressing or hot rolling processes. In this paper we present a contribution to the CALPHAD approach in intermetallic based semi-conductors suitable for thermoelectric applications. After a presentation of the modeling defects in semi-conductors, we will present the results on thermoelectric materials based on antimony system and the applications of these phase diagrams calculations.

1:30 PM • G2.1
LATTICE VIBRATION OF YTTERBIUM FILLED SKUTTERUDITES: AN INELASTIC ELECTRON TUNNELING STUDY. Jiro Nagano, Maruhou Furuki, Devajur Natraj, Tsutomu Ueda, Shoshi Takeya, Tokyo Techiana, Institute for Energy Utilization, National Institute of Advanced Industrial Science and Technology (AIST), Sapporo, JAPAN; Hiroshi Ando, Kakuei Matsuura, Dept of Electronics and Computer Science, University of Tokyo in Yamaguchi, OnoId, JAPAN; Eiji Hotta, Kiscia Mikan, Nano-electronic Laboratory, Graduate School of Engineering, Hokkaido University, Sapporo, JAPAN.
Inelastic electron tunneling experiments were performed on Yb₂Co₅Sb₁₄Al-xCexAl junctions measured at 4.2K. A peak observed at \( \sim 7 \) meV for Yb-filled samples is closely related to the vibration mode of Yb ions in the cages of skutterudite structure. This gives direct evidence that the rattling effect plays a dominant role in filled skutterudites. The phonon energies contributed from optical phonons shifts to the lower energy with increasing the Yb concentration. This observation indicates that an interaction between host lattice and guest ions is strong in Yb-filled skutterudites, which seems to be related to a valence fluctuation observed in Yb-filled skutterudites.

1:45 PM • G2.2
THERMOELECTRIC PROPERTIES OF Eu-DOPED CoSb₃. G.A. Lambertson Jr., Terry M. Trud, Dept of Physics and Astronomy, Clemson University, Clemson, SC; G.S. Nolas, Department of Physics, University of South Florida, Tampa, FL.
Resistivity and thermopower data is presented on Eu-doped CoSb₃ skutterudites over the temperature range of 10 K to 700 K. Thermal conductivity is also presented from 10 K to 700 K in order to determine the figure of merit. Eq45CoSb11, Eq4CoSb11, and Eq45CoSb11,35Ge0,5 exhibit an increased figure of merit as compared to the CoSb3 and Eu0,CoSb12. The room temperature value of ZT has been measured for the Eq45CoSb11,35Ge0,5 skutterudite as ZT \( \sim 0.26 \) and also has a value of ZT \( \sim 1 \) above 675 K. The other samples had a lower ZT at room temperature with ZT = 0.1 and ZT = 0.19 for the Eq45CoSb11,35Ge0,5 and the Eu0,CoSb12 samples respectively. These results will be discussed in relation to the potential of these materials for thermoelectric applications. Data on a series of Yb-filled CoSb₃ is underway and will also be discussed.

2:00 PM • G2.3
HIGH PRESSURE SYNTHESIS OF NEW FILLED SKUTTERUDITES. Hirotsugu Takizawa, Kenichi Okuami, Kyoko Uehda, Tadashi Endo, Tohoku Univ, Dept of Materials Chemistry, Sendai, JAPAN.
Germainium and tin atoms were inserted into the CoSb₃ skutterudite host lattice under high pressure and temperature condition using belt-type high-pressure equipment. Both atoms could be inserted in the body-centered vacant site of the host lattice, resulting in the formation of filled-skutterudites, MₓCoₓSb₁₂ (M = Ge, Sn). Complete filling was achieved in both cases at 6.8 GPa. Crystal structures of the filled-skutterudites were refined by the Rietveld analysis of the powder X-ray diffraction data. The level of thermal vibration amplitude at the body-centered position indicating a large rattling motion. On the other hand, germanium atoms locate the position slightly deviated from the ideal body-centered position. The tin-filled and germanium-filled compounds exhibit n-type semiconducting behavior. A remarkable reduction in the thermal conductivity is achieved in tin-filled compounds. It is concluded that tin atom is a better "traveller" in the CoSb₃ host lattice.

2:30 PM • G2.4
ELECTRONIC STRUCTURE AND THERMOELECTRIC PROPERTIES OF YTTERBIUM FILLED SKUTTERUDITES. Hiroshi Ando, Kumei Aiki, Kakuei Matsuura, Science Univ of Tokyo in Yamaguchi, Dept of Electronics and Computer Science, OnoId, JAPAN; George S. Nolas, Department of Physics, University of South Florida, Tampa, FL; Koji Akai, Misuru Massuara, Yamaguchi Univ, Dept of Advanced Materials Science and Engineering, Ube, JAPAN; Jiro Nagano, National Institute of Advanced Industrial Science and Technology, Institute for Energy Utilization, Sapporo, JAPAN.
We have investigated the electronic structure and transport properties of Yb-doped \( \text{CoS}_2 \) skutterudites for an understanding of the effect of Yb filling on the thermoelectric properties. The valence-band structure of Yb-doped \( \text{CoS}_2 \) has been studied by x-ray photoelectron spectroscopy. X-ray photoelectron spectroscopy measurements were performed on specimens with different Yb filling fractions by using the Mg \( K \alpha \) line (photon energy: 1253.6 eV) and a 180° hemispherical analyzer in the constant-resolution mode (pass energy: 40 eV). The photoemission spectra are compared with density-of-states calculations made by the full-potential linearized augmented-plane-wave (FLAPW) method. The effect of Yb filling on the electronic bonding properties is discussed from the analysis of valence-band and core-level spectra. The intermediate valence states of Yb between divalent and trivalent in \( \text{CoS}_2 \) were closely observed in both the core-level and valence-band spectra. The observed spectra agree qualitatively with results of band calculation. This result is consistent with the results of magnetic susceptibility and the inelastic electron tunneling measurements. The electronic properties (the carrier mobility, effective mass, etc.) and the thermal properties of Yb-doped \( \text{CoS}_2 \) are affected by the electronic states of Yb, resulting in the large thermoelectric figure of merit for Yb filling as compared to other rare-earth filling.

### Session G3: New Materials, Approaches and Measurements I

**Chair: Kevin L. Stokes**  
**Monday Afternoon, November 26, 2001**  
**Room 208 (Hynes)**

**3:30 PM G3.1**  
**Novel Thermal Transport in Stable Binary \( \text{Cd}_2 \gamma \text{Yb} \) Quasicrystals**  
A.L. Price, Terry M. Trist, Dept. of Physics and Astronomy, Clemson University, SC

Quasicrystalline materials have been investigated for application as thermoelectric materials due to their inherently low thermal conductivity. With the discovery of a new stable binary \( \text{Cd}_2 \gamma \text{Yb} \) quasicrystal, thermal and electrical transport measurements have been performed on these materials. It is found that the Wiedemann-Franz relationship is unsuitable for modeling thermal conductivity in the \( \text{Cd}_2 \gamma \text{Yb} \) quasicrystal. The electronic contribution to the thermal conductivity is calculated from the Wiedemann-Franz relationship to be comparable to or greater than the measured total thermal conductivity, thus indicating the presence of a "negligible lattice contribution". In addition, no evidence of the lattice contribution appears in the temperature dependence of the thermal conductivity. The thermal conductivity increases linearly with temperature above 75 K and proportional to \( T^{3/4} \) between 2 K and 75 K. Consequences of the breakdown of the Wiedemann-Franz relationship are discussed as well as the possibility of a minimum thermal conductivity.

### Session G4: Clathrates I

**Chair: George S. Nols**  
**Tuesday Morning, November 27, 2001**  
**Room 208 (Hynes)**

**8:30 AM G4.1**  
**Resonant Ultrasound Spectroscopy Studies of Microfabricated Heaters, Voltage and Temperature Sensors, and Phase Lock Schemes to Determine the Temperature and Voltage Oscillation in the Cross-plane Direction of Thin Films**  
These measurements are applied to Si/Ge superlattices grown by molecular beam epitaxy.
Resonant Ultrasonic Spectroscopy (RUS) measurements have been carried out for 3 cubic clathrate materials: Ba$_2$Ga$_4$Ge$_{30}$, Sr$_2$Ga$_4$Ge$_{30}$, and Ba$_2$Ga$_4$Si$_{30}$. In these materials, the Ba, Sr, and Eu ions reside in oversized atomic cages. They have attracted attention as promising thermoelectric materials, having thermoelectric conductivities comparable to glasses while maintaining crystalline electronic properties. RUS has been proven to be useful for the study of similar cage-like materials [1], identifying 2 local modes in the filled skutterudite La$_2$Al$_2$Sb$_5$. The RUS measurements we present here were carried out as a function of temperature (2-300K) on single crystals, and allow the determination of the 3 elastic moduli. The results are compared to ultrasonic attenuation measurements on Sr$_2$Ga$_4$Ge$_{30}$ and RUS measurements on filled and unfilled skutterudites. This work is supported in part by the Office of Naval Research. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725.


8:45 AM *G4.2 THERMAL PROPERTIES OF SEMICONDUCTOR CLATHRATES Mary Anne White, Liyan Qiu, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, CANADA; George Nolan, Department of Physics, University of South Florida, Tampa, FL.

Materials with low thermal conductivity due to efficient phonon coupling and high electrical conductivity (Shack’s so-called phonon glass/electron crystal, or PGE) offer promise as thermoelectric materials. Here we report thermal properties of several semiconductor clathrates: Sr$_2$Ga$_4$Ge$_{30}$, Sr$_2$Zn$_4$Ge$_{30}$, Ba$_2$Ga$_4$Sn$_{30}$, and Ba$_2$Ga$_4$Si$_{30}$. In these structures, generally as $M_aX_4Y_{30}$, $M$ is a guest host lattice formed by $X$ and $Y$. In principle, rattling of $M$ within the cages should provide efficient phonon-phonon coupling and hence low thermal conductivity. In this report, we emphasize the role of the low-frequency optical modes associated with guest rattling on the thermal properties.

9:00 AM *G4.3 THEORETICAL STUDY OF RATTLING ATOMS AND THERMODYNAMIC INFLUENCE ON THE LATTICE THERMAL CONDUCTIVITY IN CLATHRATE-FRAMEWORK SEMICONDUCTORS. Otto F. Sankey, Jianjun Dong, and Charles W. Myles, “Arizona State University, Tempe, AZ; Auburn University, Auburn, AL; Texas Tech University, Lubbock TX.

We have explored the electronic and vibrational properties of type-I and type-II semiconductor (Si, Ge, and Sn) clathrates using theoretical DFT electronic structure methods. These framework materials have open cages which harbor guest impurities, and provide local vibrations in the vibrational frequencies of the guest modes, and compare them to experiment. These modes may scatter the extended heat-carrying acoustic modes. We have investigated the effect of guests on the lattice thermal conductivity by using the linear response theory heat current correlation functions using molecular dynamics. We compare these results to results of guest-free crystals, and to amorphous materials. Our results are consistent with experiments, and have impact as a theoretical test of the “rattler” concept.

9:30 AM G4.4 PRESSURE EFFECT OF SEEBECK COEFFICIENT FOR ZINC-DOPED TIN CLATHRATES. E. Chen, K.L. Stokes, Advanced Material Research Institute, University of New Orleans, New Orleans, LA; G.S. Nolan, Department of Physics, University of South Florida, Tampa, FL.

We measured the temperature dependence of electrical conductivity ($\sigma$) and thermopower ($S$) of Cd$_2$Zn$_2$Sn$_4$ under high pressure up to 1.2 GPa. We observed the reversible gap widening, irreversible $S$ increasing under high pressure, which were similar to the behaviors of Cd$_2$Hg$_2$Sn$_4$. However, the relaxation effect of $\sigma$ for Cd$_2$Zn$_2$Sn$_4$ was negligible in contrast with that of Cd$_2$Hg$_2$Sn$_4$. We will also present the result of Rb$_2$Zn$_2$Sn$_4$ for further comparison. The results suggest that the vacancy potential plays a more important role in transport properties for tin clathrates under high pressure.

9:45 AM G4.5 Abstract WERFTRAM.
is practically based on Sb$_2$Te$_3$. It also has the tendency to replace Bi in many compounds forming a series of solid solutions. Since the electrical properties of solids depend directly on their crystallographic and electronic structure, we are looking for new materials and new compositions involving antimony. We have discovered several new ternary compounds in the A/Ph$_3$/Q (A = K, Rb, Cs, Q = S, Se, Te) system. Most of known ternary chalcogenide compounds possess wider band gaps than the corresponding bismuth compounds.

