

SYMPOSIUM G

Thermoelectric Materials 2001—Research and Applications

November 26 – 29, 2001

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* Invited paper

SESSION G1: GUIDANCE TO ADVANCED TE
RESEARCH

Chair: George S. Nolas
Monday Morning, November 26, 2001
Room 208 (Hynes)

10:45 AM *G1.1

OVERVIEW OF VARIOUS STRATEGIES FOR THE DEVELOPMENT OF NEW BULK MATERIALS FOR THERMOELECTRIC APPLICATIONS. Terry M. Tritt, Dept of Physics and Astronomy, Clemson University, Clemson, SC.

Recently, there has been a renewed interest in thermoelectric material research. There are a number of different systems of potential thermoelectric materials that are under investigation by various research groups. Some of these efforts focus on 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 pentatellurides (e.g. HfTe_5), quasicrystals (e.g. $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ and $\text{Cd}_{5.7}\text{Yb}$), half-heusler alloys (e.g. $\text{TiNiSn}_{1-x}\text{Sb}_x$), skutterudites (e.g. $\text{CeFe}_x\text{Co}_{4-x}\text{Sb}_{12}$) and clathrates (e.g. $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$). 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 *G1.2

ELECTRONIC BAND STRUCTURE CALCULATIONS FOR THE IDENTIFICATION AND OPTIMIZATION OF NOVEL THERMOELECTRICS. 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 NaCoO_2 .

11:45 AM G1.3

THERMODYNAMIC CALCULATIONS IN NEW THERMOELECTRIC MATERIALS. APPLICATION TO PROCESSES. J.C. Tedenac, M.C. Record, Laboratoire de Physico-Chimie de la Matière Condensée, Université de Montpellier 2 - Sciences et Techniques du Languedoc, Montpellier, FRANCE; S.G. Fries, ACCESS e.V. RWTH Aachen, Itzesstrasse, GERMANY.

Performances enhancement of thermoelectric modules can be obtained by a good knowledge of the materials constitution involved in their fabrication. Its depends on a relevant thermodynamic analysis of the material. Improvement of the figure of merit in thermoelectric materials depends on multiple factors (crystallographic structure, electronic structure, phonons 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: a - 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 method, we will present an overview of computational approach of the phase equilibria in multicomponent systems used in thermoelectric materials. The CALPHAD approach uses Gibbs energy descriptions in order to calculate phase equilibria as an add to optimize performance, design and tailor materials. The main objective of this method is to constitute available materials databases 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 equilibria, add to the understanding solidification and the resulting microstructures obtained by hot pressing or ball milling 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.

SESSION G2: SKUTTERUDITES I

Chair: David C. Johnson
Monday Afternoon, November 26, 2001
Room 208 (Hynes)

1:30 PM G2.1

LATTICE VIBRATION OF YTTERBIUM FILLED SKUTTERUDITES: AN INELASTIC ELECTRON TUNNELING STUDY. Jiro Nagao, Marhoun Ferhat, Devaraj Nataraj, Tsutomu Uchida, Satoshi Takeya, Tokao Ebinuma, Institute for Energy Utilization, National Institute of Advanced Industrial Science and Technology (AIST), Sapporo, JAPAN; Hiroaki Anno, Kakuei Matsubara, Dept of Electronics and Computer Science, Science University of Tokyo in Yamaguchi, Onoda, JAPAN; Eiji Hatta, Kōichi Mukasa, Nano-electronics Laboratory, Graduate School of Engineering, Hokkaido University, Sapporo, JAPAN.

Inelastic electron tunneling experiments were performed on $\text{Yb}_x\text{Co}_4\text{Sb}_{12}$ -Al oxide-Al junctions measured at 4.2K. A peak observed at $\sim 7\text{meV}$ 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 CoSb_3 . 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.

Resistivity and thermopower data is presented on Eu-doped CoSb_3 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. $\text{Eu}_{0.43}\text{Co}_4\text{Sb}_{11.59}\text{Ge}_{0.31}$ and $\text{Eu}_{0.42}\text{Co}_4\text{Sb}_{11.37}\text{Ge}_{0.5}$ exhibit an enhanced figure of merit as compared to the CoSb_3 and $\text{Eu}_{0.2}\text{Co}_4\text{Sb}_{12}$. The room temperature value of ZT has been measured for the $\text{Eu}_{0.42}\text{Co}_4\text{Sb}_{11.37}\text{Ge}_{0.5}$ skutterudite as $ZT \approx 0.26$ and also has a value of $ZT > 1$ above 675 K. The other samples had a lower ZT at room temperature with $ZT = 0.1$ and $ZT = 0.19$ for the $\text{Eu}_{0.43}\text{Co}_4\text{Sb}_{11.59}\text{Ge}_{0.31}$ and the $\text{Eu}_{0.2}\text{Co}_4\text{Sb}_{12}$ 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 CoSb_3 is underway and will also be discussed.

2:00 PM *G2.3

HIGH PRESSURE SYNTHESIS OF NEW FILLED-SKUTTERUDITES. Hirotsugu Takizawa, Ken-ichi Okazaki, Kyota Uheda, Tadashi Endo, Tohoku Univ, Dept of Materials Chemistry, Sendai, JAPAN.

Germanium and tin atoms were inserted into the CoSb_3 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, $\text{M}_x\text{Co}_4\text{Sb}_{12}$ ($\text{M}=\text{Ge}, \text{Sn}$). 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 inserted tin atoms exhibit very large 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 "rattler" in the CoSb_3 host lattice.

2:30 PM G2.4

ELECTRONIC STRUCTURE AND THERMOELECTRIC PROPERTIES OF YTTERBIUM-FILLED SKUTTERUDITES. Hiroaki Anno, Kazuhiro Ashida, Kakuei Matsubara, Science Univ of Tokyo in Yamaguchi, Dept of Electronics and Computer Science, Onoda, JAPAN; George S. Nolas, Department of Physics, University of South Florida, Tampa, FL; Koji Akai, Mitsuru Matsuura, Yamaguchi Univ, Dept of Advanced Materials Science and Engineering, Ube, JAPAN; Jiro Nagao, 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-filled CoSb₃ skutterudites for an understanding of the effect of Yb filling on the thermoelectric properties. The valence-band structure of Yb-filled CoSb₃ 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 α 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 CoSb₃ were clearly 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-filled CoSb₃ 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.

2:45 PM G2.5

SYNTHESIS AND THERMOELECTRIC PROPERTIES OF CoP₃.
Virgil Shields, Thierry Caillat, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA.

In an effort to expand the range of operation for highly efficient, segmented thermoelectric unicouples currently being developed at the Jet Propulsion Laboratory (JPL), skutterudite phosphides are being investigated as potential high temperature segments to supplement antimonide segments that limit the use of these unicouples at a hot-side temperature of about 600-700°C. We report here on the synthesis and transport properties of one of these phosphides materials, CoP₃. Large amounts of cobalt triphosphide have been prepared by direct reaction from stoichiometric powders at synthesis temperatures ranging from 600 to 950°C. The synthesized powders were analyzed by x-ray diffractometry and hot pressed at 1000°C. The samples were analyzed by microprobe analysis and electrical conductivity, Seebeck voltage and thermal conductivity measurements were performed. The thermoelectric properties are presented and discussed as a function of temperature up to 800°C. Initial thermal stability results are presented to assess the potential of this material for high temperature operation.

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 Cd_{5.7}Yb QUASICRYSTALS. A.L. Pope, Terry M. Tritt, Dept of Physics and Astronomy, Clemson Univ, Clemson, SC; R. Gagnon, J. Strom-Olsen, Dept of Physics, McGill University, Montreal, CANADA.

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 Cd_{5.7}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 Cd_{5.7}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, leaving the appearance of a "negligible lattice contribution". In addition, no semblance 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.

3:45 PM G3.2

CROSS-PLANE THERMOELECTRIC PROPERTIES OF Si/Ge SUPERLATTICES. Bao Yang, Gang Chen, Mechanical and Aerospace Engineering Department; Jianlin Liu, Kang Wang, Electrical Engineering Department, University of California, Los Angeles, CA.

In this paper, a set of methods is developed to measure the seebeck coefficient, electrical conductivity, and thermal conductivity in the cross-plane direction of thin films. The method employs

microfabricated heaters, voltage and temperature sensors, and phase lock schemes to determine the temperature and voltage oscillation in the cross-plane direction of the sample. Then, the thermal conductivity and Seebeck coefficient of thin film are determined simultaneously. The cross-plane electrical conductivity is also measured by a modified transmission line method. These methods are applied to Si/Ge superlattices grown by molecular beam epitaxy.

4:00 PM *G3.3

NANODOT MATERIALS AND DEVICES IN PbSnSeTe-BASED QUANTUM DOT SUPERLATTICES. T.C. Harman, Patrick Taylor, M.P. Walsh, B.J. Laforge and G.W. Turner, Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, MA.

High-quality PbSnSeTe-based QDSL quantum-dot superlattice (QDSL) structures have been grown by molecular beam epitaxy and investigated for high thermoelectric figures of merit ZT. Background information on the band structure and properties of PbSnSeTe-based materials (in which the 300 K energy gap can approach zero) are presented. Our initial objective of demonstrating that high ZT values with QDSL materials (conservatively estimated at 0.9 at 300 K) and 2.0 at 550 K has been achieved. We have demonstrated QDSL thermoelectric uncouple devices with greater than 17 K cooling below room temperature in highly unoptimized devices. It is anticipated that thermoelectric microcoolers, with thousands of thermocouples based on QDSL materials, should be capable of efficiently pumping up to approximately 200 W/cm² over a 20 to 50 K temperature difference.

4:30 PM G3.4

DOPING AND ALLOYING TRENDS IN NEW THERMOELECTRIC MATERIALS. Sim Loo^a, Sangeeta Lal^a, Duck-Young Chung^b, Kuei-Fang Hsu^b, Doretta Kyratsi^b, Mercuri G. Kanatzidis^b, Timothy P. Hogan^a. ^aDepartment of Electrical and Computer Engineering, Michigan State University, East Lansing, MI; ^bChemistry Department, Michigan State University, East Lansing, MI.

New thermoelectric bulk materials such as CsBi₄Te₆ have shown superior properties to traditional materials, however, optimal performance requires continuing investigations of doping and alloying trends. A recently modified high throughput measurement system is presented for doping and alloying investigations in several new thermoelectric materials. The modification includes a four-probe configuration for more accurate measurements while maintaining a relatively short sample preparation time. The system is fully computer controlled and provides flexible contacts to accommodate various sample dimensions. Optimal compositions are then identified for further investigations in thermoelectric prototype modules. The most promising materials will be further characterized for electrical conductivity, thermoelectric power, thermal conductivity, and Hall effect measurements as a function of temperature.

4:45 PM G3.5

COMMERCIAL APPARATUS FOR MEASURING THERMAL TRANSPORT PROPERTIES FROM 1.9 TO 390 KELVIN.
N.R. Dilley, R.C. Black, L. Montes, A. Wilson, M.B. Simmonds, Quantum Design, Inc., San Diego, CA.