Therefore, we also explored Sb/Bi solid solutions to tune the band gaps of these materials. The phase stability and thermoelectric properties of each compound were examined in terms of participation of bismuth in the frameworks. Also, we will present the complete physicochemical and electrical characterization of these compounds.

11:45 AM G5.5
LATTICE MISFIT STRAIN RELAXATION IN PbSeTe/PbTe
THERMOELECTRIC QUANTUM DOTTED HETEROSTRUCTURES.
Patrick J. Taylor, Theodore C. Harman, Michael P. Walsh, Brian E. LaForge, George W. Wachter. Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, MA.

Quantum dot heterostructures have the potential to improve the thermoelectric properties of a material by 1) reducing thermal conduction because of more interfacial phonon scattering and 2) increasing the electrical power factor by increasing the density of states. The extent to which this potential can be experimentally realized is influenced by, among other properties, the quantum dot size distribution, the inter-dot spacing and the amount of heterostructure lattice misfit strain relaxation. We present results from a qualitative analysis of the size and distribution of PbSeTe/PbTe quantum-dot heterostructures used in transmission electron microscopy. In addition, we present a novel film fringe contrast technique (using transmission electron microscopy) to directly determine the state of lattice misfit strain relaxation for these quantum dots within a PbTe matrix. From this analysis, we determined that the size distribution of quantum-dot diameters ranges from 5 nm to 40 nm. The quantum-dot size where lattice misfit strain relaxation appears to be essentially complete is 30 nm. For quantum-dots of diameter sufficiently small to remain coherent with the PbTe matrix, evidence was obtained for spontaneous lateral ordering within the PbTe. This work was sponsored by the Department of the Navy, the Army Research Office, and the Defense Advanced Research Projects Agency (DARPA) under AF contract number F 19628-06-00012. The opinions, interpretations, conclusions, and recommendations are those of the authors and are not necessarily endorsed by the Department of Defense.

SESSION G6 DEVICES
Chair: Thierry Cailh
Tuesday Afternoon, November 27, 2001
Room 208 (Hynes)

1:30 PM G6.1
SUPERLATTICE THIN-FILM THERMOELECTRIC DEVICES FOR ANYWHERE, ANY TIME COOLING AND HEATING.
Hanan Venkatraman. Edward Sivola, Brooks O’Quinn, Thomas Colpitts, Research Triangle Institute, Research Triangle Park, NC.

A major goal of our Thermoelectric program has been to demonstrate significant enhancement in figures-of-merit (ZT) at 300K using the concept of phonon-blocking electrons-transmitting superlattice structures. The thermal conductivity reduction arises from a complex localization-like behavior for phonons in superlattices and the electron transmission is facilitated by optimal choice of band-offsets in certain hetero-structures. Another goal of our development has been to achieve all of the material to high coefficient of performance (COP) in cooling devices and demonstrate ~1000 W/cm$^2$ cooling power densities in thin-film thermoelectric devices. The high-performance superlattice materials and the extremely low specific contact resistivities (τ<5Ω-8 Ohm-cm$^2$) achievable in devices have allowed us to demonstrate an extrinsic device figure-of-merit (ZT) of ~2.4 at 300K by the conventional Harman method in p-type Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattice thermoelectrics. We have also obtained ZT of about ~1.4 in n-type superlattice thermoelectrics at 300K. In addition, we have observed 32K and 48K sub-ambient cooling at 280K and 33K, respectively, in p-type superlattice micro-thermoelectrics. We have utilized a semi-transparent heat source for determining the coefficient of performance (COP) of thermoelectric devices; a COP of ~5 was achieved for 17.5K cooling at 300K with an estimated heat load of ~365 W/cm$^2$ for the p-type micro-thermoelectrom. We have fabricated p-n couples using these micro-thermoelectroms, obtaining sub-ambient cooling of 15.6K in our initial trials. We will demonstrate functionality of these thin-film couples in a non-laboratory environment. In addition to high performance (in terms of COP or ZT) and high-cooling power densities, these micro-thermoelectroms are also extremely fast-acting, about a factor of 20000 better than bulk thermoelectric technology. We have also allowed into the concept of high-performance anywhere, any time active cooling and heating. We will present results to demonstrate this concept with IR-imaging of superlattice micro-thermoelectroms.

1:45 PM G6.2
THERMOELECTRIC MODULE FOR LOW TEMPERATURE APPLICATIONS.
Timothy P. Hagans*, Suzanne Lai*, Sun Loo*, Duck-Young Chung*, Theodore Kyriazis, Ricardo Gutierrez, Charles Casady, "Electrical and Computer Engineering Department, Michigan State University, East Lansing, MI. 8Chemistry Department, Michigan State University, East Lansing, MI. 9Telrex Corporation, Traverse City, MI.

The possibility of a prototype thermoelectric cooling device for operation near liquid nitrogen temperatures has been explored. In these devices, the figure of merit is a combination of the properties of the two branches of the module. Here, we investigate the fabrication of a module with a low temperature material, Cu$_2$Bi$_2$Te$_3$ (p-type), and the best known low temperature n-type material Bi$_2$Se$_3$(Sb$_2$Te$_3$). Transport measurements for each of these materials show high performance at low temperatures. Known values for the figure of merit Znue of Cu$_2$Bi$_2$Te$_3$ is 3.6e$^{-10}$$^2$ $^K$/225K and for Bi$_2$Se$_3$ is 5.6e$^{-10}$$^2$ $^K$/7K. At 100K, these values drop to 2.1e$^{-10}$$^2$ $^K$/225K and 6e$^{-10}$$^2$ $^K$/7K for Bi$_2$Se$_3$ and Cu$_2$Bi$_2$Te$_3$, respectively. These materials are based on these data and show a cooling rate at 100K which is approximately three times the efficiency of a Bi$_2$Te$_3$ module at that temperature. We present transport measurements results in the fabrication of a low temperature thermoelectric module and properties of the resulting module.

2:00 PM G6.3
TRANSPORT PROPERTIES OF ELECTRODEPOSITED THICK FILM THERMOELECTRIC MATERIALS.
Jean-Pierre Fleith, Jennifer A. Herman, Nick Stoltz, G. Jeffrey Snyder, Ching-Kuei Huang and Margaret A. Ryan, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA.

Electrodeposited deposition is a promising alternative to the fabrication of novel solid-state thermoelectric microdevices that could be integrated into thermal management packages and low power, electrical power source systems. Our interest is focused on p-type Bi$_2$Se$_3$/Sb$_2$Te$_3$ alloys as well as other attractive thermoelectric materials such as PbTe$_{1-x}$S$_x$, Pb$_2$Te$_3$, and CoSb$_3$. Room temperature electrochemical techniques have been developed for the deposition from aqueous solutions of thermoelectric films 1-50 μm in thickness. In this paper, we report on the thermoelectric transport properties of the electrodeposited films as a function of temperature, film composition and post-deposition heat treatments, in particular for Bi$_2$Te$_3$ alloys. Experimental data are compared to results obtained for bulk materials and for films grown by chemical vapor deposition techniques.

2:15 PM G6.4
THERMOCURRENT GENERATION WITH AN IMPROVED EMITTER.
Yoshikazu Ishimaru, Borin Y. Moyo, Theodore H. Geballe, Stanford University, Applied Physics Dept, Stanford, CA; Thomas W. Kenny, Stanford University, Dept of Mechanical Engineering, Stanford, CA.

We consider new possibilities for cooling by vacuum tunneling of electrons. Vacuum electron emission is attractive for cooling because of the absence of lattice thermal conduction and absence of ohmic resistance. We investigate a layer of low electron affinity semiconductor which overcoats the metallic emitter. The semiconductor surface emits electrons below the Fermi level and thus produces current with a higher Peltier coefficient. The influence of the electric field in the thickness of the current’s significantly reduced due to the Schottky effect which makes it possible to produce a reasonable emission current. In this study we try to optimize the cooling efficiency by adjusting the thickness, electric constant, and electron affinities of the semiconductor. We find that large cooling currents can be obtained by a combination of energy selective tunneling and thermionic emission. Numerical simulations show that emitters covered with 50 μm of semiconductor with electron affinity of 0.5 eV can produce a cooling power of few W/m$^2$ with a Peltier coefficient of 4W/eV for electric field of 2 MV/cm.

2:30 PM G6.5
CONSERVATION OF LINEAR MOMENTUM IN HETERO-STRUCTURE INTEGRATED THERMOELECTRIC COOLERS.
Dwyer Vashisht, Ali Shikouni, University of California, Jack Baskin School of Engineering, Santa Cruz, CA.
Thin film thermionic coolers use selective emission of hot electrons over a heterostructure barrier layer from emitter to collector resulting in evaporative cooling. Since the energy distribution of emitted electrons is almost exclusively on one side of the Fermi energy, upon the current flow, strong carrier-carrier and carrier-electron scatterings tend to reverse the quasi-equilibrium Fermi distribution in the cathode by absorbing energy from the hot side and thus, cooling the emitter junction. If the internal moment of the hot electrons is conserved in thermionic emission process, only those with sufficiently enough kinetic energy perpendicular to the barrier can pass over the barrier and cool the emitter junction. However, if there’s a conservation of internal momentum, the number of electrons participating in thermionic emission will dramatically increase. We have studied electron transport in a range of 4T55K for several thin film heterostructure cooler devices and found that internal moment is partially conserved. We propose by creating a controlled roughness in the interface of the superlattice barriers one can influence the wave vector of carriers and have more electrons with sufficiently enough kinetic energy contribute in thermionic emission thereby resulting in a higher cooling efficiency.

2:45 PM G6.6 HIGH COOLING POWER DENSITY SiGe/Si THIN FILM COOLERS. Genghong Zeng, Xinfeng Fan, Edward Croke*, Chris LaBounty, Daryosh Vashahi*, Ali Shokouhi*, and John E. Bowers, Department of Electrical and Computer Engineering University of California, Santa Barbara, CA; *HRL Laboratories, LLC, Malibu, CA. $Haskin School of Engineering, University of California, Santa Cruz, CA.

For the thermal management of microelectronic and optoelectronic devices, SiGe is considered as a good material due to the compatibility with IC manufacturing techniques and its relatively high figure of merit ZT. Thin film coolers have the advantage of high cooling power density. SiGe base structure on Si or SiGe substrates by molecular beam epitaxy. This film SiGe/Si micro coolers integrated with resistive heater on top of them were fabricated using standard IC processing technology. The resistive heater was used as a thermal source to generate a temperature gradient. Cooling powers up to 800 W/cm² were measured at a heat sink temperature of 25°C for 40 K, 10 μm² devices. $This project is supported by DARPA HERETIC program and the Army Research Office.

SESSION G7 NEW MATERIALS, APPROACHES AND MEASUREMENTS II
Chair: Kukiwa Masaharu
Tuesday Afternoon, November 27, 2001
Room 208 (Hynes)

3:30 PM G7.1 REDUCTION OF LATTICE THERMAL CONDUCTIVITY IN BALL-MILLED AND SHOCK-COMPACTED TiN/Si HALF-HEUSLER ALLOYS. S. Bhattacharya, Terry M. Tran, Dept. of Physics and Astronomy, James Madison University, VA; V. N. Nunnikhoven, S.J. Poon, Dept. of Physics, Univ of Virginia, Charlottesville, VA; N. Thadhani, Dept. of MSE, Georgia Institute of Technology, Atlanta, GA.

Half-Heusler alloys are currently being investigated for their potential as thermoelectric materials. They exhibit high negative thermoelectric power (-3 to -500 μV/K) and favorable electrical resistivity (0.18 mΩ cm) at room temperature. Attractive power factors of (s/2T) of about (82.3, 1.0 W/mK) at room temperature and about 4.5 mW/K at 65 K have been reported in these materials. However, to achieve a high figure-of-merit in the half-Heusler alloys, the relatively high thermal conductivity in these materials (~10 W/mK) must be reduced. The thermal conductivity in these materials is composed primarily of a lattice contribution, with a considerably small electronic component which is not a significant part of the total thermal conductivity.

The challenge is to reduce the relatively high lattice thermal conductivity in these materials. In this paper, we report significant reduction of lattice thermal conductivity (~1.5 - 3.5 W/mK) in some Ti-based half-Heusler alloys which have been prepared by ball milling and followed by shock-compression. This process resulted into reduced grain sizes (less than 4 μm) in these materials, which corresponds to a smaller lattice thermal conductivity. These structural effects on the thermal properties of the Half-Heusler alloys will also be discussed.