We have developed an instrument which simultaneously measures the thermal conductivity κ , Seebeck coefficient α , and electrical resistivity ρ of a sample, thereby determining the thermoelectric figure of merit $Z = \alpha^2/\rho\kappa$. A Quantum Design Physical Property Measurement System (PPMS) provides the temperature control from 1.9 - 390 K and applied magnetic fields of up to 14 tesla. Two small probes mounted along the sample each contain thin film Cernox chip thermometers as well as electrical contacts to monitor the temperature and voltage drops across the sample. A third probe attached to the end of the sample provides a heater and current source to stimulate the sample both thermally and electrically. The sample's response to cyclic heat pulses is analyzed in real time using DSP techniques. A nonlinear least-squares fit is used, employing a two time-constant model to determine both the thermal conductivity and the Seebeck coefficient for the material. Data acquisition using these ac techniques are expedited since we can sweep both temperature and field during a measurement. Adaptive algorithms continually adjust the thermal and electrical stimuli applied to the sample, optimizing the speed and accuracy of the measurement. We present results from some of the materials measured so far, including thermoelectric research materials and Pb in the superconducting state.

SESSION G4: CLATHRATES I

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

8:30 AM G4.1

RESONANT ULTRASOUND SPECTROSCOPY STUDIES OF

CLATHRATE THERMOELECTRICS. Veerle Keppens, Michael McGuire, and Alem Teklu, National Center for Physical Acoustics and Dept. of Physics, The University of Mississippi, University, MS; David Mandrus and Brian Sales, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Resonant Ultrasound Spectroscopy (RUS) measurements have been carried out for 3 cubic clathrate materials: $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$, $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$, and $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$. In these materials, the Ba, Sr and Eu ions rattle in oversized atomic cages. They have attracted attention as promising thermoelectric materials, having thermal conductivities comparable to glasses while maintaining crystalline electronic properties. RUS has proven to be useful for the study of similar cage-like materials [1], identifying 2 local modes in the filled skutterudite $\text{La}_{0.75}\text{Fe}_3\text{CoSb}_{12}$. 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 $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ 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.

[1] V. Keppens et al., Nature 395, 876-878 (1998).

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 Nolas, Department of Physics, University of South Florida, Tampa, FL.

Materials with both low thermal conductivity due to efficient phonon coupling and high electrical conductivity (Slack's so called phonon glass/electron crystal, or PGEC) offer promise as thermoelectric materials. Herein we report thermal properties of several semiconductor clathrates: $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$, $\text{Sr}_8\text{Zn}_8\text{Ge}_{38}$, $\text{Cs}_8\text{Ga}_8\text{Sn}_{38}$ and $\text{Ba}_8\text{Ga}_{16}\text{Si}_{30}$. In these structures, generalized as $\text{M}_8\text{X}_a\text{Y}_{46-a}$, M is a guest in a 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 optic modes associated with guest rattling on the thermal properties.

9:00 AM *G4.3

THEORETICAL STUDY OF RATTLING ATOMS AND THEIR INFLUENCE ON THE LATTICE THERMAL CONDUCTIVITY IN CLATHRATE-FRAMEWORK SEMICONDUCTORS. Otto F. Sankey^a, Jianjun Dong^b, and Charles W. Myles^c, ^aArizona State University, Tempe, AZ; ^bAuburn University, Auburn, AL; ^cTexas 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 produce local vibrational modes. We search for trends 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 evaluating 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. F. Chen, K.L. Stokes, Advanced Material Research Institute, University of New Orleans, New Orleans, LA; G.S. Nolas, Department of Physics, University of South Florida, Tampa, FL.

We measured the temperature dependence of electrical conductivity (σ) and thermopower (S) of $\text{Cs}_8\text{Zn}_4\text{Sn}_{42}$ 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 $\text{Cs}_8\text{Sn}_{44}$. However, the relaxation effect of σ for $\text{Cs}_8\text{Zn}_4\text{Sn}_{42}$ was negligible in contrast with that of $\text{Cs}_8\text{Sn}_{44}$. We will also present the result of $\text{Rb}_8\text{Zn}_4\text{Sn}_{42}$ for further comparison. The results suggest that the vacancy played an important role in transport properties for tin clathrates under high pressure.

9:45 AM G4.5

Abstract Withdrawn.

SESSION G5: CHALCOGENIDES I

Chair: Tim P. Hogan

Tuesday Morning, November 27, 2001
Room 208 (Hynes)

10:30 AM *G5.1

SEARCH FOR NEW THERMOELECTRIC MATERIALS THROUGH EXPLORATORY SOLID STATE CHEMISTRY.

Mercouri G. Kanatzidis, Dept. of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, MI.

Our current focus in solid state exploratory synthesis involves the search for new phases with superior thermoelectric applications. Particularly, the chemistry of complex ternary and quaternary systems of heavy element (Pb and Bi) main group chalcogenides is under investigation and several new materials have been discovered. Our synthetic strategy and selection criteria will be outlined and recent results will be reported. The new materials have complex compositions and structures and they routinely possess very low thermal conductivity. The main challenges lie in increasing the power factor and in several cases we have met these challenges. We will present the structures and properties of these systems and give an initial assessment of their properties. Finally, we will report doping studies on CsBi_4Te_6 which we reported previously that it has favorable properties for low temperature thermoelectric applications. *This work is supported by ONR and DARPA.

11:00 AM G5.2

ELECTRICAL AND THERMAL TRANSPORT OF RARE EARTH DOPED PENTATELLURIDES. Nathan D. Lowhorn, Terry M. Tritt, R.T. Littleton IV, Dept. of Physics and Astronomy, Clemson Univ, Clemson, SC; J.W. Kolis, Dept. of Chemistry, Clemson Univ, Clemson, SC.

The transition metal pentatellurides HfTe_5 and ZrTe_5 exhibit a broad resistive anomaly as a function of temperature. This behavior is also reflected in the thermopower as it changes from a large positive value below room temperature to a large negative value at lower temperatures with the zero crossing corresponding well with the peak temperature of the resistive anomaly. The large values of the thermopower at low temperatures ($T \approx 150$ K) have made these materials attractive for investigation for potential low temperature thermoelectric applications. The magnitude of the resistive peak and the peak temperature are highly sensitive to doping as well as external influences such as magnetic field and pressure. In this study we examine the effect of doping with various rare elements and the subsequent effects on the electrical and thermal transport properties such as the electrical resistivity, thermopower, and thermal conductivity. These results will be discussed in relation to potential thermoelectric performance of these materials.

11:15 AM G5.3

RAMAN SCATTERING IN Sb DOPED TRANSITION METAL PENTATELLURIDES $\text{ZrTe}_{5-x}\text{Sb}_x$. K. McGuire, Nathan Lowhorn, T.M. Tritt, A.M. Rao, Clemson Univ, Dept of Physics & Astronomy, Clemson, SC.

The resistivity anomaly and the corresponding thermopower in ZrTe_5 are sensitive to doping with Sb[1]. A series of doped $\text{ZrTe}_{5-x}\text{Sb}_x$ have been prepared with $0 < x < 0.2$, where x is the nominal Sb concentration. X-ray diffraction data revealed that the pentatelluride structure prevails at all doping concentrations. We have measured the Raman spectra of $\text{ZrTe}_{5-x}\text{Sb}_x$ in the 90-300 cm^{-1} range and compared them to the corresponding spectrum for the parent material ZrTe_5 . With increasing Sb concentration, the line widths for three of the four peaks observed at 115, 120, 147 cm^{-1} in the parent material are severely broadened with insignificant change in the line width for the fourth peak at 180 cm^{-1} . Interestingly, the peak intensity for the mode at 180 cm^{-1} gradually diminishes in $\text{ZrTe}_{5-x}\text{Sb}_x$ up to $x=0.15$, and is completely vanished in the $x=0.20$ compound. Implications of the disappearance of the resistivity anomaly with concomitant vanishing of 180 cm^{-1} Raman mode in the $x=0.20$ compound will be presented. [1] R.T. Littleton et al., Phys. Rev. B (in press).

11:30 AM G5.4

SYNTHETIC INVESTIGATIONS IN THE A/Sb/Q (A = K, Rb, Cs; Q = Se, Te) SYSTEM AND COMPOSITIONAL MANIPULATIONS FOR GOOD THERMOELECTRIC PROPERTIES. Duck-Young Chung, Theodora Kyratsi, Mercouri G. Kanatzidis, Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, MI; John Ireland, Carl R. Kannewurf, Department of Electrical Engineering and Computer Science, Northwestern University, Evanston, IL.

Antimony is an important element in the field of thermoelectric materials. The p-type leg of a room temperature thermoelectric device

is practically based on Sb_2Te_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/Sb/Q (A = K, Rb, Cs; Q = Se, Te) system. Most of known antimony 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-DOT HETEROSTRUCTURES. Patrick J. Taylor, Theodore C. Harman, Michael P. Walsh, Brian E. LaForge, Richard L. Slattery, George W. Turner, 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 hetero-interface 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 quantitative analysis of the size and distribution of PbSeTe/PbTe quantum-dot heterostructures by transmission electron microscopy. In addition, we present a novel Mire fringe contrast technique (using transmission electron microscopy) to directly determine the state of lattice misfit strain relaxation of PbTeSe quantum dot heterostructures 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 No. F19628-00-0002. The opinions, interpretations, conclusions, and recommendations are those of the authors and are not necessarily endorsed by the Department of Defense.

SESSION G6: DEVICES I

Chair: Thierry Caillat
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. Rama Venkatasubramanian, Edward Siivola, Brooks O'Quinn, Thomas Colpitts, Research Triangle Institute, Research Triangle Park, NC.

A major goal of our Thermoelectrics program has been to demonstrate significant enhancement in figure-of-merit (ZT) at 300K using the concept of phonon-blocking electron-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 translate the high ZT of the material to high coefficient of performance (COP) in cooling devices and demonstrate $\sim 1000 \text{ W/cm}^2$ cooling power densities in thin-film thermoelectric devices. The high-performance superlattice materials and the extremely low specific contact resistivities ($\rho_c < 3 \times 10^{-8} \text{ Ohm-cm}^2$) achievable in devices have allowed us to demonstrate an extrinsic device figure-of-merit (ZTe) of as much as ~ 2.4 at 300K by the conventional Harman method in p-type $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattice thermoelements. We have also obtained ZTe of about ~ 1.2 to 1.4 in n-type superlattice thermoelements at 300K. In addition, we have obtained 32K and 40K sub-ambient cooling at 298K and 353K, respectively, in p-type superlattice micro-thermoelements. We have utilized a semi-infinite heat source for determining the coefficient of performance (COP) of thermoelements; a COP of ~ 5 was deduced for 17.5K cooling at 360K with an estimated heat load of $\sim 535 \text{ W/cm}^2$ for the p-type micro-thermoelements. We have fabricated p-n couples using these micro-thermoelements, 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-thermoelements are also extremely fast-acting, about a factor of 23000 better than bulk thermoelectric technology. These results have allowed us to extend into the concept of high-performance anywhere, any time active cooling and heating TM. We will present results to demonstrate this concept with IR-imaging of superlattice micro-thermoelements.