3:45 PM G7.2 RECENT RESEARCH AT OAK RIDGE ON NOVEL THERMOELECTRIC MATERIALS. Brian Sales, Bryam Chakoumakos, David Mavros, Rongying Jin, Jim Thompson, Solar State Division, ORNL, Oak Ridge, TN; Naveen R. Raja, National Center for Physical Acoustics, University of Mississippi, Oxford, MS.

Cage compounds such as the skutterudites and semiconductor clathrates, ternary tellurides, mixed-valence rare earth compounds and Kondo insulators have been investigated in our group over the past several years as thermoelectric materials for power generation or refrigeration applications. The most recent research on these materials will be discussed with an emphasis on understanding the physics of these complex materials. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725.

4:15 PM G7.3 LARGE THERMOELECTRIC POWER FACTOR IN TiS2 SINGLE CRYSTALS. Hideto Imai, Yutichi Shimakawa and Yoshimi Kubo, NEC Corporation, Fundamental Research Laboratories, Tsukuba, JAPAN.

A TiS₂ crystal, which has a CdI₂-type layered structure, was found to have a large thermoelectric power factor comparable to that of the best thermoelectric material, Bi₂Te₃-Sb₂Te₃ alloy. Its power factor in-plane, ρS²/σ, at 300 K was 37.1 μW/K cm with ρ = 1.7 mΩ cm and σ = 565 mΩ cm⁻¹. The lattice thermal conductivity showed a relatively low and highly anisotropic behavior, suggesting that the electronic structure of this compound has a quasi-two-dimensional nature. The carrier density was 2.8 x 10¹⁹ cm⁻³, which is one order of magnitude larger than that of optimally doped (Bi,Sb)₂Te₃. It is noted that a large power factor comparable to that of (Bi,Sb)₂Te₃ was observed, though the carrier density was significantly different. Both strong inter-valley scattering and strong electron-phonon coupling in the two-dimensional electronic state seem to play an important role in enhancing this crystal's thermopower. Despite the large power factor, the figure of merit ZT, at 300 K was 0.16 because of the relatively large in-plane thermal conductivity, 60 mW/Kcm. Since the contribution of electron carriers to thermal conductivity is estimated to be ~4 mW/Kcm by Wiedemann-Franz law, most of the thermal conductivity is contributed by the lattice. In the light of the "phonon-glass electron-crystal" concept, the lattice-thermal conductivity of TiS₂ could be reduced by introducing rattling atoms between the conjugate layers, leading to a large ZT. Atom intercalation into the van der Walls gap is a promising approach, and we will also report on the results.

4:30 PM G7.4 THERMAL AND ELECTRICAL PROPERTIES OF COCHRALSKI GROWN GeSi SINGLE CRYSTALS. Ichiro Yonemura, Takuya Akashi, Toshiaki Goto, Institute for Materials Research, Tohoku University, Sendai, JAPAN.

Germanium-silicon (GeSi) alloy is an important material for high temperature thermoelectric devices with environmental compatibility, and has been successfully used as a power generator within deep space probes Voyager, Galileo, etc. The target for wider applications is to enhance the figure of merit as a thermoelectric element. In this paper we show that the thermoelectric parameters, thermal conductivity, electrical conductivity and Seebeck coefficient of high quality bulk single crystals of Ge₁₋ₓSbx alloys in the various composition 0.8 < x < 1 were investigated in the temperature range 630°C to 1200°C. These results Highest figure of merit 3.0 for x = 0.68 was obtained at a high performance thermoelectric device. Single crystals of the alloys heavily doped with B, Ga, and P impurity were grown by the Czochralski technique. The thermal conductivity was mainly controlled by the phonon scattering at point-like defects, showing a minimum at x = 0.5 ± 0.6. The electrical conductivity of alloys was well controlled to be almost constant with a high magnitude by suitable doping. The Seebeck coefficient was 300 - 400 μV/K at 600°C in the heavily impurity-doped Ge₁₋ₓSbx alloys. The dependence of the Seebeck coefficient on the electrical conductivity was revealed. The dimension-less figure of merit of 0.65 was evaluated in the impurity-doped single crystals of Ge₇S₃ alloys.

4:45 PM G7.5 SYNTHESIS OF HEAVY DOPED SILICON-GERMANIUM ALLOY WITH UNIFORM STRUCTURE BY SPLAT SOLIDIFICATION IN MICROGRAVITY. Hidemi Nakayama, Masakatsu Sawaishi, Toshiaki Otsutani, AIST, Microgravity Materials Lab., Sapporo, JAPAN.

SiGe alloy have been studied as a thermoelectric semiconductor. However, it is difficult to synthesize the uniform SiGe alloy because of a wide separation between liquidus and solidus in its phase diagram and the differences in the densities of Si, Ge and dopant. In microgravity environment, homogeneous melt can be obtained because of no thermal convection and no segregation caused by differences in the densities of the constituent elements. By rapidly solidification of this homogeneous melt, it is possible to synthesize the uniform SiGe alloy with heavy dopant. In this study, heavily doped SiGe alloy (Si/Ge = 4 in atomic ratio) was synthesized by splat solidification on the rotating copper block in vacuum. The starting material of SiGe alloy was prepared by arc melting in Ar atmosphere. Arc melted ingot was mixture of Si rich and Ge rich phase. The starting SiGe melt was kept in 1.2 microgravity using 1 tm drop tower and dropped...
from aminole at the braking of dye capsule, the solidified sample had uniform structure and similar composition to the starting material. The solidified sample was stirred with spark plasma sintering technique at 1273K for 5 min. The sintered sample had many holes and its thermal conductivity was lower than that of as-sintered one. The electrical conductivity of the sintered sample was similar to that of as-sintered one. Other thermoelectric properties will be presented at this meeting.

SESSION G8 POSTER SESSION
TE MATERIALS AND DEVICE R&D
Chairs: George S. Nolms, David C. Johnson,
David G. Maudras, Brian S. Sales, Jean-Pierre Fleurlat
and Jeff W. Shley
Tuesday Evening, November 27, 2001
8:00 PM
Exhibition Hall D (Hyatt)

G8.1 NON-EQUILIBRIUM ELECTRONS AND PHONONS IN HETEROSTRUCTURE INTEGRATED THERMOELECTRIC COOLERS.
Djoucky Vlahou, Ali Shokouri, University of California, Jack Baskin School of Engineering, Santa Cruz, CA.
The effect of hot carriers on electron transport in single barrier thermoelectric emission coolers is studied theoretically. By studying nonequilibrium characteristics of electrons and phonons in the device, fundamental limitation of the cooler performance is analyzed. In particular, we investigated the effect of various boundary conditions at heterojunctions on the electron and phonon temperature distributions. These boundary conditions have significant impact on the device performance. Thin film devices under high voltage or in high current density are examples of situations where electrons and phonons are not in equilibrium and a coupled transport equation should be solved for an accurate determination. In a thermoelectric/thermionic device one can consider the lattice temperature while cooling happens in the electron gas. Although at low currents electrons and phonons have the same equilibrium temperature, by increasing the current, they tend to different temperatures, which can lead to a reduction in cooling power density. We will show that in materials with faster electron energy relaxation, i.e. higher electron-phonon coupling, thermionic cooling performance is less affected by high current injection, and argue that SiGe thin film coolers are not limited by hot carrier effects.

G8.2 THERMOELECTRIC BEHAVIOR OF CARBON FIBER POLYMER-MATRIX COMPOSITE LAMINATES IN THE FIBER AND THROUGH-THICKNESS DIRECTIONS. Shoukai Wang, Chee Chung Liew, Victor H. Guerrero, D.L. Chang, Composite Materials Research Laboratory, University at Buffalo, The State University of New York, Buffalo, NY.
Polymer-matrix composites containing continuous carbon fibers are important for lightweight structures. This paper is aimed at developing theoretical models for combined thermoelectric and structural applications. The composites studied are laminates with carbon fibers in unidirectional or crossply configurations. The thermoelectric behavior in both the fiber and through-thickness directions of a laminate are addressed. The thermoelectric behavior in the fiber direction is governed by the fibers; intercalation of the fibers greatly enhances the behavior and provides n-type and p-type composites. The behavior in the through-thickness direction is governed by the extent of contact between fibers of adjacent laminae, and by the presence of interlaminar additives. Thermocouples have been made by using the interface between laminae of dissimilar fibers as the thermocouple junction and using the thermoelectric behavior of the lamina in the fiber direction.

G8.3 MICROSTRUCTURE EFFECTS ON THE THERMOELECTRIC PROPERTIES OF BASED PbTe FILMS PREPARED BY PULSED LASER DEPOSITION. Anne Dauscher, Bertrand Lenoir, Alexandre Jacquet, L.P.M., Ecole des Mines, Parc de Staurupt, Nancy, FRANCE, Mario Basnou, NILPRA, Laser Department, Bucharest, ROMANIA.
Lead telluride (PbTe) thin films, as well as PbTe and Bi2Te3 multilayers, were prepared by pulsed deposition from a Nd:YAG laser working at a wavelength of 522 nm. The films were deposited under vacuum onto silicon/silicon (111) and baryum fluoride (111) at 150°C, temperature at which congruent transfer from target to substrate occurs. Strong influence of substrate nature and annealing on the structure and morphology of the PbTe films was observed. The effect of these microstructure changes as well as the presence of additional thin Bi or Te layers on the transport properties of PbTe will be presented and discussed.

G8.4 MICROSTRUCTURAL AND THERMOELECTRIC PROPERTIES OF p-TYPE Bi2S3-Te3 and n-TYPE Bi2Te2S3 FILMS DEPOSITED BY PULSED LASER ABLATION. M.S. Bhatwadekar, J. Kangnamdram, North Carolina State University, Department of Materials Science, Raleigh, NC; B.C. Sales, Oak Ridge National Laboratory, Solid State Division, Oak Ridge, TN; H. Wang, Oak Ridge National Laboratory, High Temperature Materials Laboratory, Oak Ridge, TN.
Thin films of p-type Bi2S3-Te3 and n-type Bi2Te2S3 were deposited on Si substrates using Nd:YAG pulsed laser ablation at temperatures ranging from 500°C to 500°C. The films were characterized using X-ray diffraction, SEM, and TEM. X-ray mapping and EDS were used to determine the stoichiometry. The films showed uniform thickness and high crystalline quality with a preferred (00l) alignment with the substrates. The film quality in terms of stoichiometry and structural perfection is studied as a function of growth temperature. It was found that films deposited at 350°C gave the best stoichiometry. The Seebeck coefficient, thermal conductivity and electrical resistivity were measured as a function of temperature and compared with the measurements from the bulk. Correlation of thermoelectric properties with microstructure is discussed.

G8.5 DISCRETE STATE SIMULATION OF THE PELTIER EFFECT FOR INTERFACES BETWEEN ARBITRARY BAND STRUCTURES. Peter P.P. Rozakowski III, Timothy D. Sands, Graduate Group in Applied Science and Technology, University of California, Berkeley, CA.
The Pellet Heating and Cooling Effects are generated by external electric potentials applied across junctions between two materials characterized by different electronic conduction band structures. At these interfaces, there are significant changes in the density of states. The flow of charge density across an isothermal junction is accompanied by the exchange of heat with the lattice. The direction of the charge carriers and the details of the band structure determine whether phonons are absorbed or emitted. The magnitude of Pellet Cooling is further influenced by the lattice heat conduction within the separate materials and by the transport of phonons across the interface. Analytic treatments of these processes are often restricted to interfaces between simple band structures. The presented discrete state simulation addresses interfaces between band structures of arbitrary complexity. Each side of the interface is described by a discrete (tabular) set of energy/number density electron and phonon states. Transport within each material and across the interface is governed by commensurate hopping between discrete electron and phonon states in both real and reciprocal lattice spaces. Hopping probabilities are expressed as precalculated lookup tables. Hopping represents quantum mechanical scattering and occurs in both real and reciprocal lattice spaces. The electron and phonon conductances are explicitly coupled by the scattering terms. The aggregate charge and heat current densities are determined as a function of the applied external field and temperature. The resultant Peltier Coefficient is determined not only by the discontinuity in the separation of the Fermi levels in the two structures but also by the specific transport characteristics of the interface itself. By considering a one-dimensional interface between simple band structures, a comparison is made between the predictive capabilities of the discrete state simulation and relaxation time approximations of Boltzmann's equations. The extension of this method to more complicated band structures is presented.