1:45 PM G6.2

THERMOELECTRIC MODULE FOR LOW TEMPERATURE APPLICATIONS. Timothy P. Hogan^a, Sangeeta Lal^a, Sim Loo^a, Duck-Young Chung^b, Theodora Kyratsi^b, Mercouri G. Kanatzidis^b, Charles Cauchy^c, ^aElectrical and Computer Engineering Department, Michigan State University, East Lansing, MI; ^bChemistry Department, Michigan State University, East Lansing, MI; ^cTellurex 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 involves a combination of the properties of the two branches of the module. Here, we investigate the fabrication of a module with a new low temperature material, CsBi_4Te_6 (p-type), and the best known low temperature n-type material $\text{Bi}_{15}\text{Sb}_{15}$. Transport measurements for each of these materials show high performance at low temperatures. Known values for the figure of merit Z_{max} of CsBi_4Te_6 is $3.5 \times 10^{-3}/\text{K}$ at 225K and for $\text{Bi}_{15}\text{Sb}_{15}$ is $\sim 6.5 \times 10^{-3}/\text{K}$ at 77K. At 100K these values drop to $2.0 \times 10^{-3}/\text{K}$ for CsBi_4Te_6 and $\sim 6.0 \times 10^{-3}/\text{K}$ for $\text{Bi}_{15}\text{Sb}_{15}$. Theoretical simulations based on these data show a cooling of $\Delta T = 12\text{K}$ at 100K, which is almost three times the efficiency of a Bi_2Te_3 module at that temperature. We present transport measurements of elements used 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 FILMS OF THERMOELECTRIC MATERIALS. Jean-Pierre Fleurial, Jennifer A. Herman, Nick Stoltz, G. Jeffrey Snyder, Chen-Kuo Huang and Margaret A. Ryan, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA.

Electrochemical deposition is a promising alternative approach 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 interests focus on n-type and p-type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ alloys as well as other attractive thermoelectric materials such as $\text{PbTe}_{1-x}\text{Se}_x$, 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_2Te_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

THERMIONIC REFRIGERATION WITH AN IMPROVED EMITTER. Yoshikazu Hishinuma, Boris Y. Mozyzhes, 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 resistivity. We investigate a layer of low electron affinity semiconductor which overcoats the metallic emitter. The semiconductor surface eliminates emission of electrons below the Fermi level and thus produces current with a higher Peltier coefficient. Under the influence of a strong electric field ($10^6 - 10^7 \text{ V/cm}$), the height of the potential barrier is 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, dielectric 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 calculations show that emitters covered with 50Å of semiconductor with electron affinity of 0.5eV can produce a cooling power of few W/cm^2 with a Peltier coefficient of $\sim 0.4\text{V}$ for electric field of 2 MV/cm.

2:30 PM G6.5

CONSERVATION OF LATERAL MOMENTUM IN HETERO-STRUCTURE INTEGRATED THERMIONIC COOLERS. Daryoosh Vashaee, Ali Shakouri, 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-lattice scatterings tend to restore the quasi-equilibrium Fermi distribution in the cathode by absorbing energy from the lattice, and thus, cooling the emitter junction. If the lateral momentum 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 is no conservation of lateral momentum, the number of electrons participating in thermionic emission will dramatically increase. We have studied electrical transport in a range of 4-350K for several thin film heterostructure cooler devices and found that lateral momentum 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 total 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. Gehong Zeng, Xiaofeng Fan, Edward Croke^a, Chris

LaBounty, Daryoosh Vashae^b, Ali Shakouri^b, and John E. Bowers, Department of Electrical and Computer Engineering University of California, Santa Barbara, CA; ^aHRL Laboratories, LLC, Malibu, CA; ^bBaskin 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/Si superlattice structure was grown on 5-inch silicon substrates by molecular beam epitaxy. Thin 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 load and also as a temperature sensor. Cooling power density up to 600 W/cm² was measured at a heat sink temperature of 25°C for 40 X 40 μm² devices. * This project is supported by DARPA HERETIC program and the Army Research Office.

SESSION G7: NEW MATERIALS, APPROACHES AND MEASUREMENTS II

Chair: Kakuei Matsubara
Tuesday Afternoon, November 27, 2001
Room 208 (Hynes)

3:30 PM G7.1

REDUCTION OF LATTICE THERMAL CONDUCTIVITY IN BALL-MILLED AND SHOCK-COMPACTED TiNiSn HALF-HEUSLER ALLOYS. S. Bhattacharya, Terry M. Tritt, Dept of Physics and Astronomy, Clemson Univ, Clemson, SC; Y. Xia, V. Ponnambalam, S.J. Poon, Dept of Physics, Univ of Virginia, Charlottesville, VA; N. Thadhani, Dept of MS&E, Georgia Institute of Technology, Atlanta, GA.

Half-Heusler alloys are currently being investigated for their potential as thermoelectric materials. They exhibit high negative thermopower (40-250 μV/K) and favorable electrical resistivity (0.1-8 mΩ·cm) at room temperature. Attractive power factors ($\alpha^2\sigma T$) of about (0.2-1.0 W/m·K) at room temperature and about 4.5 W/m·K at 650 K have been reported in these materials. However, in order to achieve a high figure-of-merit in the half-Heusler alloys, the relatively high thermal conductivity in these materials (~10 W/m·K) must be reduced. The thermal conductivity in these materials is composed primarily of a lattice contribution, with a comparatively small electronic component. 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/m·K) in some Ti-based half-Heusler alloys which have been prepared by ball milling and followed by shock-compaction. This process resulted into reduced grain sizes (less than 4 μm) in these materials, which corresponds to a smaller lattice thermal conductivity. These microstructural 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, Bryan Chakoumakos, David Mandrus, Rongying Jin, Jim Thompson, Solid State Division, ORNL, Oak Ridge, TN; Veerle Keppens, National Center for Physical Acoustics, University of Mississippi, Oxford, MS.

Cage compounds such as the skutterudites and semiconducting

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 CRYSTAL. Hideoto Imai, Yuichi 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), S^2/ρ , at 300 K was 37.1 μW/K²cm with $\rho = 1.7$ mΩcm and $S = -251$ μV/K. Its electrical resistivity showed metallic and highly anisotropic behavior, suggesting that the electronic structure of this compound has a quasi-two-dimensional nature. The carrier density was 2.8×10^{20} 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 conductive layers, leading to a large ZT. Atom intercalation into the van der Waals gap is a promising approach, and we will also report on the results.

4:30 PM G7.4

THERMAL AND ELECTRICAL PROPERTIES OF CZOCHRALSKI GROWN GeSi SINGLE CRYSTALS. Ichiro Yonenaga, Takaya Akashi, Takashi 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 the thermoelectric parameters, thermal conductivity, electrical conductivity and Seebeck coefficient of high quality bulk single crystals of Ge_{1-x}Si_x alloys in the various composition 0.8 < x < 1 were investigated in the temperature range 300 ~ 1000 K for application to 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 GeSi 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 GeSi alloys.

4:45 PM G7.5

SYNTHESIS OF HEAVY DOPED SILICON-GERMANIUM ALLOY WITH UNIFORM STRUCTURE BY SPLAT SOLIDIFICATION IN MICROGRAVITY. Hideaki Nagai, Yoshinori Nakata, Hideki Minagawa, Masataka Sasamori, Takeshi Okutani, AIST, Microgravity Materials Lab., Sapporo, JAPAN.

Si-Ge alloy have been studied as a thermoelectric semiconductor. However, it is difficult to synthesize the uniform Si-Ge 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 difference in the densities of the constituent elements. By rapidly solidification of this homogeneous melt, it is possible to synthesize the uniform Si-Ge alloy with heavy dopant. In this study, heavy doped Si-Ge alloy (Si/Ge=4 in atomic ratio) was synthesized by splat solidification on the rotating copper block in vacuum. The starting material of Si-Ge alloy was prepared by arc melting in Ar atmosphere. Arc melted sample was mixture of Si rich phase and Ge rich phase. When Si-Ge melt was kept in 1.2s microgravity using 10m drop tower and dropped

from alumina nozzle at the braking of drop capsule, the solidified sample had uniform structure and similar composition to the starting material. The solidified sample was sintered by 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-arc melted one. The electric conductivity of the sintered sample was similar to that of as-arc melted one. Other thermoelectric property will be presented at this meeting.

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

G8.1
NON-EQUILIBRIUM ELECTRONS AND PHONONS IN
HETEROSTRUCTURE INTEGRATED THERMIONIC COOLERS.
Daryoosh Vashaee, Ali Shakouri, University of California, Jack Baskin
School of Engineering, Santa Cruz, CA.

The effect of hot carriers on electron transport in single barrier thermionic 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 a strong impact on the device operation. 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 analysis. In a thermoelectric/thermionic device one measures 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 current 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.D.L. Chung, 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 these composites 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 laminae 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 Jacquot, L.P.M., Ecole des Mines, Parc de Saurupt, Nancy,
FRANCE; Maria Dinescu, NILPRP, Laser Department, Bucharest,
ROMANIA.

Lead telluride (PbTe) thin films, as well as Te/PbTe and Bi/PbTe multilayers, were prepared by pulsed deposition from a Nd:YAG laser working at a wavelength of 532 nm. The films were deposited under vacuum onto silica/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 Bi_{0.5}Sb_{1.5}Te₃ AND n-TYPE Bi₂Te_{2.7}Se_{0.3} FILMS
DEPOSITED BY PULSED LASER ABLATION. M.S. Raghuvveer, K.
Jagannadham, North Carolina State University, Department of
Materials Science and Engineering, 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 Bi_{0.5}Sb_{1.5}Te₃, n-type Bi₂Te_{2.7}Se_{0.3} and n-type with SbI₃ doping were deposited on mica substrates using Nd-YAG pulsed laser ablation at temperatures ranging from 300°C to 500°C. These 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 (00n) alignment with the substrates. The film quality in terms of stoichiometry and crystal 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.F. Radkowski III, Timothy D. Sands,
Graduate Group in Applied Science and Technology, University of
California, Berkeley, CA.

The Peltier 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 Peltier 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/wavenumber electron and phonon states. Transport within each material and across the interface is governed by coordinated 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 currents 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 dissimilarity of the separate band 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. Jun Wang, Daniel Marshall,
Motorola Labs, Physical Sciences Research Labs, Tempe, AZ; Nikolay
Zein, Gregory Khrenov, Soft-Tec, Moscow, RUSSIA.

The electronic structure of a crystalline boron carbide has an energy forbidden gap of ~3eV and 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 bipolaron through localized defects were developed, accordingly. Although the bipolaron electrical conductivity model does not rely on any specific types of defect, the bipolaron formation in boron carbide is believed to be a defective C-B-B intraicosahedral chain in connection with a B₁₁C icosahedron. The current study examined the existing theory of bipolaron electrical conductivity by performing a systematical study on the formation energies of the defects in boron carbide using a state-of-the-art *ab-initio* electronic structure method. The studied defects cover a) stoichiometric variations 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 $B_{11}C$ icosahedra connected by C-B-C intricosahedral chains, *i.e.* consistent with the reported structural model of B_4C . When carbon concentration is reduced, however, the population of C-B-C chain is found to be intact, while the population of $B_{11}C$ icosahedron is reduced by the replacements of B_{12} icosahedron. This observation is fundamentally different from the existing 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.

G8.7

SYNTHESIS OF BORON-RICH METAL BORIDES AND THEIR THERMOELECTRIC PROPERTIES. Masatoshi Takeda, Ferrer Domingo, Takahiro Miura, Tadahiro Fukuda, Nagaoka University of Technology, Dept of Mechanical Engineering, Niigata, JAPAN.

Polycrystalline metal borides $AlMgB_{14}$, MB_6 ($M = Ca$ and rare earth metals), and MB_2 ($M =$ transition metals) were prepared by using PECS (Pulse Electric Current Sintering) technique. Single phase of orthorhombic $AlMgB_{14}$, which contains B_{12} icosahedral clusters as building blocks, was obtained at sintering temperatures between 1573 K and 1823 K, while higher sintering temperatures lead to the appearance of $\gamma-AlB_{12}$ -type phase. Seebeck coefficient (α) and electrical conductivity (σ) of the $AlMgB_{14}$ at room temperature was about 600 ($\mu V/K$) and 10^{-1} ($1/\Omega m$), respectively. Such large α and low σ are comparable to those of metal doped β -rhombohedral boron. MB_2 -type materials such as TiB_2 and VB_2 , which have layered structure comprising interleaved two-dimensional boron and metal layers, were also synthesized. They have metallic property with large σ (more than 10^6 ($1/\Omega m$)), and their α was enhanced up to 20 ($\mu V/K$) by substituting metal atoms with other metals. Further increase is expected. The MB_6 hexaborides are cubic phase whose structure is a three-dimensional skeleton constituted of B_6 octahedral clusters, and the interstices of which are filled by metal atoms. The α and the σ of the synthesized CaB_6 were about 200 ($\mu V/K$) and 10^4 ($1/\Omega m$) 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.

G8.8

FORMATION OF BISMUTH-SILICA NANOCOMPOSITE VIA HIGH-ENERGY BALL MILLING. Matthew A. Meitl, 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 composites via high-energy ball milling in argon with a Spex 8000 Mixer/Mill. As determined by transmission electron microscopy (TEM), the average diameter of the bismuth particles decreased to 10 nm after 16 hours of milling. By 40 hours, the X-ray diffraction peaks vanish, and finally, after 62 hours, the Bi nanoparticles are not observed in TEM samples due either to the formation of a Bi-silica solid solution or the oxidation of Bi metal to bismuth oxide. The 10 nm Bi nanoparticles formed after 16 hours of milling should be sufficiently small to exhibit quantum confinement. Measurements of the electronic properties of these nanophase Bi-silica composite materials as a function of milling time and Bi volume fraction are currently underway.

G8.9

THE FABRICATION AND THERMOELECTRIC PROPERTIES OF AMORPHOUS Si/Ge BULK SAMPLES. Sangmin Lee, Yoichi Okamoto, Toshio Kawahara, Jun Morimoto, National Defense Academy, Dept of MS&E, Yokosuka, JAPAN.

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

G8.10

HIGH TEMPERATURE ELECTRICAL TRANSPORT PROPERTIES OF Eu AND Yb-DOPED SKUTTERUDITES. R.H. Tedstrom, 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. Sample 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.

G8.11

ANNEALING STUDIES OF Re DOPED $AlPdMn$ QUASICRYSTALS. D.W. Winkler, A.L. Pope, Terry M. Tritt, Dept of Physics and Astronomy, Clemson Univ, Clemson, SC; R. Gagnon, J. Strom-Olsen, Dept of Physics and Astronomy, McGill Univ, Montreal, CANADA.

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. $AlPdMn$ quasicrystal samples were prepared with various levels of Re substitution for the Mn ($AlPdMn_{1-x}Re_x$) 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, $10 K < T < 300 K$. The relationship between the electrical and thermal transport properties and microstructure will be presented and discussed.

G8.12

THERMOELECTRIC PROPERTIES OF $AlCuFe$ QUASICRYSTALS AND THEIR APPROXIMANTS. P.N. Alboni, A.L. Pope, Terry M. Tritt, Clemson Univ, Clemson, SC; A.R. Ross, C. Jenks, P. Thiel, Ames National Laboratory, Ames, IA.

In the search for new thermoelectric materials, quasicrystals have been investigated due to their inherently low thermal conductivity. Crystalline phases closely related to the quasicrystals, however, have largely been ignored. These closely related phases are approximants that have similar structure, 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 are presented. The viability of the $i-AlCuFe$ quasicrystalline system and the ω and β approximant phases as thermoelectric materials is discussed.

G8.13

MICROSTRUCTURAL EVOLUTION OF La-DOPED SiB_6 HIGH TEMPERATURE THERMOELECTRIC MATERIAL DURING A SPARK PLASMA SINTERING. D.W. Lee, J.H. Won, J.K. Park, K.H. Kim, J. Matsushita^a, K.B. Shim, CPRC Hanyang Univ, Seoul, KOREA. ^aTokai Univ, JAPAN.

SiB_6 has proved to be a potentially useful material because of its excellent thermoelectrical properties above 700°C, low specific gravity, high degree of hardness, and moderate melting point. SiB_6 , which has poor sinterability with a conventional sintering technique due to the covalent characteristic, has been successfully densified fully using a spark plasma sintering (SPS) method. The SPS-processed specimens consisted of SiB_6 , SiB_4 and Si_2B_3 phases. Pure SiB_6 powder were densified fully at the sintering temperature of 1600°C. In particular, it was formed that the rare earth element was very effective in evolving the microstructure of SiB_6 phase, resulting in reducing the sintering temperature and controlling grain growth. These effects were discussed in details in terms of microstructure evolution during the SPS process.

G8.14

THERMOELECTRIC PERFORMANCE OF DOPED Ni-Co-O POLYCRYSTALLINE OXIDES. Junbo Wu, Jun Nan, and Ce Wen Nan, Tsinghua Univ, Dept of Mater Sci & Eng, Beijing, CHINA; Wuhan Univ of Tech, Adv Mater Res Inst, Wuhan, CHINA.

Thermoelectric oxide semiconductors have recently been paid much attention in the literature. In this paper, Na- and Li-doped Ni-Co-O based polycrystalline samples were studied. The oxide powder was prepared by a soft chemical approach, and then was sintered in form of compressed pellets. 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 conductivity. 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.

G8.15

CHEMICAL SYNTHESIS OF $Ca_9Co_{12}O_{28}$ AND THERMOELECTRIC PROPERTIES. Shengli Chen, Jun Nan, and Ce Wen Nan, Tsinghua Univ, Dept of Mater Sci & Eng, Beijing,

CHINA and Wuhan Univ of Tech, Adv Mater Res Inst, Wuhan, CHINA.

Composite oxide $\text{Ca}_9\text{Co}_12\text{O}_{28}$, 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 a CaO layer and CoO₂ 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 from 573K up to 1073K. The Seebeck coefficient increases dramatically with increasing temperature. The results indicate that the thermoelectric properties can be improved further by optimizing the preparation method.

G8.16

SYNTHESIS AND THERMOELECTRIC PROPERTIES OF $(\text{Na}_x\text{Ca}_{1-x})_3\text{Co}_4\text{O}_{9+\delta}$ ($x=0.05-0.2$) POLYCRYSTALLINE OXIDES. Jun Nan, Xisong Zhou, Junbo Wu and Ce Wen Nan, Dept of Mater Sci & Engineering, Tsinghua Univ, Beijing, CHINA and Adv Mater Res Institute, Wuhan Univ of Tech, Wuhan, CHINA.

Oxides ceramics have recently been attracted much attention as promising thermoelectric material due to their special potential of applications in power generation using waste heat. In this paper, $(\text{Na}_x\text{Ca}_{1-x})_3\text{Co}_4\text{O}_9$ ($x=0.05-0.2$) 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. The electrical conductivity and the power factor increase with increasing temperature. The Seebeck coefficients decrease with increasing Na dopant amount. The figure of merit of the oxide samples is smaller than that of traditional thermoelectric alloys, which is about 210-4 1/K at 700.

G8.17

THERMOELECTRIC PROPERTIES AND STRUCTURAL CHARACTERIZATION IN $\text{SnTe-Bi}_2\text{Te}_3$ ALLOY. Xisong Zhou, Jun Nan, Junbo Wu, and Ce Wen Nan, Tsinghua Univ, Dept of Mater Sci & Eng, Beijing, CHINA; Wuhan Univ of Tech, Adv Mater Res Inst, Wuhan, CHINA.

Modern high efficient thermoelectric cooling device calls for development of steady materials with higher ZT. One of the novel promising approaches is to combine bismuth telluride with other elements and to synthesis new ternary compounds. In this paper $\text{SnTe-Bi}_2\text{Te}_3$ 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 layers. Among all of the compounds, SnBi_2Te_4 exhibits better thermoelectric performance around 400K. Thermal conductivity is extremely low beyond conventional judgment. With Sb doping the carrier concentration can be optimized, and hence the total electrical conductivity increases. There is still room for enhancing the thermoelectric performance.

G8.18

THERMOELECTRIC PROPERTIES OF PbSe EPITAXIAL THIN FILMS AND PbSe/EuS HETEROSTRUCTURES. Mildred S. Dresselhaus, Gene Dresselhaus, MIT, Dept of Physics, Cambridge, MA; Elena I. Rogacheva, Tatyana V. Tavrina, Sergey N. Grigorov, Konstantin A. Nasedkin, Valentine V. Volobuev, Alexander Yu. Sipatov, National Technical University "Kharkov Polytechnic Institute", Kharkov, 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 present work is preparation of PbSe epitaxial thin films and PbSe/EuS 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). PbSe thin films were prepared by thermal evaporation of PbSe in vacuum and subsequent deposition onto (001) KCl surfaces at 570 K. EuS was grown on PbSe layers using electron-beam evaporation. Electron microscopy studies revealed a "vapor-crystal" mode of film growth in the [001] 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 freshly 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 oxygen forms on the film surface. Covering PbSe films with a 30 nm thick EuS layer fully protects a PbSe film from oxidation. In PbSe/EuS heterostructures, extrema in

behavior were observed in the dependences of the thermoelectric parameters on d and explained by the transition from an island-like film structure to a continuous film and by a self-organization effect that was most pronounced at certain thicknesses (30 nm). The magnetoresistance also has pronounced extrema at the indicated thicknesses. These observations provide additional means for controlling properties of PbSe-based thin film structures.

G8.19

TEMPERATURE AND THICKNESS DEPENDENCES OF THERMOELECTRIC PROPERTIES OF PbS/EuS BILAYERS.

Elena I. Rogacheva, Sergey N. Grigorov, Tatyana V. Tavrina, Olga N. Nashchekina, Yegor O. Vekhov, Alexander Yu. Sipatov, Valentine V. Volobuev, National Technical University "Kharkov Polytechnic Institute", Kharkov, UKRAINE; Mildred S. Dresselhaus, MIT, Dept of Physics, Cambridge, MA.