G8.6 DEFECT FORMATION IN BORON CARBIDE: AN AB INITIO ELECTRONIC STRUCTURE STUDY. Jan Wang, Daniel Marshall, Motorola Labs, Physical Sciences Research Labs, Temple, AZ; Nikolay Zein, Gregory Kirenen, Sci-Tec, Moscow, RUSSIA.
The electronic structure of a crystalline boron carbide has an energy forbidden gap of ~3eV and it is hence a good insulator. But, on the other hand, the electrical conductivity of boron carbide is measurable. It is therefore believed that the defects formation in boron carbide is responsible for its electrical conductivity and a theory of hopping conduction of biholes through localized defects were developed, accordingly. Although the biholes and electron conduction models do not rely on any specific types of defects, the bihole or electron formation in boron carbide is believed to be a defect C-B intrasublattice chain in connection with a C-B intrasublattice chain. The current study investigated the existing theory of conduction in boron carbide by performing a systematic study on the formation energies of defects in boron carbide using a state-of-the-art ab initio electronic structure method. The studied defects cover a) stoichiometric vacancies of carbon concentration, b) missing boron atoms, and c) distribution of carbon atoms in the materials. It is found that the
ground state of a fully carbonated boron carbide consists of B12C icosahedra connected by C-B-C intramolecular chains, i.e. consistent with the reported structural model of B4C. When carbon concentration is reduced, however, the population of C-B-C chains is found to be intact, while the population of B12C icosahedron is reduced by the replacements of B12C icosahedron. This observation is fundamentally different from the earlier model of boron-rich boron carbide. The localized states associated with missing boron atoms are identified and the electrical conductivity through these localized defects states is studied.

GS.7 SYNTHESIS OF BORON-RICH METAL BORIDES AND THEIR THERMOELECTRIC PROPERTIES. Masahiro Takeda, Ferrer Domingo, Takashi Mura, Takashi Fukuda, Nagoya University of Technology, Dept. of Mechanical Engineering, Nishitaga, JAPAN.

Polycrystalline metal borides Al2MoB4, MoB4 (M = Cr and rare earth metals), and MoB8 (M = transition metals) were prepared by using PECS (Pulse Electric Current Sintering) technique. Single phase of orthorhombic Al2MoB4, which contains B12 icosahedral clusters as building blocks, was obtained at sintering temperatures between 1523 K and 1823 K, while higher sintering temperatures lead to the appearance of γ-Al2B2 type phase. Seebeck coefficient (α) and electrical conductivity (σ) of the Αl2MoB4 at room temperature was about 600 μV/K and 10^3 (S/m), respectively. Such low α and low σ are comparable to those of metal doped β-ternary carbides. MoB4-type materials such as Ti2B2 and VB2, which have layered structure comprising interleaved two-dimensional boron and metal layers, were also synthesized. These have metallic property with large α (more than 10^4 μV/K), and their α was enhanced up to 200 μV/K by substituting metal atoms with other metals. Further increase is expected. The Mo6B16 hexaborides are cubic phase whose structure is a three-dimensional skeleton constituted of B6 octahedral clusters, and the tetrahedra of which are filled by metal atoms. The α and the σ of the synthesized CaB6 were about 200 μV/K and 10^4 (S/m) at room temperature, respectively. Substituting Ca atoms with rare earth metals will enable us to improve these thermoelectric properties. Details of the results and discussion will be presented at the meeting.

GS.8 FORMATION OF BISMUTH-SILICA NANOcomposite VIA high-Energy BALL MILLING. Matthew A. Mehl, Timothy M. Dellinger, Paul V. Braun, Department of Materials Science, University of Illinois, IL.

Nanostructured bismuth has received much attention as a possible thermoelectric material due to its high figure of merit and its ability to display quantum confinement effects at length scales up to 50 nm. Here, we present the synthesis of nanostructured bismuth-silica composite via high-energy ball milling in argon with a Spex 8000 Micer/Mill. As determined by transmission electron microscopy (TEM), the average diameter of the bismuth particles decreased to 10 nm (from 1 μm in starting), and finally, after 62 hours, the Bi nanoparticles are not observed in TEM samples due to the formation of a Bi-silica solid solution or the oxidation of Bi metal to bismuth oxide. The 10 nm Bi nanoparticles were identified after 16 hours of milling should be sufficiently small to exhibit quantum confinement. Measurements of the electronic properties of these nanophase Bi-SiO2 composite materials as a function of milling time and Bi volume fraction are currently underway.

GS.9 THE FABRICATION AND THERMOELECTRIC PROPERTIES OF AMORPHOUS SiGe BULK SAMPLES. Sangjin Lee, Yoko Okamoto, Toshio Kawanaka, Jun Morimoto, National Defense Academy, Dept. of MSE, Yokosuka, JAPAN.

We have already reported that the SiGe amorphous superlattice thin film which shows the extremely large power factor and the anomalously large power factor comes from the SiGe amorphous phase, we have tried to fabricate the amorphous SiGe bulk sample using the melt spinning method.

GS.10 HIGH TEMPERATURE ELECTRICAL TRANSPORT PROPERTIES OF Eu- AND Yb-DOPED SKUTTERUDITES. R.H. Twidstrom, G.A. Lamberton Jr., Terry M. Tritt, Dept of Physics and Astronomy, Clemson Univ, Clemson, SC. G.S. Nolas, Department of Physics, University of South Florida, Tampa, FL.

Skutterudites have shown promise for potential thermoelectric applications due to their high power factors. In this paper thermopower and resistivity is measured and presented on a series of Eu and Yb-doped skutterudites over a temperature range of approximately 100 K to 700 K using our high temperature thermoelectric probe. Simple measurement techniques are briefly discussed. Data from various levels of Eu and Yb dopings will be presented and compared in order to show trends that point towards improvements in these skutterudites for potential thermoelectric applications.


Quasicrystals have properties associated with both crystalline and amorphous materials. These properties appear to be sensitive to both composition and annealing conditions. Therefore, it is important to investigate the influence of the microstructure on the electrical and thermal transport properties of quasicrystals. AlPnMn quasicrystals were prepared with various levels of Al substitution for the Mn (AlPnMn-1_xMg_x) and then subjected to different annealing conditions. Electrical resistivity, thermopower and thermal conductivity were measured on each as grown and annealed sample over a broad range of temperature, 1K < T < 300K. The relationship between the electrical and thermal transport properties and microstructure will be presented and discussed.


In the search for new thermoelectric materials, quasicrystals have been investigated due to their inherently low thermal conductivity. Crystalline phases closely related to the quasicrystal, however, have largely been ignored. These phases offer a new class of materials that share similar structural, yet the periodicity of a crystal. In this paper, we have investigated an icosahedral I-AlCuFe quasicrystalline phase as well as two of its corresponding approximant phases (ω and β). Electrical and thermal transport properties of these materials were measured. The visibility of the I-AlCuFe quasicrystalline system and the ω and β approximant phases as thermoelectric materials is discussed.

GS.13 MICROSTRUCTURAL EVOLUTION OF La-DOPED SiB6 HIGH TEMPERATURE THERMOELECTRIC MATERIAL DURING A SPARK PLASMA SINTERING. D.W. Lee, J.H. Wei, J.K. Park, K.H. Kim, J. Joo, Shih, C.P. Hwang, Yuung, Seoul, KOREA. “Tokai Univ, JAPAN.

SiB6 has proved to a potentially useful material because of its excellent thermoelectric properties above 700°C, low specific gravity, high degree of hardness, and moderate melting point. SiB6, which has poor sintering characteristics, is often used in a spark plasma sintering (SPS) method. The SPS-processed specimens consisted of SiB6, SiB6 and Si-Doped pure SiB6 powder were densified fully at the sintering temperature of 1600°C. In particular, it was found that the rare earth element was very effectively in the microstructure of SiB6 phase, resulting in reducing the sintering temperature and controlling grain growth. These effects were discussed in detail in terms of microstructure evolution during the SPS process.


Thermoelectric oxide semiconductors have recently been receiving much attention in the literature. In this paper, Na and La-doped NaCoO based polycrystalline samples were studied. The oxide powder was prepared by a soft chemical approach, and then was sintered in air under a pressure of 1 atm. The chemical processing greatly shortens the overall preparation time period. We carried out x-ray diffraction and electron microscopy analysis, and measured their electrical conductivity. Seebeck coefficient and thermal properties. The influence of various dopants and processing routes on their microstructure and thermoelectric properties were investigated in high temperature region. The novel chemical processing is effective to prepare the oxide ceramics.

GS.15 CRYSTALLINE SYNTHESIS OF CaSnO2.5 AND THERMOELECTRIC PROPERTIES. Shengli Chen, Jun Nan, and Ce Wen Nan, Tsinghua Univ, Dept of MSE Sci & Eng, Beijing,
CHINA and Wuhan Univ of Tech, Adv Mater Res Inst, Wuhan, CHINA.

Composite oxide CaSe/12O28, as a class of novel thermoelectric oxides, was synthesized via a sol-gel process, following by a hot-pressing and sintering procedure. This material is a layered oxide consisting of CaO layer and CaO22 block, which is believed to act as an electrical conduction layer. The phase composition was characterized by means of X-ray diffraction and microscopy analysis. The Seebeck coefficient and electrical conductivity of the samples were measured by conventional method. The Seebeck coefficient increases dramatically with increasing temperature. The results indicate that the thermoelectric properties can be improved further by optimizing the preparation method.

**GS.16 SYNTHESIS AND THERMOELECTRIC PROPERTIES OF (Na0.85, Ca0.15)CeO2+δ (x=0.05 or 0.2) Pb2CoCr2O6 CRYSTALLINE OXIDES.**
Jun Nan, Xian Li, Wei Li, and Wei Xu, Wuhan Univ, Wuhan, China

Oxides ceramics have recently been attracted much attention as promising thermoelectric material due to their special potential applications in power generation using waste heat. In this paper, (Na0.85, Ca0.15)CeO2+δ (x=0.05 or 0.2) polycrystalline samples with a layered structure were prepared by a sol-gel method followed by a low-temperature sintering procedure. The electrical properties and Seebeck coefficients were measured from 400 to 800 °C. The electrical conductivity and the power factor increase with increasing temperature. Both the Seebeck coefficients decrease with increasing Na-doping amount. The figure of merit of the oxide samples is smaller than that of traditional thermoelectric alloys, which is about 216.4 /K at 700°C.

**GS.17 THERMOELECTRIC PROPERTIES AND STRUCTURAL CHARACTERIZATION IN Sc1−xBi2−xTc4 Alloys.** Xia Rong, Jun Nan, Jun Nan, Jun Nan, Wei Li, and Wei Wu, Wuhan Univ, Wuhan, China

Modern high efficient thermoelectric cooling devices call for development of steady materials with higher ZT. One of the novel promising approaches is to combine bismuth telluride with other elements and to synthesize new ternary compounds. In this paper Sc1−xBi2−xTc4 alloys were prepared by a rapid quenching of the melt followed by a sintering procedure of compacted pellets. The microstructure in this system seems to be described as lagers. Among all of the compounds, Sc1−xBi2−xTc4 exhibits better thermoelectric performance around 400K. Thermal conductivity is extremely low beyond conventional judgment. With Sc doping the carrier concentration can be optimized, and hence the total electrical conductivity is increased. There is work room for enhancing the thermoelectric performance.

**GS.18 THERMOELECTRIC PROPERTIES OF Pb/Se EPITAXIAL THIN FILMS AND Pb/Se/Eu HETEROSTRUCTURES.** Milred S. Dresselhaus, Gene Dresselhaus, MIT, Dept of Physics, Cambridge, MA; Elena I. Rogacheva, Tatiana V. Tvarin, Sergey N. Grigorov, Konstantin A. Nomakin, Valeriy V. Volosov, Alexander Yu. Sipans, National Technical University “Kharkiv Polytechnic Institute”, Kharkiv, UKRAINE

Theoretical prediction and subsequent experimental confirmations of the possibility of significant enhancement in the thermoelectric figure of merit in low-dimensional structures based on IV-VI compounds stimulates further interest in studying lead chalcogenides. The goal of the presented work is preparation of PbSe epitaxial thin films and PbSe/Eu heterostructures and studying the dependences of their thermoelectric properties (electrical conductivity, the Hall coefficient, charge carrier mobility, and the Seebeck coefficient) on the PbSe layer thickness d (d=5-200 nm). PbTe thin films were prepared by thermal evaporation of PbSe in vacuum and subsequent deposition onto (100) KCl surfaces at 570 K. EuS was grown on PbSe layers using electron-beam evaporation. Electron microscopy studies revealed a “vapor-crystal” model of film growth in the [010] orientation without coalescence. At about a 40 nm thickness, PbSe films are practically continuous although they contain voids and pores. It was established that oxidation of thus prepared films of PbSe in air at 300 K leads to an inversion of the conductivity sign from n to p type in films with thicknesses d<100 nm. The observed dependences of the thermoelectric properties on d were explained by the existence of compensating acceptor states, which appear on the surfaces of PbSe films.