A significant increase in the thermoelectric power factor upon decreasing the PbS well width in PbS/EuS superlattices attracts attention to a detailed study of both the growth mechanisms and the optimization of the thermoelectric parameters of these superlattices. In particular, it is important to study the role of the PbS buffer layer in determining the kinetic properties of the superlattices. In the present work, the influence of the PbS thickness d (varying between 2 and 200 nm) with a fixed thickness of the EuS layer (about 30 nm) on the thermoelectric properties of PbS/EuS bilayers grown by thermal evaporation and vacuum deposition on (001)KCl substrates was studied. The temperature dependences of the electrical conductivity, the Hall coefficient, charge carrier mobility, and thermopower in the range of 77-300 K were measured. Electron microscopy studies showed that PbS grows on KCl in the island-like fashion and forms a continuous film at 40 nm thickness. All the studied bilayers manifested n -type electrical conductivity. The dependences of the thermoelectric properties on d were found to be non-monotonic: at $d = 15$ nm, extrema in the properties and the highest values of the thermoelectric power factor were observed. This phenomenon was attributed to percolation effects connected with the transition from an island-like film to a continuous film and with the defect formation in the film. It was found that the character of the temperature dependences of the thermoelectric properties changes qualitatively with increasing d . At $d < 10$ nm, PbS/EuS bilayers have a negative thermal coefficient of resistance. The possibility of potential barriers giving rise to an activated conductivity at small d is discussed. In the temperature dependences of films with thicknesses corresponding to the extrema in the thermoelectric parameters, non-monotonic behavior in the form of steps and oscillations is observed, indicative of system instability.

G8.20

THERMOELECTRIC NANOWIRES BY ELECTROCHEMICAL DEPOSITION. Oded Rabin^a, Yu-Ming Lin^b, Stephen B. Cronin^c, Mildred S. Dresselhaus^{b,c}, Massachusetts Institute of Technology, MA; ^aDept. of Chemistry; ^bDept. of Electrical Engineering and Computer Science; ^cDept. of Physics, Cambridge, MA.

Nanowires made of thermoelectric-relevant materials were grown by electrochemical deposition. Their diameter and ordering are dictated by the porous alumina template that is fabricated on the working electrode prior to the deposition. The composition of the nanowires is controlled by the composition of the electrolyte and the deposition potential. This technique offers unique opportunities in the range of structures and materials that can be employed. The structural and transport properties of these wires will be presented, and comparison will be made to nanowires synthesized by other techniques.

G8.21

Abstract Withdrawn.

G8.22

Abstract Withdrawn.

G8.23

THERMOELECTRIC PROPERTIES AND CRYSTAL AND ELECTRONIC STRUCTURES OF A LAYERED-STRUCTURE MATERIAL InGaZnO_4 . Hideto Imai, Hidekazu Kimura, Yuichi Shimakawa, 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 (2-D) electronic state. An YFe_2O_4 -type layered InGaZnO_4 , which consists of InO_2 and GaZnO_2 layers, was expected to show such 2-D characteristics. A small amount of oxygen defects produces highly conductive carriers in the 2-D InO_2 layers. The insulating nature of the GaZnO_2 layer, on the other hand, is thought to come from the small overlapping between the 4s orbitals of Ga and Zn due to the difference of the z -coordinates of Ga and Zn in the GaZnO_2 layers[1]. In the present study, we investigated thermoelectric properties of

InGaZnO₄ and its dimensionality by transport measurements, structure analysis and the electronic band structure calculation. Electron-doped (In_{0.9}Sn_{0.1})GaZnO_{4-δ} was found to have the highest figure-of-merit, ZT , 0.04 at 300 K with ρ of 5 mΩcm, S of -68 μV/K, κ of 42 mW/Kcm, and n of 6×10^{18} cm⁻³. Both magnitude and T -dependence of S are well explained in terms of the 3-D effective-mass approximation using the measured carrier density, and no enhancement of S was observed; that is, the result of transport measurement suggests 3-D nature of the material. Structure analysis by neutron-diffraction data and EXAFS studies revealed that the z -coordinates of Ga and Zn were different by 3~4% as speculated by Orita *et al.*[1] However, the band-structure calculation using the obtained structural parameters predicted a considerable 3-D conduction due to the overlapping of the In $5s$ and Ga $4s$ orbitals. This result is consistent with our transport results, but in sharp contrast with the previous speculation of 2-D electronic structure from cluster-model calculation [1].
[1] M. Orita, *et al.*, PRB **61**, 1811 (2000).

G8.24
THERMOELECTRIC PROPERTIES OF Bi-Sb-Te-X COMPOUNDS PREPARED BY MA-PDS METHOD. Yong-ho 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-Sb-Te materials doped with Ag, BN and Ag&BN. 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%Bi₂Te₃-75%Sb₂Te₃ alloy by doping a small amount of Ag. The doping content was optimized at 0.01-0.02wt%, which corresponds to the maximum figure-of-merit of 3.4×10^{-3} /K. Doping of BN or Ag&BN, however yields extremely low values of Seebeck coefficient, finally resulting in a low figure-of-merit.

G8.25
STRUCTURE AND THERMOELECTRIC PROPERTIES OF NEW LAYERED COMPOUNDS IN THE QUATERNARY SYSTEM Cs-Pb-Bi-Te. Kuei-Fang Hsu, Duck-Young Chung, Antje Mrotzek, 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 CsBi₄Te₆ exhibits promising thermoelectric properties. In an effort to explore the ultimate performance of this compound, we introduce Pb metal into its layered framework. Consequently, the four new compounds of CsPbBi₃Te₆ (**1**), CsPb₂Bi₃Te₇ (**2**), CsPb₃Bi₃Te₈ (**3**) and CsPb₄Bi₃Te₉ (**4**) were obtained by the reactions of CsBi₄Te₆ with increasing content of PbTe. The four compounds adopt novel layered 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_mBi₃Te_{5+m} ($m = 1$ to 4).

G8.26
HALL CARRIER MOBILITY OF THERMOELECTRIC AgBiTe₂-Ag₂Te COMPOSITES. T. Sakakibara, Aisin Seiki Co., Ltd., Aichi, JAPAN and Univ. of Miyazaki, Miyazaki, JAPAN; Y. Takigawa, Osaka Electro-Communication Univ., Dept of Electronics Engineering, Osaka, JAPAN; K. Kurosawa, Univ. of Miyazaki, Dept of Electrical and Electronics Engineering, Miyazaki, JAPAN.

In order to realize higher speed and larger capacity optical communication systems, performance of thermoelectric devices must be improved for diode laser refrigeration. However, the figure-of-merits for thermoelectric materials have not been remarkably improved for thirty years. The most popular means to improve the figure of merits are increasing the effective mass or mobility of carriers or decreasing the lattice thermal conductivity. [1] In this paper, we propose a novel way to increase the carrier mobility by forming composites. We prepared a series of (AgBiTe₂)_{1-x}(Ag₂Te)_x ($0 \leq x \leq 1$) composite materials by means of melt and cool down. [2] Hall coefficients and electrical conductivity were measured by a standard van der Pauw technique in the temperature rang from 93K to 283K, and then Hall carrier mobility were calculated from these data. The mobility of Ag₂Te is much larger than that of AgBiTe₂. A composite (AgBiTe₂)_{0.125}(Ag₂Te)_{0.875} showed the higher value than Ag₂Te below 243K. Around 143K at which the carrier type changes from

p-type to n-type with increasing the temperature in Ag₂Te, there is a competition between the negative and positive carriers in both phases, resulting in enhancement of the mobility.
[1] R.P. Chasmar and R. Stratton, J. Electron. Control, 7, 52 (1959)
[2] Y. Takigawa, T. Imoto, T. Sakakibara, K. Kurosawa, Mat. Res. Soc. Symp. Proc., Vol. 545, p105 (1999).

G8.27
GEOMETRIC EFFECTS ON THE TRANSIENT COOLING OF THERMOELECTRIC COOLERS. R.G. Yang, G. Chen, Mechanical and Aerospace Engineering Department, University of California at Los Angeles, Los Angeles, CA; G.J. Snyder, J.-P. Fleurial, Jet Propulsion Laboratory-California Institute of Technology, Pasadena, CA.

Transient thermoelectric cooling effect has been proposed and demonstrated for decades [1]. Changing transient pulse shape [2] and using conical shape thermoelectric legs [3] have been conjectured to further decrease the minimum transient temperature. In this paper, we investigated systematically the current pulse shape effects and thermoelectric shape effects on the transient performance including minimum transient temperature, the time that the cold junction stays at the lowest temperature and duty cycle. We found numerically that the lowest temperature can be obtained for thermoelectric cooler with prism legs does not vary much for different pulse shapes, but the time that the cold junction stays at the lowest temperature deviates for different pulse shapes. Conical-shaped thermoelectric legs with cross section area at the cold junction smaller than that at the hot junction can slightly decrease the minimum transient temperature. However, holding time can be increased by several times for conical shape thermoelectric legs with cross section area at the cold junction larger than that at the hot junction. These effects are further studied by integrating thermoelectric coolers with the lasers to show the possibility of increasing laser firing time. This work is supported by DARPA HERETIC Project. References: 1. H.J. Goldsmid, Electronic Refrigeration, Pion Limited, London, 1986. 2. K. Landecker and A.W. Findlay, Study of the Fast Transient Behavior of Peltier Junctions, Solid-State Electronics, Vol. 3 pp239-260, 1961. 3. G.E. Hoyos, K.R. Rao and D. Jerger, Fast Transient Response of novel Peltier Junction, Energy Conversion, 17, pp.45-54, 1977.

G8.28
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, CA.

The well-established theoretical model on thermoelectric transport in low-dimensional systems, such as superlattice, deals with the quantum effect on figure-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 electron Boltzmann 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 inputting the superlattice property with that of Si/Ge, the result obtained are compared with previous works considering quantum effect on the same material system. This work is supported by ONR MURI on Thermoelectrics (N00014-97-1-0516). Keywords: Thermoelectric, Superlattices, Boltzmann equation, Thin Films

G8.29
A METHOD FOR FINE TUNING OF THERMOELECTRIC PERFORMANCE. C. Gravalides, E. Hatzikraniotis, Dept. of Physics, Aristotle University of Thessaloniki, Thessaloniki, GREECE; P. Lostak, L. Kudelka, University of Pardubice, Pardubice, CZECH REPUBLIC.

In this work we present a method that allows a direct and continuous fine tuning of the thermoelectric properties. 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 an insertion reaction and the free carrier concentration is gradually changed by continuous 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 can be applied to one and single sample, as charge transfer can gradually change it from p-to-n type. The method has been applied to a series of bismuth or antimony tellurides and solid solutions. Due to controllable charge transfer, a smooth and continuous change from p-type to n-type material has been observed. Two types of insertion-modification technique were applied, either by direct lithiation (direct reaction with butyl lithium) to by exposure to hydrated hydrazine. As charge transfer gradually changes p-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.

G8.30

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

E. Hatzikraniotis, C. Gravalides, 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 the experimentally measured values of electrical conductivity in a p-to-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 experimentally measured data of 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-to-n transition is in a very good agreement with separately measured ones.

G8.31

PELTIER JUNCTION USING AN YBCO HIGH T_c SUPERCONDUCTOR. J.E. Rodriguez and A. Mariño, Department of Physics, Universidad Nacional de Colombia, Bogota, COLOMBIA.

A junction between bismuth-antimonide alloy as active leg and YBa₂Cu₃O_{7- 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 1.2T) on these transport parameters are discussed.