**GS.19 THERMOELECTRIC PROPERTIES AND CRYSTAL AND ELECTRONIC STRUCTURES OF A LAYERED STRUCTURE MATERIAL InGaZnO4 Heterostructure.** Hideko Imaa, Hideki Kimura, Yuchi Shimokawa, and Yoshimi Kubo, NEC Corporation, Fundamental Research Laboratories, Tsukuba, JAPAN

A layered-structure material can be a good thermoelectric, because the thermopower, S, is enhanced with the two-dimensional (2D) electronic state. An InP-O2 type layered InGaZnO4, which consists of InO2 and GaZnO2 layers, was expected to show such 2D characteristics. A small amount of highly conductive carriers in the 2D InO2 layers. The insulating nature of the GaZnO4 layer on the other hand, is thought to come from the small overlapping between the orbitals of Ga and Zn, due to the difference of the z-coordinates of Ga and Zn in the Ga2O3 layers[1]. In the present study, we investigated thermoelectric properties of
InGaZnO$_4$ and its dimensionality by transport measurements, structure analysis and the electronic band structure calculation. Electron-doped (In$_{x}$Ga$_{1-x}$ZnO$_4$) and hole-doped (Ga$_{y}$In$_{1-y}$ZnO$_4$) with the highest figures-of-merit, $ZT$, 0.04 at 300 K with $\rho$ of 5 m$\Omega$ cm, $S$ of 0.8 $\mu$V/K, $\kappa$ of 42 mW/Km, and $n$ of 6 $\times$ 10$^{17}$ cm$^{-3}$. Both magnitude and $S$-dependence of $ZT$ are well explained in terms of the 3D-effective-mass and carrier density, and no enhancement of $ZT$ was observed; that is, the result of transport measurement suggests 3D nature of the material. Structure analysis by neutron-diffraction data and EXAFS studies revealed that the $z$-coordinate of $S$-atom in Ga$_2$O$_4$ were different by 3 $\pm$ 0.2% as speculated by Oriin et al.[1] However, the bond-structure calculation using the obtained structural parameters predicted a considerable 3D conduction due to the overlapping of the In 3s and Ga 4s orbitals. This result is consistent with our transport results, but in sharp contrast with the previous speculation of 3D electronic structure from chaser-model calculation [1].


GS 24

THERMOELECTRIC PROPERTIES OF Bi$_x$Sb$_{1-x}$Te$_2$X COMPOUNDS PREPARED BY MA-PDS METHOD. Yong-Jae Park, Xuedong Liu, National Institute of Advanced Industrial Science and Technology, Sendai, JAPAN.

In this work, we employed a new processing technique, mechanical alloying (MA)-pulse discharge sintering (PDS), to fabricate the bulk Bi$_x$Sb$_{1-x}$Te$_2$X materials doped with Ag, BN, and AgBiBN. The electrical, thermal and thermoelectrical properties of the doped samples were systematically investigated as a function of the doping content and temperature. Based on these studies, we identified a great potential for further improving the thermoelectric performance of the mother 25%Bi$_2$Te$_3$+75%Sb$_2$Te$_3$ alloy by doping a small amount of Ag. The doping content was optimized at 0.10-0.15%Ag, which corresponds to the maximum $ZT$ of 3.3 at 700 K and 0.64 at 300 K of AgBiBN, however yields extremely low values of Seebeck coefficient, finally resulting in a low figure-of-merit.

GS 26

STRUCTURE AND THERMOELECTRIC PROPERTIES OF NEW LAYERED COMPOUNDS IN THE QUATERNARY SYSTEM Cs-Ph-Bi$_2$Te$_4$, Kuo-Fang Hsu, Duck-Yong Chang, Antje Mrozek, Mercouri G. Kanatzidis, Michigan State Univ, Dept of Chemistry and Center for Fundamental Materials Research, East Lansing, MI; Sangeeta Lal, Tim Hogan, Michigan State Univ, Dept of Electrical and Computer Engineering, East Lansing, MI.

We are interested in ternary or quaternary bismuth chalcogenides because of their rich structural chemistry and potentially promising thermoelectric properties. These materials may exhibit the essential features required for high figure of merit by virtue of their complex electronic structures, crystal structures and compositions. Recently, we reported that the doped compound CsBi$_2$Te$_4$ exhibits promising thermoelectric properties. In an effort to explore the ultimate performance of this compound, we introduce Pb$_{1-x}$Te$_x$ into its layered framework. Consequently, the four new compounds CsPb$_{1-x}$Bi$_x$Te$_4$ (1), CsPb$_2$Bi$_2$Te$_4$ (2), CsPb$_3$Bi$_3$Te$_4$ (3) and CsPb$_4$Bi$_4$Te$_4$ (4) were obtained by the reactions of CsBi$_2$Te$_4$ with increasing content of Pb$_{1-x}$Te$_x$. The four new compounds adopt novel structures built up of anionic slabs with progressively increasing thickness. We will present the four compounds as members of the brand-new homologous series CsPb$_m$Bi$_m$Te$_{4m}$ (m = 1 to 4).

GS 28

CLASSICAL SIZE EFFECT ON IN-PLANE THERMOELECTRIC PROPERTY IN SUPERLATTICES. W. L. Liu, G. Chen, Mechanical and Aerospace Engineering Department, University of California at Los Angeles, Los Angeles, CA.

The well-established theoretical model on thermoelectric transport in low-dimensional systems, such as superlattice, deals with the quantum effect on figures-of-merit enhancement. However, the classical size effect may still exist and have effects on transport properties. In this paper, we will report a theoretical approach to investigate the classical size effect on in-plane thermoelectric transport properties. An atomic Bohrman transport model at in-plane direction is established in superlattice system. Partial specular and partial diffuse interface scattering boundary condition are included in the solution. By using the superlattice property with that of Si/Ge, the result obtained are compared with previous works considering the classical size effect on the same material system. This work is supported by ONR MURI on Thermoelectrics (N00014-97-1-0615). Keywords: Thermoelectric, Superlattices, Bohrman equation, Thin Films.

GS 29

A METHOD FOR FINE TUNING OF THERMOELECTRIC PERFORMANCE. C. Gribinakis, E. Heikkala, Dept. of Physics, Aristotle University of Thessaloniki, Thessaloniki, GREECE; P. Losta, L. Kudela, University of Pardubice, Pardubice, CZECH REPUBLIC.

In this work we present a method that allows a direct and continuous fine tuning of thermoelectric performance. The method is applied to an already grown material, and allows the direct change and monitor of the free carrier concentration. The sample under study is exposed to a direct laser reaction and the free carrier concentration is gradually changed by controllable and controllable charge transfer from inserted species to host lattice. Conductivity, Hall effect and Seebeck measurements can be in-situ measured during the insertion process. The main advantage of the method is that it the necessary to use one and single sample, as charge transfer can gradually change it from p-type to n-type. The method has been applied to a series of bismuth or bismuth tellurides and solid solutions. Due to controllable charge transfer, a smooth and continuous change from p-type to n-type, the peak on power factor is clearly observed experimentally both for p and for n type of material.
In this work we present results on a series bismuth or antimony tellurides and solid solutions, estimate ZT performance in each case and compare with known optimized compositions.

**GS.30**

**A SIMPLE METHOD FOR THE EVALUATION OF THERMOELECTRIC PERFORMANCE BASED ONLY ON ELECTRICAL CONDUCTIVITY MEASUREMENTS.**

E. Harikirakan, C. Granakis, Dept. of Physics, Aristotle University of Thessaloniki, Thessaloniki, GREECE.

In this work we present a simple, yet accurate method that allows a direct evaluation of thermoelectric properties from a minimum set of experimental data. The method, a numerical algorithm, uses experimentally measured values of electrical conductivity in a p-n transition. The algorithm assumes a two band model and directly calculates the p and n carrier contributions, in two steps. In the first step, a simple parabolic approximation is adopted. Based on experimental data from electrical conductivity, the first step separates the contributions of p and n carriers, and directly calculates the thermoelectric performance of both the p and the n region. In the second step, a refinement of the first, the calculated values are corrected for account of carrier degeneracy and of non-parabolicity of the bands. The efficiency of the method is tested against simulated and real data and results are presented. Though, the algorithm uses a minimum set of data, i.e only of electrical conductivity, the calculated values for Seebeck coefficient, Hall effect and mobility, in the full range of the p-n transition is in a very good agreement with separately measured ones.

**GS.31**

**PELTIER JUNCTION USING A YBCO HIGH Tc SUPERCONDUCTOR.** J.E. Rodriguez and A. Manrique, Department of Physics, Universidad Nacional de Colombia, Bogota, COLOMBIA.

A junction between bismuth-antimony alloy as active leg and YBa2Cu3O7-δ as passive leg, which operate at around liquid nitrogen temperatures has been built. Measurements of electrical conductivity, thermoelectric power and thermal conductivity of YBCO and Bi-Sn were carried out and their influence on the thermoelectric merit figure (ZT) were analyzed. The effect of the applied magnetic field (up to 1 T) on these transport parameters are discussed.

**GS.32**

**GROWTH OF PbTe FILMS BY MAGNETRON SPUTTERING.** A. Jinov, J. Pipela, Z. Dusek, and R. Stolc, Department of Materials Engineering, Ben Gurion University of the Negev, Beer Sheva, ISRAEL.

The monolithic integration of narrow gap IV-VI semiconductors and Si devices is highly attractive for IR optoelectronic and thermoelectric applications. The growth of epitaxial PbTe is constrained by the large difference of -19% between the lattice parameters of PbTe and the Si substrate and the considerable difference in their thermal expansion coefficient. In recent years, the epitaxial growth of IV-VI semiconductors on Si substrates has been successfully realized using fluoride buffer layers and bilinear IR sensors have been fabricated. However, epitaxial growth of PbTe films directly on Si wafer is desirable for simplification of the process. In our research we used RF magnetron sputtering for thin film preparation. Si (111) wafers were used as substrates and PbTe films were deposited at constant power for different times and at various power levels. The growth of PbTe films with thickness 80-200 nm was performed at substrate temperature ≤400°C with a deposition rate of about 0.1 nm/s. Films were studied by X-ray diffraction (XRD) using a Rigaku diffractometer A combination of 400W and 30min sputtering time and heating the substrate at ≤400°C provided a highly textured film. The only peak was that of (200) thus indicating the possibility of obtaining epitaxial growth of lead telluride under the above conditions by magnetron sputtering. The results were reproducible. Other power/time combination is presently under investigation in order to test other possibilities of obtaining epitaxial films. The films were characterized also by scanning electron microscopy (SEM) and Auger spectroscopy.

**GS.33**

**SYNTHESIS OF NONSTRUCTURED BISMUTH COMPOUNDS IN LIOTHROIC LIQUID CRYSTALS.** Tim M. Dollinger, Paul V. Braun, University of Illinois at Urbana Champaign, Dept. of MSE, Urbana IL.

Liothropic liquid crystals selforganize to form ordered mesophas of consisting of hydrophobic and hydrophilic nano-domains. When chemistries are chosen which operate exclusively in one of these domains, the domains serve as nanoreactors that can limit the size and shape of material produced in the liquid crystals. The specific mesophases we investigated were formed by mixing amphiphilic polymers or oligomers with aqueous based solutions containing bismuth precursors (typically bismuth salts). Chemical and electrochemical syntheses based on the reduction of bismuth salts were performed in lamellar, hexagonal, and inverse hexagonal phases of oligo(ethylene oxide) olef other based lyotropic liquid crystals. The various lyotropic phases were created by varying the relative ratio of the components making up the mesophase. By varying the phase of the liquid crystal, the dimensionality and connectivity of the water rich domains in which the bismuth is formed can be varied from zero to three dimensions, controlling the size of the solids formed. The resulting nanostructured bismuth was examined with transmission electron microscope and showed improved thermoelectric figure of merit (ZT) due to quantum confinement within these nanostructures.

**GS.34**

**EXPERIMENTAL THERMOPOWER OF QUANTUM WIRES.** M.V. Vedemnov, O.N. Dzyubin, B.M. Goldtman, Yu. V. Ivanov, Yu. A. Kuznetsov, IPPE, Ioffe Technical-Physical Institute, S. Petersburg, RUSSIA.

Thermopower of semiconductor nanowires with diameter of about 5 nm was measured. The results for InAs nanowires were used for nanowire preparation. These nanowires were filled by the melted semiconductors. Temperature dependence of thermopower and the reduced resistance of nanowire bundle were measured. Due to a maximization of the necessary characteristics from corresponding dependencies of bulk semiconductors, the obtained results and the literature data indicate that transport properties of quantum wires have a quantum character, they are described better by the Luttinger liquid model than by the usual Fermi-gas one.

**GS.35**

**Si$_2$N$_4$: A PROMISING NEW THERMOELECTRIC MATERIAL: ELABORATION AND CHARACTERIZATION.** Véronique Izard, Marie-Christine Record, Julien Haines, Jean-Claude Tedennac, UMI, Laboratoire de Physico-chimie de la Matière Condensée, Montpellier, FRANCE.

Zinc-antimony alloys have interesting thermoelectric properties. Si$_2$N$_4$ is a high performance p-type thermoelectric material that appears to be a promising substitute for PbTe due to a higher factor of merit (ZT = 1.3 at 670K$^{[1]}$) and due to the advantage of being Pb-free. As the literature reports this compound as being multi-phase$^{[2][3]}$, we have investigated its stability range by means of DSC measurements, X-ray diffraction and electron microscope analysis; our experimental results supported by Russwud research was used to determine the stability range with precision. In order to elaborate the thermoelectric material, two techniques of sample preparation were carried out: conventional synthesis in silicron tube sealed under vacuum and mechanical alloying. Due to a minimization of the necessary number of steps, the latter technique is more relevant to commercial processing; moreover, by involving reduction of grain size, it leads to an improvement of the thermoelectric material$^{[2][3]}$. A formation process is proposed for powders produced in this way. Elaboration of this n-type material are also presented. References$^{[1]}$ T. Caillat, J.P. Fleurial and A. Borchuckevich, J. Phys. Chem. Solids, 58 (7), 1113-1125, 1997$^{[2]}$ V. Poreev, K.A Dobryden, Izv. Akad. Nauk SSSR, Neorg. Mater., 6 (2), 203-210, 1970$^{[3]}$ K.A. Dobryden, Izv Akad. Nauk SSSR, Neorg. Mater., 10 (4), 543-557, 1974$^{[4]}$ M. Tapiero, S. Narashiki, J.G. Ges, C. Noguet, J.P. Ziegler, M. Jouch, J.L. Loison, M. Robine, Solne Energy Materials, 12, 257-274, 1985$^{[5]}$ K. Sridhar, K. Chattergha, J. Alloys and Compounds, 261, 262-268, 1998$^{[6]}$ D.M. Rowe, C.M. Brandhult, Appl. Phys. Letters, 47 (3), 255-257, 1985.

**GS.36**

**FORMATION, CRYSTAL STRUCTURE AND PHYSICAL PROPERTIES OF NOVEL THERMOELECTRIC SKUTTERUDITE Eu$_2$Fe$_4$As$_3$, Ni$_2$Ge$_3$, Andry Grytsay, Peter Rogl, Universitats Wien, Institut für Physikalische Chemie, AUSTRIA, Stefan Berger, Christoph Paul, Ernst Bauer, T.U. Wien, Institut für Experimentalphysik, AUSTRIA; Claude Godart, CNRS-UPR209, Thin, FRANCE; Bingfan Ni, Molins Abels-Elmegaid, Universität Köln, Physikalisches Institut, GERMANY, Andriana Saeone Rezende, Ricardo Ferro, Università di Genova, Dipartimento di Chimica e Chimica Industriale, ITALY; Derek Kuczorowski, W. Trzebinski, Institute For Low Temperature and Structure Research Polish Academy Of Sciences, Wroclaw, POLAND.

Alloys from the solid solution Eu$_2$Fe$_4$As$_3$, Ni$_2$Ge$_3$ were synthesized by arc-melting followed by long term annealing. From quantitative X-ray powder Russwud refinements ofsticyum was established in all

Thermoelectric materials provide an important means for reliable solid state refrigeration and for the generation of power. The skutterudite compound CoSb₃ is a thermoelectric material whose thermal and electrical properties may be decoupled through doping to produce a skutterudite structure. It has been shown that two dimensional electronic quantum confinement can enhance materials thermoelectric figure of merit and the effect for one dimensional confinement is predicted to be greater. We report the fabrication of CoSb₃ nanowire arrays by electrolytic deposition from dimethyl sulfoxide (DMSO) solutions. The wires were deposited into porous alumina templates, which were either purchased or formed in our lab by the anodization of polished aluminum sheets, to produce wire diameters of 200 nm, 100 nm, and 50 nm. The concentration, deposition time, and potential were adjusted to achieve the stoichiometric CoSb₃ composition both through the codeposition of Co and Sb from single solutions and by the deposition of alternate Co and Sb layers from separate solutions. X-ray diffraction, EDS, and SEM experiments confirmed the formation of the CoSb₃ skutterudite nanowires.

SESSION G10: NANOWIRES
Wednesday Morning, November 28, 2001
Room 208 (Hynes)

10:15 AM *G10.1
THERMOELECTRIC POTENTIAL OF BI AND BIₓ₋ₓSbₓ NANOARRAYS. M.S. Dresselhaus, Y.-M. Lin, O. Rubin, S.B. Cronin, M.R. Black, and J.Y. Ying, Massachusetts Institute of Technology, Cambridge, MA.

Alloying Bi with Pb provides another important variable in controlling the band structure of Biₓ₋ₓSbₓ nanowires and their transport properties. By varying the Bi concentration and the wire diameter, the thermoelectric figure of merit ZT can be optimized. Theoretical calculations have predicted encouraging ZT values (> 1) at 77K for Biₓ₋ₓSbₓ nanowires of easily achievable wire diameters (≈400 nm) and x in the range 0.11 ≤ x ≤ 0.15. Theoretical predictions for optimizing ZT for Bi and Biₓ₋ₓSbₓ nanowires are presented, emphasizing the unusual situation where the extremum of 10 hole pockets at the L-points, H-points and T-point are simultaneously degenerate. Experimentally, Biₓ₋ₓSbₓ nanowire arrays are fabricated by a templated-assisted process using micro-alumina membranes. Measurements of the Seebeck coefficient and of the resistance of Biₓ₋ₓSbₓ nanowire arrays over a wide range of temperatures (4K ≤ T ≤ 300K) and magnetic fields (0 T ≤ B ≤ 6T) are briefly reviewed within the context of the aforementioned model. Characterization measurements using optical spectroscopy and other techniques are summarized. The potential of the Biₓ₋ₓSbₓ nanowire system for thermoelectric applications is assessed.

10:45 AM *G10.2
SYNTHESIS AND PROPERTIES OF LEAD SELENIDE NANOCRYSTALS. L. Solodov, L. Solodova, G. Chen, W. Zhou and J. Feng, Advanced Materials Research Institute, University of New Orleans, New Orleans, LA; Christopher B. Murray, IBM T.J. Watson Research Center, Yorktown Heights, NY.
We present results of our investigation of the synthesis, structural properties and electrical transport properties of lead selenide (PbSe) nanocrystals. Stable colloidal suspensions of PbSe nanocrystals with sizes on the order of 5-10 nm were synthesized using a ligand-free thermal growth method in high-temperature organic solvents (1100°C - 2000°C). The nanocrystalline PbSe powder was characterized by X-ray scattering (WAXS/XRD/SAXS), electron microscopy and optical absorption. Thin films were formed by precipitation of the nanoparticles from solution onto insulating substrates. Depending on the deposition conditions, monodisperse or aggregated structures are formed. We show results of the macroscopic and microscopic morphology of these sintered PbSe films.

RESULTS OF ELECTRICAL CONDUCTIVITY AND SEEDED COEFFICIENT MEASUREMENTS ON THE SINTERED FILMS WILL BE DISCUSSED.

11:00 AM 10.3
PATTERN SHAPE-CONTROLLED SELF-ASSEMBLY OF PbSe, SnSe NANOCRYSTALLITES: Jie Fang, Kevin L. Stokes, Jihao He and Charles J. O’Connor. Advanced Materials Research Institute, University of New Orleans, LA.

Binary metal telluride-antimony is a very important thermoelectric material. In this work, nanocrystalline PbSe, SnSe have been prepared using a high-temperature organic solution reducing method by the presence of proper capping/stabilizing agents. By using this technique, we are able to produce PbSe, SnSe nanoparticles as small as ~12 nm in size in a monodisperse way through a size-selection post treatment. TEM characterization reveals that the as-prepared particles possess a high crystallinity in single rhombohedral phase as well as a high reproducibility. The particle size and morphology of PbSe, SnSe were then determined in our laboratory. The further engineer these particles toward the application in thermoelectric device, we have, for the first time, also demonstrated that we are able to control the pattern shape of PbSe, SnSe self-assembly from 3D to 2D by employing different solvent systems with variation of the ratio between polar and nonpolar components.

11:15 AM 10.4
THERMOELECTRIC TRANSPORT PROPERTIES OF INDIVIDUAL BISMUTH NANOWIRES: S.B. Crimin 1, Y. Lin 1, M.S. Sinder 1, R. Gronsky 1, A.M. Stone 1, O. Rubin 1, M.R. Black 1, M.S. Dresselhaus 1, 2, 3, 4. 1Department of Physics, 2Department of Electrical and Computer Engineering, 3Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA; 4Department of Materials Science, University of California, Berkeley, CA.

Bismuth nanowires have been predicted to have a high thermoelectric figure of merit due to quantum confinement of electrons and increased scattering of phonons at the wire boundary. We have synthesized Bi nanowires by filling amorphous alumina templates with molten Bi using a pressure injection method. Nanowires with diameters between 10 and 200 nm are fabricated using this scheme. In order to assess the thermoelectric transport properties accurately, the nanowires are removed from the template and the measurements are carried out on individual Bi nanowires. 4-point resistivity measurements, as well as measurements of the Seebeck coefficient, are reported for various nanowire diameters as a function of temperature. We have also fabricated Bi nanowires by electroetching Bi thin films in templates. The thermoelectric transport properties are also reported for the Bi thin film nanowire.

We gratefully acknowledge the support of MURI subcontract 0295G-7A114-01, NSF grants CTS-9527223 and DMR-98-04734, and the US Navy contract N00167-92-K-0052.

11:30 AM 10.5
PREPARATION AND CHARACTERIZATION OF Bi 2–x Sb x NANOWIRE ARRAYS: Shao Ren, Lin Hong, Zhongshan Univ, Dept of Physics, Guangzhou, PR. CHINA; Li Sun, P.C. Sorensen, Johns Hopkins Univ, Dept of Materials Sci and Eng, Baltimore, MD.

The Bi2–x Sb x nanowire arrays were synthesized by electrodeposition in amodic alumina templates. The electrolytes consisted of BiCl3, SbCl3, 0.1 M, and HCl 2.4 M in aqueous medium, with the expected molar ratio of bismuth to antimony. Three bath composition were used to synthesize nanowire arrays, that is 5%, 13%, and 50% in Sb. The composition of the wires, their crystal structure and morphology were determined by XRD, SEM, and TEM. The results was compared with the Bi:Sb film electroplated with the same electrochemical parameters and bath composition. The volume resistivity and Seebeck coefficient were studied as a function of bath composition with XRD, SEM, and TEM. The result is shown in Table 1. The obtained nanowires are different from the thin films. The films have a (102) preferred orientation when the concentration of antimony between 25% and 100% in bath solution.

11:45 AM 10.6
THERMOELECTRIC PROPERTIES OF Bi2–x Sb x NANOWIRE ARRAYS: Su-Ming Lin, Dept. of Electrical Engineering and Computer Science, G. Rubin, Dept. of Chemistry, S. Cronin, Dept. of Physics; J.Y. Ying, Dept. of Chemical Engineering, M.S. Dresselhaus, Dept. of Physics, Massachusetts Institute of Technology, Cambridge, MA.

Bi2–x Sb x alloy nanowires constitute a promising 1D system for thermoelectric applications. Recently, low-dimensional systems have been exploited extensively due to their enhanced thermoelectric performance compared to bulk materials and their potential for microcoolers which can be integrated into electronic devices.

Bi-related nanowires form an especially intriguing family of low dimensional systems because of the numerous favorable transport properties, such as small electron effective masses and high carrier mobilities, and high-quality samples have been fabricated by a rather inexpensive approach. By alloying Bi with Sb, the band structure of Bi2–x Sb x nanowires and their transport properties can be varied by varying the Sb concentration and the wire diameter to optimize ZT.