G8.32

GROWTH OF PbTe FILMS BY MAGNETRON SPUTTERING. A. Jdanov, J. Pelleg, Z. Dashevsky and R. Shneck, 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 the 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 a constant power for different times and at a constant time 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 40W 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.

G8.33

SYNTHESIS OF NANOSTRUCTURED BISMUTH COMPOUNDS IN LYOTROPIC LIQUID CRYSTALS. Tim M. Dellinger, Paul V. Braun, University of Illinois at Urbana-Champaign, Dept. of MS&E, Urbana IL.

Lyotropic liquid crystals self-organize to form ordered mesophases consisting of hydrophilic and hydrophobic nano-domains. When chemistries are chosen which operate exclusively in one of these domains, the domains serve as nano-reactors that can limit the size and shape of solid phases 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) oleyl ether 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 compounds may exhibit an enhanced thermoelectric figure of merit "Z" due to quantum confinement within these nanostructures.

G8.34

EXPERIMENTAL THERMOPOWER OF QUANTUM WIRES.

M.V. Vedernikov, O.N. Uryupin, B.M. Goltsman, Yu. V. Ivanov, Yu. A. Kumzerov, A.F. Ioffe Physical-Technical Institute, St. Petersburg, RUSSIA.

Thermopower of semiconductor nanowires with diameter of about 5 nm was studied experimentally for the first time at temperature 77-300 K. Asbestos nanotubes were used for a nanowire preparation. These nanotubes were filled by the melted semiconductors. Temperature dependencies of thermopower and the reduced resistance of nanowire bundle were measured. These dependencies differ qualitatively 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.

G8.35

Sb₃Zn₄, A PROMISING NEW THERMOELECTRIC MATERIAL: ELABORATION AND CHARACTERIZATION. Veronique Izard, Marie-Christine Record, Julien Haines, Jean-Claude Tedenac, UMII, Laboratoire de Physico-chimie de la Matière Condensée, Montpellier, FRANCE.

Zinc-antimony alloys have interesting thermoelectric properties. Sb₃Zn₄ 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^[2,3,4], we have investigated its stability range by means of DSC measurements, X-ray diffraction and electron microprobe analysis; our experimental results supported by Rietveld refinements allowed us to determine the stability range with precision. In order to elaborate this thermoelectric material, two techniques of sample preparation were carried out : conventional synthesis in silica tube sealed under vacuum and mechanical alloying. Due to a minimisation 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^[5,6]. A formation process is proposed for powder elaborated in this way. In both cases, sintering conditions are discussed and physical characterizations are presented. XANES spectroscopy gave us information about the antimony atoms environment in Sb₃Zn₄ and permitted us to propose a doping element for this compound. Elaboration and characterization of this n-type material are also presented. References [1] T. Caillat, J.P. Fleurial and A. Borshchevsky, J. Phys. Chem Solids, 58(7), 1119-1125, 1997 [2] V.I. Psarev, K.A. Dobryden, Izv. Akad. Nauk SSSR, Neorg. Mater., 6(2), 230-236, 1970 [3] K.A. Dobryden, Izv. Akad. Nauk SSSR, Neorg. Mater., 19(4), 549-557, 1983 [4] M. Tapiero, S. Tarabichi, J.G. Gies, C. Noguét, J.P. Zielinger, M. Joucla, J.L. Loison, M. Robino, Solar Energy Materials, 12, 257-274, 1985 [5] K. Sridhar, K. Chattopadhyay, J. Alloys and Compounds, 264, 293-298, 1998 [6] D.M. Rowe, C.M. Bandhari, Appl. Phys. Letters, 47 (3), 255-257, 1985

G8.36

FORMATION, CRYSTAL STRUCTURE AND PHYSICAL PROPERTIES OF NOVEL THERMOELECTRIC SKUTERUDITE Eu₉Fe_{4-x}Ni_xSb₁₂. Andriy Grytsiv, Peter Rogl, Universität Wien, Institut für Physikalische Chemie, AUSTRIA; Stefan Berger, Christoph Paul, Ernst Bauer, T.U. Wien, Institut für Experimentalphysik, AUSTRIA; Claude Godart, CNRS-UPR209, Thiais, FRANCE; Bingfan Ni, Mohsen Abd-Elmeguid, Universität Köln, Physikalisches Institut, GERMANY; Andriana Saccone, Riccardo Ferro, Università di Genova, Dipartimento di Chimica e Chimica Industriale, ITALY; Darek Kaczorowski, W. Trzebiatowski, Institute For Low Temperature and Structure Research Polish Academy Of Sciences, Wroclaw, POLAND.

Alloys from the solid solution Eu₉Fe_{4-x}Ni_xSb₁₂ were synthesized by argon arc-melting followed by long term annealing. From quantitative X-ray powder Rietveld refinements isotypism was established in all

cases with the partially filled skutterudite-type structure, $\text{LaFe}_4\text{P}_{12}$. The Eu-content of the samples was determined from combined data obtained by Rietveld refinements and electron microprobe measurements. These investigations confirmed a systematic trend for the Eu-occupancy y in the parent lattice, revealing a gradual decrease of the Eu-content from nearly full occupancy, $y = 0.83$, in $\text{Eu}_{0.83}\text{Fe}_4\text{Sb}_{12}$ to $y = 0.28$ for $\text{Eu}_{0.28}\text{Fe}_{2.16}\text{Ni}_{1.84}\text{Sb}_{12}$. The alloys have been studied with respect to transport properties (electrical resistivity (T,H,p); thermal conductivity (T), Cp(T,H); Seebeck coefficient (T)) and magnetism. Europium valence was checked by L_{111} -XAS and Mössbauer spectroscopy. $\text{Eu}_{0.83}\text{Fe}_4\text{Sb}_{12}$ orders magnetically below 84 K and the transition temperature decreases as a function of the Fe/Ni substitution. Concomitantly, the transition metal exchange increases the Seebeck coefficient significantly, hence the figure of merit enhances. Moreover, electronic transport crosses over from a hole conductivity regime into electron dominated behavior.

SESSION G9: SKUTTERUDITES II
Chair: Jihui Yang
Wednesday Morning, November 28, 2001
Room 208 (Hynes)

8:30 AM *G9.1

THE PERFORMANCE OF A SEGMENTED THERMOELECTRIC CONVERTOR USING Yb-BASED FILLED SKUTTERUDITES AND Bi_2Te_3 -BASED ALLOYS. Kakuei Matsubara, Science University of Tokyo in Yamaguchi, Dept. of Electronics, Yamaguchi, JAPAN.

In collaboration with industries, we are currently pursuing a broad search to develop advanced thermoelectric materials for waste heat recovery of the automobile engines exhaust gas. This joint program started in 1995, several families of compounds have been developed and optimized. Among these materials, heavily-doped CoSb_3 and filled skutterudites with a chemical formula of $\text{RM}_4\text{Sb}_{12}$ ($\text{R}=\text{Yb,Ce}$; $\text{M}=\text{Co,Fe}$) are particularly promising. Recent results on these advanced materials have demonstrated that dimensionless figure of merit ZT -values are substantially larger than 0.8 for $\text{YbCo}_4\text{Sb}_{12}$ and 1.0 for $\text{Yb}_x\text{Co}_{4-y}\text{Pt}_y\text{Sb}_{12}$ ($x=0.5, y=0.005$), respectively. The purpose of this program is to make sure of a feasibility of the thermoelectric convertor for the engines waste heat recovery of the automobile. Judging the power out put of the convertor by a life-cycle, the energy balance should be plus. Based on this requirement, our goal is set in a 5-10% in the overall efficiency, which is given by the product of the efficiency of a thermoelectric module and that of a heat exchanger. To attain this purpose, our recent study focus on a segmented thermoelectric module using Yb-based filled skutterudites and Bi_2Te_3 -based alloys. This segmentation achieves higher ZT values (about 0.9) in a wide temperature range from 300K to 920K, and allows to operate the convertor at higher temperature. In the convertor design, special brazing alloys are used to ensure a low electrical resistance contact between the metallic electrode and the thermoelectric materials. The performance of the convertor is seriously affected by heat transfer, so that this problem is also considered to maximize the power output of the convertor for a given thermal input. @Overview of recent results obtained in this joint program will be reported in this symposium.

9:00 AM G9.2

SKUTTERUDITE AND SEGMENTED THERMOELECTRIC UNICOUPLES FOR POWER GENERATION APPLICATIONS. Thierry Caillat, Alex Borschhevsky, Jeff Snyder, and Jean-Pierre Fleurial, Jet Propulsion Laboratory/California Institute of Technology, Pasadena, CA.

Highly efficient, segmented thermoelectric uncouple incorporating advanced thermoelectric materials with superior thermoelectric figures of merit are currently being developed at the Jet Propulsion Laboratory (JPL). Both segmented uncouples (including a combination of state-of-the-art thermoelectric materials based on Bi_2Te_3 and novel p-type Zn_4Sb_3 , p-type $\text{CeFe}_4\text{Sb}_{12}$ -based alloys and n-type CoSb_3 -based alloys) and skutterudite-only are under development at JPL. This paper describes the various fabrication techniques and electrical and thermal testing for these advanced uncouples with a maximum predicted thermal to electrical efficiency of about 15% for a hot-side temperature of 975K and a cold-side temperature of about 300K. I-V curves have been generated for selected uncouples and are presented and discussed. Several potential applications for these advanced uncouples are reviewed.

9:15 AM G9.3

ELECTRONIC STRUCTURE AND THERMOELECTRIC PROPERTY OF SKUTTERUDITE CoSb_3 . K. Koga, K. Akai, K. Oshiro, and M. Matsuura, Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube-City, JAPAN.

Electronic structure of CoSb_3 is calculated by means of full-potential linearized augmented plane wave (FLAPW) method with the generalized gradient approximation (GGA). The calculated band gap of CoSb_3 with the consideration of spin-orbit (SO) interaction is 110meV, which is about a half of that without SO interaction. Calculated electronic structure shows that there exist one valence and three conduction bands across the band gap. These bands are fitted very well by the simple band model with the Kane's nonparabolic valence and conduction bands and two parabolic conduction bands. Using the simple band model, thermoelectric properties are calculated. With the constant relaxation time approximation reasonable result for the Seebeck coefficient is obtained only at the low temperature region. For the improvement at higher temperature region, the microscopic scattering mechanisms such as acoustic and optical phonon scatterings and the impurity scattering are taken into account. Obtained results show some improvements, but there still exist large discrepancy between the theoretical and experimental results for higher temperature.

9:30 AM G9.4

ELECTROCHEMICAL DEPOSITION OF CoSb_3 NANOWIRES FROM NON-AQUEOUS SOLUTIONS. J.P. Klitzke, R. Gronsky, T. Sands, University of California, Berkeley, Dept. of Materials Science & Mineral Engineering, M.S. Martín-González, A. Prieto, A. Stacy, University of California, Berkeley, Dept. of Chemistry, Berkeley, CA.