Theoretical calculations have predicted encouraging ZT values (> 1) at 77 K for Bi2–x Sb x nanowires of attainable wire diameters (< 400 nm). The Bi2–x Sb x nanowire arrays are fabricated by a template-assisted approach in amodic alumina membranes. Experimental measurements of the Seebeck coefficient and of the thermoelectric power of Bi2–x Sb x nanowire arrays will be presented for a wide range of temperatures (4 K < T < 300 K) and diameters; there will be a short period where the wire is supercooled before the Joule heating reaches the cold end. In this way, a current pulse applied to a cooler running at maximum ZT can temporarily achieve and maintain a temperature difference of several hundred degrees Celsius.

SESSION 11: DEVICES II
Chair: Ali Shakeri

Wednesday, November 28, 2001
Room 208 (Hyne's)

1:45 PM G11.1
SUPERCOOLING OF THERMOELECTRIC DEVICE USING A CURRENT PULSE: G. Jeffrey Snyder, Jean-Pierre Freulich, Thierry Cuillers, Jet Propulsion Laboratory, California Institute of Technology. Pasadena, CA.

In a thermoelectric cooler, the Peltier effect is normally used to cool the device in the thermoelectric element, such that a maximum temperature difference, ΔT, is achieved at a particular current I_mew. During steady state operation, if the currents are increased above I_mew, the inrush Joule heating will be greater than the increased Peltier cooling resulting in a net decrease of ΔT. However, since Peltier cooling occurs instantaneously at the cold junction, when Joule heating occurs throughout the length of the device and not just at the cold end, there will be a short period where the cold junction is supercooled before the Joule heating reaches the cold end. In this way, a current pulse applied to a cooler running at maximum ZT can temporarily achieve and maintain a temperature difference of several hundred degrees Celsius.

2:00 PM G11.2
FULLY-INTEGRATED MICRO-SIZED THIN-FILM HEATER AND COMPUTER-BASED ACCURATE MEASUREMENT OF TEMPERATURE PROFILE BY USING THIN-FILM THERMOCOUPLES: Byung-Koo Kim, Hyojoo Jung, Jung-Sik Lee, Sang-Ki Joe, School of Materials Science and Engineering, Seoul National University, Seoul, KOREA.

The integrated thin film heater and thin film thermocouple have potential MEMS applications, such as miniaturized pressure sensor, flow meter, medical surgery, inkjet printer head, and so on. Thus, much research has been performed on this topic. Metallaclaid (TaSi2 and TaSi2) heater with micro-meter wide was fabricated using photolithography process and its thermal response behavior by applying a square pulse of voltage at variable frequencies (up to several hundreds Hz) using a function generator was investigated. Also, the spatial temperature profile was measured by thin film thermocouples made by sputtering. We actually made and compared metal silicide heater and polycrystalline silicon heater. It turned out that metallaclaid heater was superior in thermal response and thermal accumulation side effect caused by repeatedly applied voltage pulses. To measure accurate temperature, the silicon heater was passivated with SiO2 layer before the deposition of thin film thermocouples to prevent the thermoelectric power of the thin-film thermocouple from being interfered with pulse input power. An array

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of K-type (alumel and chromel) thermocouples was deposited by sputtering and patterned by photolithography. The thermocouples had multiple junctions that could measure the temperature at different points, simultaneously. This array of thermocouple outputs were synchronized with voltage pulses and monitored by computer-based measurement tools through specially designed probing system. The composition of thin film thermocouple was analyzed by Auger depth profile system and thermoelectric power was calibrated against commercially available thermocouple in furnace. Also, it was confirmed that the composition of thin film thermocouple was the same as that of commercially available one. In this work, we show metallic-alloy heater and also thin film thermocouple is powerful tool in monitoring the temperature profiles of heater and/or any type of integrated device of which we want to know the real temperature.

2:15 PM G11.3
THIN FILM DISPENSER CATHODES FOR THERMIONIC MICRO-DEVICES. Kevin R. Zawadzki, and Donald B. King, Sandia National Laboratories, Albuquerque, NM

Energy conversion, high frequency microwave transmission, and directed energy applications would all benefit from the development of a thermionic micro-device that utilizes an electron emissive thin film. High fluence, state-of-the-art emitters are dispensable structures based on CuO impregnation into a porous W matrix. This type of macro-cathode is not amenable to incorporation into a micro-device.

We demonstrate a method of producing emissive films that mimic the structure and properties of a macro-dispenser using RF sputter deposition. The films are deposited on chemically oxidized W and BaCuxOy (4:1:1.5 Ba:Cu:O) layers with various metal terminating layers. We find the resulting films are electron emissive at temperatures ranging from 800 to 1300 K. Grating array sputter ion guns were used to show the micro-film structure, and chemistry evolve with film annealing producing free Ba due to W reduction of the ternary oxide, W layer coalescence into particles and void formation. (Photo)electron spectroscopies and current/voltage characterization show that emission is defined by surface dipole formation due to Ba population, as well as other additives of the surface. The emission properties can be tuned by controlling both the individual metal and oxide layer thickness and the deposition conditions to yield either metal or oxide terminated surfaces. These surfaces show low, uniform work functions ranging from 1.5 to 2.2 eV and moderate apparent emission coefficients of 6 A/cm²Kelv. Recent efforts are focused on incorporating Re and SrC at the surface to further minimize the work function. Our work demonstrates that the mechanisms used for Ba generation and transport in nano-dispenser cathodes can also be built into thin film structures. Sandia is a multi-program laboratory operated by Sandia Corporation; a Lockheed Martin Company, for the U.S. Department of Energy under contract DE-AC04-94AL85000.

SESSION G12: OXIDES
Chair: Terry M. Tritt
Wednesday Afternoon, November 28, 2001
Room 208 (Hynes)

3:00 PM G12.1
GROWTH MECHANISM AND THERMOELECTRIC PROPERTIES OF LONG CO-BASED OXIDE WHISKERS. Ryoji Fumihashi, Ichiro Matsubara, Minshiro Shikano, National Institute of Advanced Industrial Science and Technology, Kawasaki, Osaka, JAPAN

Thermoelectric power generation using waste heat is expected to develop as a valuable energy source in the next few decades. Recently, CuO-based layered oxides have attracted much attention as promising thermoelectric materials because of their excellent properties and high chemical stability at high temperature in air. Two kinds of single-crystalline whiskers of (Bi,Sr)Oy (BiO2)2 (BC-222) and (Ca,Cu)Oy (CaO2)2 (CaO2-222) phases were grown from the surface of glassy and crystallized precursors by annealing in an Ar gas flow. The phases of the whiskers can be controlled by the Co content of the precursors. The average compositions of the whiskers grown from the glassy precursors are Bi1.5 (Sr,Ca)1.5 CuO2-y and (Ca, Sr, Bi)1.5 CuO2-y. Although the Co-222 whiskers are 1.0 mm at the longest, the BC-222 whiskers reach lengths of as much as 1.0 cm. The length of the whiskers depends on the microstructure of the precursor phases. The result of microstructural characterization indicates that the growth points of the whiskers are their bases. Seebeck coefficient and resistivity of both of Co-222 and BC-222 whiskers are higher than 200 μV/K and 100 μΩ cm, respectively. The whisker phases seem to have a pseudomorphic relationship at the Nernst level of which the formation is effective to enhance Seebeck coefficient. Thermal conductivity of the Co-222 and BC-222 samples is suppressed to low values at high temperature because of their layered structure. The Co-222 and the BC-222 are model compounds of phonon-glass and electron-crystal. Oxides are promising thermoelectric materials for high temperature application.

3:15 PM G12.2
EFFECTS OF CATION DOPING ON THE THERMIELECTRIC PROPERTIES IN Cu2O: Ichiro Matsubara, Ryoji Fumihashi, Minshiro Shikano, National Institute of Advanced Industrial Science and Technology, Osaka, JAPAN, Kei Sasaki, Osaka Electro-Communication University, Osaka, JAPAN

Since the discovery of a large power factor in Na2CoO2, extensive studies on Co-based oxides with a layered structure have been carried out. Very recently, it has been reported that p-type Sr- and Bi-doped Ca2-O single crystal whiskers have a figure of merit ZT of over 1.2 at T > 800°C in air. This compound has a layered structure, in which triple rock salt-type (Ca, Sr)CuO2 layers and single Cd-type CaO2 layers are stacked alternately. Due to the high ZT value of the whisker, this type of material is expected to be applied to thermoelectric power generators. In this study, we have investigated the effects of cation doping on the thermoelectric properties of the compound using co-doping. Two types of material were examined, a commercial sample and a sample prepared by a combinatorial approach to synthesize the cation doped Ca2O thin films rapidly and evaluated the solid solution range. In the compounds of Ca2+Mn+2CoO2 (M = Mg, Sr, Ba, and Bi), pure phase was formed for x < 0.5. For Sr and Bi co-doped Ca2O-CoO2 sample shows the highest power factor.

3:30 PM G12.3
THERMOELECTRIC PROPERTIES OF CdIn2Se5 (A = In+4, Ln+3 AND Bi+3) CERAMICS. Weiling Luo, Yue Jin Shan, Meauro Jock, Hiroki Izumi Department of Applied Chemistry, Faculty of Engineering, Usanomiy University, Suita, Osaka, JAPAN

CdTeO2 is a perovskite-type oxide with 1:1 Baite ordered structure. Pure CdTeO2 is commonly regarded as a good insulator because its comprising cations, Cd2+ and Te4+, possess the same closed-shell electronic configurations as 10-electrons. It was accidentally found by us that its electric conductivity could be decreased or increased by a few orders of magnitude with the varying of temperature. To modify its electric properties, we tried to dope electrons into CdTeO2 by way of introducing oxygen vacancies and subsequent O2- ions by thermal treatment, such as In2+3, Ln3+ and Bi3+. Polycrystalline samples of Cd5+2A3Te5 (A = In3+, Ln3+ and Bi3+) were synthesized by a solid state reaction method. The element consturations of samples were determined by IC and they were investigated and compared with that of pure CdTeO2. The conductivities of Cd5+2A3Te5 (A = In3+, Ln3+ and Bi3+) showed a metallocopic behavior with very slight temperature dependence and were higher than that of three other cubic phases, Cd5+2O3Te5, which indicates the doped-samples become to semiconductors. Moreover, it was found that the conductivity of the samples could be increased by several orders by annealing under nitrogen flow. The resistivities of CdIn2Se5 measured in nitrogen at 800°C were at the order of mΩ cm at room temperature. The negative Seebeck coefficients obtained from all samples indicate that electrons are the charge carriers. The absolute values of these Seebeck coefficients are less than 10 μV/K, which is very small. The CdTeO2 can be obtained with tetragonal crystal structure in various proportions containing lanthanide ions. These results indicate that CdTeO2 is a promising material for thermoelectric applications.

3:45 PM G12.4
SYNTHESIS AND CHARACTERIZATION OF SINGLE CRYSTALINE NANOWIRES OF SILVER SELENIDE THROUGH A SOLID PHASE REACTION. Byron Gross, Nouran Xia, Univ of Washington, Dept of Chemistry, Seattle, WA, Vicying Wu, Peiking Yang, Univ of California, Dept of Chemistry, Berkeley, CA

We have recently demonstrated a topotactic reaction, through which single crystal nanowires of trigonal selenium could be converted to silver selenide (a well-known thermoelectric material) with almost no change in the morphology and crystallinity. The silver selenide nanowires could exist in a tetragonal or orthorhombic phase, depending on the dimensions of these nanowires. We will present the experimental procedure, as well as some preliminary results on the thermoelectric properties of these nanowires.
4:00 PM GI12.5
LARGE THERMOPOWER IN METALLIC MISFIT COBALT OXIDES, L. De Angelis, S. Hébert, A. Maguin, D. Pellegin, M. Hervieu and B. Raveau, Laboratoire CERMAT, UMR CNRS 1584, 6508, Cen, FRANCE.

The misfit cobalt oxides crystallize in composite structures built of CoO$_2$ layers of the CdI$_2$ type stacked with rock salt (RS) type layers. Although these cobalt oxides exhibit metallic behavior, their room-temperature thermopower (TEP) is large (typically -10/N K) and their thermoelectrical conductivity is low (~2W/Km) at 300K. Among this class of layered oxides, physical properties of the Bi, Pb)/Sr/Co/O and Ca/Co/O misfits have been mainly studied. More recently, we have studied the T/Co/O misfit. Interestingly, the transport and magnetic properties of this oxide are remarkable. This oxide is metallic and paramagnetic down to 2K and its magnetoresistance is positive whereas, at low temperature, all the other misfits exhibit reentrant resistivities and large negative magnetoresistance. The thermoelectrical transport and magnetic of the Tebased misfit is also very large. In order to understand the underlying physics governing the properties of the oxide misfits, cationic substitutions at the level of Bi, Pb/Pb-1, T/Co/O layers have been attempted. Although the structures, studied by transmission electron microscopy, are kept unchanged by these substitutions, modifications in the transport properties are evidenced. On the one hand, the large TEP is ascribed to the unusual low-spin state configurations of the mixed-valent $\text{Co}^{2+}$/Co$^{3+}$ which are stabilized in the Co$_2$Ir$_2$O$_7$ lattice. On the other hand, changes in the $a_2g$ and e$_g$ band filling induced by cationic substitutions are responsible for the existence of spin-polarized transport at low temperature in the magnetically ordered state explaining the large negative magnetoresistance observed in substituted T/Co/O misfit.

SESSION GI13: CHALCOGENIDES II
Chair: Mercouri G. Kanatzidis
Thursday Morning, November 29, 2001
Room 208 (Hynes)

8:30 AM GI13.1
ELECTRONIC STRUCTURE OF $\text{K}_2\text{Bi}_2\text{Se}_3$ J. Larson, D. Bicum, S.D. Mahanth, Michigan State University, Department of Physics and Astronomy, East Lansing, MI; M.G. Kanatzidis, Michigan State University, Department of Chemistry, East Lansing, MI

$\text{K}_2\text{Bi}_2\text{Se}_3$ belongs to a class of complex Bi-Te-Se systems which have great potential for thermoelectric performance. This compound forms in two distinct crystal structures, orthorhombic Bi$_2$Te$_2$Se$_3$ with space group P11 and monoclinic with space group P2$_1$/n. To understand their thermoelectric properties we have carried out band structure calculations within ab initio density functional theory (DFT) and a linearized augmented plane wave (LAPW) method implemented in WIEN97 code. Both scalar relativistic correction and spin-orbit interaction (SOI) were included. For exchange and correlation, we used Perdew-Burke-Ernzerhof potential which incorporate gradient approximation (GGA). The effect of the SOI on the band structure of $\text{K}_2\text{Bi}_2\text{Se}_3$ is to shift the conduction band down relative to the valence band and thereby decrease the gap from 0.76 eV to 0.47 eV, which is smaller than the experimental value (0.75 eV). There are however direct gaps at the X point (0.76 eV) and at the V point (0.72 eV) in the Brillouin zone. The low electrical conductivity and high thermopower are consistent with the gap found in this system. The effective mass calculations show a highly anisotropic (2D) electron transport and small anisotropy in the hole transport. This suggests better thermoelectric properties for the electron-doped systems. $\text{K}_2\text{Bi}_2\text{Se}_3$ has a mixed occupancy of Bi and K atoms within unit cells of the crystal structure. The measured gap in this compound is 0.56 eV. We have calculated the electronic structure for different configurations with assumed extreme occupancy of the two misfit sites stated above. How the band structure depends on these assumptions will be discussed in detail. While the Bi-K disorder has been suspected to reduce thermal conductivity, this disorder also can have a profound effect on the electronic structure near the Fermi energy.

Work supported by ONR/DARPA

8:45 AM GI13.2
CRYSTAL GROWTH, STRUCUTURAL CHARACTERIZATION AND THERMOELECTRIC PROPERTIES OF $\text{K}_2\text{Bi}_2\text{S}_3$ SOLID SOLUTIONS, Theodora Kyrs, Dung-Yang Chang, Mercouri G. Kanatzidis, Dept of Chemistry, Michigan State University, MI; Jeffrey S. Dyck, Olav Uher, Dept of Physics, University of Michigan, Ann Arbor, MI; Konstantinos M. Patsakisopoulos, Dept of Physics, Aristotle University of Thessaloniki, Thessaloniki, GREECE.

Our efforts to improve the thermoelectric properties of $\text{K}_2\text{Bi}_2\text{Se}_3$, led to systematic studies of solid solutions of the type $\text{K}_2\text{Bi}_2\text{S}_{1-x}\text{Se}_x$. Crystallographic data of selected members of the solid solutions were collected in order to determine the distribution of $\text{Se}$ and $\text{Bi}$ in the lattice sites. Results show that these materials are not true solid solutions as judged by the inhomogeneous $\text{Se}/\text{Bi}$ distribution in the structure. The charge transport, semiconducting band gaps, melting points and thermoelectrical conductivities were studied as a function of $x$. A modified peak current technique was used to obtain well-oriented ingots for charge transport and thermal conductivity measurements. The thermoelectric properties of these materials are strongly anisotropic. Doping studies aimed to improve the power factor will be presented.

9:00 AM GI13.3
THE MECHANICAL CHARACTERIZATION OF BISMUTH TELLURIDE BASED THERMOELECTRIC MATERIALS, Wodi Brotwos, Kevin P. Mennd, Univ of North Texas, Laboratory of Advanced Materials & Optimized Materials, Dept of Materials Science, Denton, TX; John B. White, Marlow Industries Inc, Dallas, TX.

The thermoelectric properties of bismuth telluride based thermoelectric (TE) materials are well-characterized, but comparatively little has been published on the mechanical and thermo-mechanical properties of these materials. In this paper, we present the initial dynamic mechanical analysis (DMA) data for type and p-type bismuth telluride based TE materials. The effect of sample height on flexural 3-point bending results was quantified and storage modulus, loss modulus and tan delta data are presented. The data suggest that the DMA geometry factor b does not sufficiently compensate for differing sample dimensions under these test conditions. Flexural 3-point bending results for one n-type material with sample dimensions of 5.2 mm by 4.8 mm showed a storage modulus of 63 MPa in the direction parallel to the van der Waals planes and 40 MPa in the perpendicular direction. Tan delta data gives information about energy dissipation modes and for these TE materials include grain boundaries, crack defects caused by intergranular failures, and also the van der Waals or cleavage planes associated with the microstructure of the Brégman growth method. In general, samples measured perpendicular to the van der Waals planes appear to have higher tan delta values. The tan delta values for these TE materials approach that of glassy or crystalline polymers and are greater than ten times the tan delta of structural metals. We also present flexural and compressive DMA results for materials that show changes in mechanical properties that correlate to specific differential scanning calorimetry (DSC) thermal transitions. The DMA data also show a change in modulus as a function of temperature.

9:15 AM GI13.4
INITIAL ASSESSMENT OF THE THERMOELECTRIC PROPERTIES FOR THE MIXED SYSTEM $\text{Rb}_2\text{Bi}_2\text{S}_3$ $\text{K}_2\text{Bi}_2\text{Se}_3$, John R. Ireland, C.R. Kranewurf, Dept of Electrical and Computer Engineering, Northwestern University, Evanston, IL; Theodora Kyrs, Mercouri G. Kanatzidis, Dept of Chemistry and Center for Materials Research, Michigan State University, East Lansing, MI.

Previous studies of the K-BiSe based compounds with various dopants have resulted in several compositions with promising transport characteristics for thermoelectric applications. The specific system $\text{Rb}_2\text{Bi}_2\text{S}_3$, $\text{K}_2\text{Bi}_2\text{Se}_3$, exhibits both a promising electrical conductivity and Seebeck coefficient at room temperature and shows with significant improvements in the power factor achieved through the introduction of n-type dopants. Further this study has continued with the solid solutions of $\text{Rb}_2\text{Bi}_2\text{Se}_{1-x}\text{S}_x$, (0 ≤ x ≤ 2). It is known that in the neighborhood of X = 1 there is a structure change; thus this study enhances changes in thermoelectric properties both as a function of X and as a function of the type and amount of dopant introduced into the system. Where possible samples of both single crystal and polycrystalline ingot material were employed in the transport measurements. Some additional comparisons will be made to the results obtained for other systems. Research at both NU and MSU was supported by the ONR (N0014-98-1-0431) and by DARPA through ARPA (DAAG55-05-1-0184). Work at NU made use of Central Facilities supported by the NSF through the Materials Research Center (DMR-0107616).

9:30 AM GI13.5

There is a promising future for the application of thermoelectric materials in energy conversion devices because they offer cooling and electricity generation capabilities in compact, solid-state devices.
Nevertheless, their applications are limited because they can achieve only 10% of the Carnot efficiency. However, it has been demonstrated that reduced thermal conductivity is the primary reason for the low square efficiency. For this reason, our study focuses on using porous alumina templates to obtain ordered arrays of thermoelectric nanowires. The best opportunity for creating commercially viable nanowire devices is to employ Si and Se doped Bi$_2$Te$_3$ nanowires. The electrochemical behavior of these materials will be presented as well as their characterization using X-Ray diffraction (XRD), scanning electron microscopy (SEM) in conjunction with energy dispersive spectroscopy (EDS).

SESSION GI4 - CLATHRATES II
Chair: Otto F. Staley
Thursday Morning, November 29, 2001
Room 208 (Hynes)

10:15 AM GI4.1
C$_8$H$_8$ AND Cu$^{2+}$/Na$^{2+}$ NM R STUDIES OF Cu$_8$(Na$_8$)Ge$_{16}$
CLATHRATES. R.F. Marsalek, Arizona State Univ., Dept. of Physics, Tempe, AZ; G.S. Nolte, Department of Physics, University of South Florida, Tampa, FL; J. Gryko, Jacksonville State Univ., Jacksonville, AL.

C$_8$(Na$_8$)Ge$_{16}$ clathrate shows large paramagnetic shift for cesium in C$_8$H$_8$ NM R spectrum and no paramagnetic shift for sodium in NaZB resonance. Germium clathrate is different from C$_8$(Na$_8$)Si$_{16}$ (NaZB) that shows large shift for both cesium and sodium signals. We investigate the nature of these shifts as a function of sodium content and temperature.

10:30 AM GI4.2
PURIFICATION AND THERMOELECTRIC STUDY OF TYPE I Ge CLATHRATES. J. Daniel Bryan, Galen D. Stucky, Dept. of Chemistry, University of California, Santa Barbara, CA; Bo B. Iversen, Dept. of Chemistry, University of Arkansas, Arkansas C, DENMARK.

Impurity concentrations in the synthesized inorganic clathrate compounds Mg$_2$Ge$_2$Ge$_2$ (M = Ba, Sr) have been largely dictated by the parts per thousand impurities found in the alkaline earth elements. In semiconductors, these levels of impurity can be responsible for orders of magnitude change in the transport properties. To isolate and estimate the contributions by these impurities to the thermoelectric properties, we have prepared purified samples of Ba$_2$Ge$_2$Ge$_2$ by zone melting. This technique brings the impurity levels down to parts per million. We present a thermoelectric study of these compounds as a function of chemical purity and compare this data to the known literature values.

10:45 AM GI4.3
MAXIMUM-ENTROPY METHOD ANALYSIS OF THERMAL MOTION AND DISORDER IN THERMOELECTRIC CLATHRATE Ba$_8$Ga$_6$Sb$_3$O$_3$. Bo B. Iversen, Anders Bentien, Department of Chemistry, University of Arkansas, DENMARK; Dan Bryan, Galen Stucky, Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA; Anders E.C. Palmqvist, Department of Applied Surface Chemistry, Chalmers University of Technology, SWEDEN; Art Schultz, Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, IL.

By applying the Debye and Einstein models, Sales and coworkers [1] have shown that for framework structures even the most basic crystallographic parameters (Uco) can provide a quite accurate estimate of the lattice thermal conductivity as well as the Einstein temperature for the "rattler". However, while standard anisotropic atomic displacement parameters (ADPs) are obtained in every crystallographic study, no study has attempted a detailed experimental analysis of the thermal motion of a thermoelectric framework material. Accurate crystallographic data allow evaluation of not only the harmonic components of the atomic motion, but also the anharmonic effects [2]. The conventional approach to thermal motion analysis is reciprocal space structure factor fitting, where parameters describing harmonic as well as anharmonic components of the atomic motion are introduced in the structure factor expression. The maximum entropy method (MEM) provides an alternative approach [3]. MEM analysis of neutron diffraction data yields the direct space nuclear density distribution (NDD), which can be analyzed with probability density function models. For the present study of Ba$_8$Ga$_6$Sb$_3$O$_3$ single crystal neutron diffraction data at 15, 100, 150, 200, 300, 450, 600, 900 K were collected on the SCD instrument at IPNS. Reciprocal space structure factor fitting (including anharmonic Grune-Charlier coefficients) as well as direct space fitting to One Particle Potential models of the MEM nuclear density has been carried out. The analysis provides experimental estimates of the guest atom force constants, and reveals that Ba[2] has a temperature dependent disorder. It is shown that anharmonicity