Thermoelectric materials provide an important means for reliable solid state refrigeration and for the generation of power. The skutterudite compound CoSb_3 is a thermoelectric material whose thermal and electrical properties may be decoupled through doping to produce a filled skutterudite structure. It has been shown that two dimensional electronic quantum confinement can enhance a materials thermoelectric figure of merit and the effect for one dimensional confinement is predicted to be greater. We report the fabrication of CoSb_3 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 cation concentration, deposition time, and potential were adjusted to achieve the stoichiometric CoSb_3 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 CoSb_3 skutterudite nanowires.

SESSION G10: NANOWIRES

Chair: David G. Mandrus
Wednesday Morning, November 28, 2001
Room 208 (Hynes)

10:15 AM *G10.1

THERMOELECTRIC POTENTIAL OF Bi AND $\text{Bi}_{1-x}\text{Sb}_x$ NANOWIRE ARRAYS. M.S. Dresselhaus, Y.-M. Lin, O. Rabin, S.B. Cronin, M.R. Black, and J.Y. Ying, Massachusetts Institute of Technology, Cambridge, MA.

Alloying Bi with Sb provides another important variable in controlling the band structure of $\text{Bi}_{1-x}\text{Sb}_x$ nanowires and their transport properties. By varying the Sb concentration and the wire diameter, the thermoelectric figure of merit ZT can be optimized. Theoretical calculations have predicted encouraging ZT values (> 1) at 77 K for $\text{Bi}_{1-x}\text{Sb}_x$ nanowires of easily achievable wire diameters (~ 40 nm) and x in the range $0.11 \leq x \leq 0.15$. Theoretical predictions for optimizing ZT for n-type and p-type $\text{Bi}_{1-x}\text{Sb}_x$ nanowires are presented, emphasizing the unusual situation where the extrema of 10 hole pockets at the L-points, H-points and T-point are simultaneously degenerate. Experimentally, $\text{Bi}_{1-x}\text{Sb}_x$ nanowire arrays are fabricated by a template-assisted approach in anodic alumina membranes. Measurements of the Seebeck coefficient and of the resistance of $\text{Bi}_{1-x}\text{Sb}_x$ nanowire arrays over a wide range of temperatures ($4\text{K} \leq T \leq 300\text{K}$) and magnetic fields ($0\text{T} \leq B \leq 6\text{T}$) are briefly reviewed within the context of this theoretical model. Characterization measurements using optical spectroscopy and other techniques are summarized. The potential of the $\text{Bi}_{1-x}\text{Sb}_x$ nanowire system for thermoelectric applications is assessed.

10:45 AM G10.2

SYNTHESIS AND PROPERTIES OF LEAD SELENIDE NANOCRYSTAL SOLIDS. Kevin L. Stokes, Feng Chen, Weilie Zhou and Jiye Fang, 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) nanoparticle-derived solids. Stable colloidal solutions containing crystalline PbSe particles with sizes on the order of 5-10 nm were synthesized using an organometallic lyothermal growth method in high-temperature organic solvents (100°C - 200°C). The nanoparticle powders have been characterized by X-ray scattering (WAXS/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, mesoscopically ordered or amorphous structures are formed. We show results of the macroscopic and microscopic morphology of these sintered PbSe films. Results of electrical conductivity and Seebeck coefficient measurements on the sintered films will be discussed.

11:00 AM G10.3

PATTERN SHAPE-CONTROLLED SELF-ASSEMBLY OF $\text{Bi}_{0.9}\text{Sb}_{0.1}$ NANOCRYSTALLITES. Jiye Fang, Kevin L. Stokes, Jibao He and Charles J. O'Connor, Advanced Materials Research Institute, University of New Orleans, LA.

Binary-metal of bismuth-antimony is a very important thermoelectric material. In this work, nanometer-sized $\text{Bi}_{0.9}\text{Sb}_{0.1}$ has been prepared using a high-temperature organic solution reducing method by presence of proper capping/stabilizing agents. By using this technique, we are able to produce $\text{Bi}_{0.9}\text{Sb}_{0.1}$ nanoparticles as small as ~12 nm in size with monodispersity through a size-selection post treatment. TEM characterization reveals that the as-prepared particles possess a high crystallinity in single rhombohedral phase as well. Followed on this preparation, self-assembled patterns of $\text{Bi}_{0.9}\text{Sb}_{0.1}$ were successfully achieved in our laboratory. To further engineer those particles toward to the application in thermoelectric device, we have, for the first time, also demonstrated that we are able to control the pattern-shape of $\text{Bi}_{0.9}\text{Sb}_{0.1}$ self-assembly from 2D to 1D by employing different solvent system with variation of the ratio between polar and non-polar components.

11:15 AM G10.4

THERMOELECTRIC TRANSPORT PROPERTIES OF INDIVIDUAL BISMUTH NANOWIRES. S.B. Cronin^a, Y.M. Lin^b, M.S. Sander^d, R. Gronsky^e, A.M. Stacy^d, O. Rabin^c, M.R. Black^b, M.S. Dresselhaus^{a,b}, ^aDepartment of Physics, ^bDepartment of Electrical Engineering and Computer Science, and ^cDepartment of Chemistry, Massachusetts Institute of Technology, Cambridge, MA; ^dDepartment of Chemistry, ^eDepartment 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 nanowire arrays by filling anodic alumina templates with molten Bi using a pressure injection method. Nanowires with diameters between 10 and 200nm 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_2Te_3 nanowires by electrochemically filling alumina templates. The thermoelectric transport properties are also reported for the Bi_2Te_3 nanowire system.

We gratefully acknowledge the support of MURI subcontract 0205-G-7A114-01, NSF grants CTS-9257223 and DMR-98-04734, and the US Navy contract N00167-92-K0052.

11:30 AM G10.5

PREPARATION AND CHARACTERIZATION OF $\text{Bi}_{1-x}\text{Sb}_x$ NANOWIRE ARRAYS. Shan Ren, Lan Hong, Zhongshan Univ, Dept of Physics, Guangzhou, P.R. CHINA; Li Sun, P.C. Searson, Johns Hopkins Univ, Dept of Materials Sci and Eng, Baltimore, MD.

The $\text{Bi}_{1-x}\text{Sb}_x$ nanowire arrays were synthesized by electrodeposition in anodic alumina templates. The electrolytes consisted of BiCl_3 , SbCl_3 0.1M, EDTA 0.03M and HCl 2.4M in aqueous medium, with the expected molar ratio of bismuth to antimony. Three bath composition were used to synthesize nanowire arrays, that is 5%at, 12%at and 90%at Sb. The composition of the wires, their crystal structure and preferred orientation, and morphology were studied as a function of bath composition with XRD, SEM, and TEM. The result was compared with the Bi-Sb film electrodeposited with the same electrochemical parameters and bath composition. The voltammetric analytical study was carried out about the Bi-Sb films systematically. It is shown that the structure of the obtained nanowires is some different from the thin films. The films have a (012) preferred orientation when the concentration of antimony between 22%at and 100%at in bath solution.

11:45 AM G10.6

THERMOELECTRIC PROPERTIES OF $\text{Bi}_{1-x}\text{Sb}_x$ NANOWIRE ARRAYS. Yu-Ming Lin, Dept. of Electrical Engineering and Computer Science; O. Rabin, Dept. of Chemistry; S.B. Cronin, Dept. of Physics; J.Y. Ying, Dept. of Chemical Engineering; M.S. Dresselhaus, Dept. of Physics, Massachusetts Institute of Technology, Cambridge, MA.

$\text{Bi}_{1-x}\text{Sb}_x$ 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 micro-coolers which can be integrated into other electronic devices. Bi-related nanowires form an especially intriguing family of 1D systems because Bi has 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 $\text{Bi}_{1-x}\text{Sb}_x$ nanowires and their transport properties can be engineered by varying the Sb concentration and the wire diameter to optimize ZT . Theoretical calculations have predicted encouraging ZT values (> 1) at 77 K for $\text{Bi}_{1-x}\text{Sb}_x$ nanowires of attainable wire diameters (~ 40 nm). The $\text{Bi}_{1-x}\text{Sb}_x$ nanowire arrays are fabricated by a template-assisted approach in anodic alumina membranes. Experimental measurements of the Seebeck coefficient and of the resistance of $\text{Bi}_{1-x}\text{Sb}_x$ nanowire arrays will be presented for a wide range of temperatures ($4\text{ K} \leq T \leq 300\text{ K}$) and magnetic fields ($0\text{ T} \leq B \leq 6\text{ T}$). The T -dependent resistance shows an unusual trend as the Sb concentrations varies. These results will be discussed and compared with our modeling calculations.

SESSION G11: DEVICES II

Chair: Ali Shakouri

Wednesday Afternoon, November 28, 2001

Room 208 (Hynes)

1:45 PM G11.1

SUPERCOOLING OF THERMOELECTRIC DEVICE USING A CURRENT PULSE. G. Jeffrey Snyder, Jean-Pierre Fleurial, Thierry Caillat, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA.

In a thermoelectric cooler, the Peltier cooling is hampered by Joule heating in the thermoelectric elements, such that a maximum temperature difference, ΔT , is achieved at a particular current I_{max} . During steady state operation, if the current is increased above I_{max} , the increase 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, while Joule heating occurs throughout the thermoelectric elements, 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 ΔT can temporarily achieve and additional ΔT_{pulse} , due to the current pulse. Such a cooler has been built using $(\text{Bi,Sb})_2\text{Te}_3$ materials and tested for its pulse cooling properties. A pulse cooling of 15K has been achieved. The response profile and the important material and geometric parameters will be discussed and compared to theoretical predictions. Applications include cooling of an infra-red laser for gas sensing.

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. Byoung-Dong Kim, Hunjoon Jung, Jang-Sik Lee, Seung-Ki Joo, 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, ink-jet printer head, and so on. Thus, much research has been performed on this topic. Metal-silicide (TiSi_2 and TaSi_2) heater with micro-meter width 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 metal-silicide heater was superior in thermal response and thermal accumulation side effect caused by repeatedly applied voltage pulses. To measure accurate temperature, the silicide heater was passivated with SiO_2 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

of K-type (alumel and chromel) thermocouples was deposited by sputtering and patterned by photolithography. The thermocouples had multiple junctions, so we could measure the temperature at several 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 metal-silicide heater can be used as thermal source for local heating in thin film devices 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. Zavadil, and Donald B. King, Sandia National Laboratories, Albuquerque, NM.

Energy conversion, high frequency microwave transduction 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 dispenser-style structures based on BaO 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. These films are deposited as compositionally modulated W and BaCaAlO_x (4:1:1 BaO:CaO:Al₂O₃) layers with various metal terminating layers. We find the resulting films are electron emissive at temperatures ranging from 800 to 1300 K. Grazing angle x-ray diffraction and cross-section electron microscopy show that the bulk film structure and chemistry evolves 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/cm²K². Recent efforts are focused on incorporating Re and Sc at the surface to further minimize the work function. Our work demonstrates that the mechanisms used for Ba generation and transport in macro-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 Funahashi, Ichiro Matsubara, Masahiro Shikano, National Institute of Advanced Industrial Science and Technology, Kansai, Osaka, JAPAN.

Thermoelectric power generation using waste heat is expected to develop as a valuable energy source in the next few decades. Recently, Co-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 (Bi₂Sr₂O₄)_x(CoO₂)₂ (BC-222), and (Ca₂CoO₃)_xCoO₂ (Co-225) phases were grown from the surfaces of glassy and crystallized precursors by annealing in an O₂ 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 Bi_{3.0}(Sr,Ca)_{3.1}Co_{2.0}O_{9+δ} and (Ca, Sr, Bi)_{1.9}Co_{2.0}O_{5+δ}. Although the Co-225 whiskers are 1.2 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 plates. The result of microstructural observation indicates that the growth points of the whiskers are their bases. Seebeck coefficient and resistivity of both of Co-225 and BC-222 whiskers are higher than 200 μV/K⁻¹ and suppressed to a few mΩcm at high temperature in air, respectively. These phases seem to have a pseudogap at the Fermi level of which the formation is effective to enhance Seebeck coefficient. Thermal conductivity of the Co-225 and BC-222 samples is suppressed to low values at high temperature because of their layered

structure. The Co-225 and the BC-222 are model compounds of phonon-glass and electron-crystal. These oxides are promising thermoelectric materials for high temperature application.

3:15 PM G12.2

EFFECTS OF CATION DOPING ON THE THERMOELECTRIC PROPERTIES IN Ca-Co-O. Ichiro Matsubara, Ryoji Funahashi, Masahiro Shikano, National Institute of Advanced Industrial Science and Technology, Osaka, JAPAN; Kei Sasaki, Osaka Electro-Communication Univ, Osaka, JAPAN.

Since the discovery of a large power factor in NaCo₂O₄, 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 Ca-Co-O single crystal whiskers have a figure of merit ZT of over 1.2 at T > 600°C in air. This compound has a layered structure, in which triple rock salt-type (Ca, Sr, Bi)₂CoO₃ layers and single CdI₂-type CoO₂ layers are stacked alternately. Due to the high ZT value of the whiskers, 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 Ca-Co-O in order to tune the chemical composition. We have adopted a combinatorial approach to synthesize the cation doped Ca-Co-O thin films rapidly and evaluated the solid solution range. In the compounds of (Ca_{1-x}M_x)₃Co₄O₂ (M = Mg, Sr, Ba, and Bi), pure phase was formed for x ≤ 1.0 (M = Mg), x ≤ 0.8 (M = Sr), and x ≤ 0.4 (M = Bi). On the other hand, no solid solution range was obtained for M = Ba series. We have evaluated the high temperature thermoelectric properties for some selected samples and found that the Sr and Bi codoped Ca-Co-O sample shows the highest power factor.

3:30 PM G12.3

THERMOELECTRIC PROPERTIES OF Cd_{3-x}A_xTeO₆ (A = In³⁺, La³⁺ AND Bi³⁺) CERAMICS. Weiling Luan, Yue Jin Shan, Mitsuru Itoh^a, Hideo Imoto Department of Applied Chemistry, Faculty of Engineering, Utsunomiya University, Utsunomiya, JAPAN. ^aMaterials and Structure Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN.

Cd₃TeO₆ is a perovskite-type oxide with 1:1 B-site ordered structure. Pure Cd₃TeO₆ is commonly regarded as a good insulator because its comprising cations, Cd²⁺ and Te⁶⁺, possess the same closed-shell electric configurations as 4d¹⁰. It was accidentally found by us that its electric conductivity could be decreased or increased by a few orders of magnitudes with the varying of temperature. To modify its electric properties, we tried to dope electrons into Cd₃TeO₆ by way of introducing oxygen vacancies and substituting Cd²⁺ by trivalent cations, such as In³⁺, La³⁺ and Bi³⁺. Polycrystalline samples of Cd_{3-x}A_xTeO₆ (A = In³⁺, La³⁺ and Bi³⁺) were synthesized by a solid-state reaction method. The element constitutions of samples were determined by ICP analysis. Their electric properties were investigated and compared with that of pure Cd₃TeO₆. The conductivities of Cd_{3-x}A_xTeO₆ (A = In³⁺, La³⁺ and Bi³⁺) showed a metallic behavior with very slight temperature dependence and were higher by more than three orders of magnitudes than that of Cd₃TeO₆, which indicates the doped-samples become to semiconductors. Moreover, it was found that the conductivities of the samples could be increased by several orders by annealing under nitrogen flow. The resistivities of Cd_{3-x}A_xTeO₆ samples annealed 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 50% of the value observed in Cd₃TeO₆. Fortunately, their conductivities are high enough to provide good thermoelectric conversion factor, which is described as S²σ (S and σ are the Seebeck coefficient and the conductivity, respectively). This result is close to that of the current best n-type thermoelectric material-Ba_{0.4}Sr_{0.6}PbO₃. In conclusion, Cd_{3-x}A_xTeO₆ (A = In³⁺, La³⁺ and Bi³⁺) ceramics are excellent new n-type thermoelectric materials.

3:45 PM G12.4

SYNTHESIS AND CHARACTERIZATION OF SINGLE CRYSTALLINE NANOWIRES OF SILVER SELENIDE THROUGH A SOLID TOPOTACTIC REACTION. Byron Gates, Younan Xia, Univ of Washington, Dept of Chemistry, Seattle, WA; Yiyang Wu, Peidong Yang, Univ of California, Dept of Chemistry, Berkeley, CA.

We have recently demonstrated a topotactic reaction, through which single crystalline nanowires of trigonal selenium could be converted into 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 diameters of these nanowires. In this talk, we will present the experimental procedure, as well as some preliminary results on the thermoelectric properties of these nanowires.

4:00 PM G12.5

LARGE THERMOPOWER IN METALLIC MISFIT COBALT OXIDES. L.B. Wang, S. Hébert, A. Maignan, D. Pelloquin, M. Hervieu and B. Raveau, Laboratoire CRISMAT, UMR CNRS ISMRA 6508, Caen, FRANCE.

The misfit cobalt oxides crystallize in composite structures built of CoO₂ layers of the CdI₂ type stacked with rock salt (RS) type layers. Although these cobalt oxides exhibit metallic behaviors, their room-temperature thermopower 'TEP' is large (typically ~10⁻⁴V/K) and their thermal conductivity is low [~ 2W/(K.m) 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 Tl/Sr/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. In contrast, the RT thermopower of the Tl-based misfit is also very large. In order to understand the underlying physics governing the properties of the misfit oxides, cationic substitutions at the level of RS [Tl/Pb and Tl/Bi] and CoO₂ [Co/Cu] 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 Co³⁺/Co⁴⁺ which are stabilized in the Co triangular lattice. On the other hand, changes in the a_{1g} 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 Tl/Sr/Co/O misfit.

SESSION G13: CHALCOGENIDES II

Chair: Mercouri G. Kanatzidis

Thursday Morning, November 29, 2001

Room 208 (Hynes)

8:30 AM G13.1

ELECTRONIC STRUCTURE OF K₂Bi₈Se₁₃. P. Larson, D. Bilc, S.D. Mahanti, Michigan State University, Department of Physics and Astronomy, East Lansing, MI; M.G. Kanatzidis, Michigan State University, Department of Chemistry, East Lansing, MI.

K₂Bi₈Se₁₃ 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 α -K₂Bi₈Se₁₃ (trigonal with space group P-1) and β -K₂Bi₈Se₁₃ (monoclinic with space group P2₁/m). To understand their thermoelectric properties we have carried out band structure calculations within *ab initio* density functional theory (DFT) using full potential 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-Ernserhof potential which incorporates a generalized gradient approximation (GGA). The effect of the SOI on the band structure of α -K₂Bi₈Se₁₃ is to shift the conduction band down relative to the valence band and thereby decrease the gap from 0.8eV to 0.47eV, which is smaller than the experimental value (0.76eV). There are however direct gaps at the X point (0.74eV) and at the V point (0.72eV) 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. β -K₂Bi₈Se₁₃ has a mixed occupancy of Bi and K atoms within two sites of the crystal structure. The measured gap in this compound is 0.59eV. We have calculated the electronic structure for different configurations with assumed extreme occupancy of the two mixed sites stated above. How the band structure depends on these assumed configurations 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 G13.2

CRYSTAL GROWTH, STRUCTURAL CHARACTERIZATION AND THERMOELECTRIC PROPERTIES OF K₂Bi_{8-x}Sb_xSe₁₃ SOLID SOLUTIONS. Theodora Kyratsi, Duck-Young Chung, Mercouri G. Kanatzidis, Dept of Chemistry, Michigan State University, Lansing, MI; Jeffrey S. Dyck, Ctirad Uher, Dept of Physics, University of Michigan, Ann Arbor, MI; Konstantinos M. Paraskevopoulos, Dept of Physics, Aristotle University of Thessaloniki, Thessaloniki, GREECE.

Our efforts to improve the thermoelectric properties of β -K₂Bi₈Se₁₃, led to systematic studies of solid solutions of the type

β -K₂Bi_{8-x}Sb_xSe₁₃. Crystallographic data of selected members of the solid solutions were collected in order to determine the distribution of Sb and Bi in the lattice and study possible preference on specific lattice sites. We find that these materials are not true solid solutions as judged by the inhomogeneous Sb/Bi distribution in the structure. The charge transport, semiconducting band gaps, melting points and thermal conductivities were studied as a function of x. The Bridgman 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 G13.3

THERMOMECHANICAL CHARACTERIZATION OF BISMUTH TELLURIDE BASED THERMOELECTRIC MATERIALS. Witold Brostow, Kevin P. Menard, Univ of North Texas, Laboratory of Advanced Polymers & 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 thermomechanical properties of these materials. In this paper, we present the initial dynamic mechanical analysis (DMA) data for n-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 correct for differing sample dimensions under these analysis 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 gives information about energy dissipation modes and for these TE materials include grain boundaries, crystal defects such as dislocations and vacancies, and also the van der Waals or cleavage planes associated with the mica-like structure of Bridgman grown material. 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 G13.4

INITIAL ASSESSMENT OF THE THERMOELECTRIC PROPERTIES FOR THE MIXED SYSTEM Rb_{2-x}K_xBi₈Se₁₃. John R. Ireland, C.R. Kannewurf, Dept. of Electrical and Computer Engineering, Northwestern University, Evanston, IL; Theodora Kyratsi, Mercouri G. Kanatzidis, Dept. of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, MI.

Previous studies of the K-Bi-Se based compounds with various dopants have resulted in several compositions with promising transport characteristics for thermoelectric applications. The specific system β -K₂Bi₈Se₁₃ exhibits both a promising electrical conductivity and Seebeck coefficient at room temperature and above with significant improvements in the power factor achieved through the introduction of n-type dopants. To further improve these results, this study has continued with the solid solutions of Rb_{2-x}K_xBi₈Se₁₃, (0 ≤ X ≤ 2). It is known that in the neighborhood of X ≈ 1 there is a structure change; thus this study evaluates 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 (N00014-98-1-0443) and by DARPA through ARO (DAAG55-97-1-0184). Work at NU made use of Central Facilities supported by the NSF through the Materials Research Center (DMR-0076097).

9:30 AM G13.5

40 nm Sb AND Se-DOPED Bi₂Te₃ NANOWIRES BY ELECTRODEPOSITION. M.S. Martin-Gonzalez, A.L. Prieto, Dept of Chemistry, R. Gronsky, T. Sands, Dept of Materials Science & Mineral Engineering; A.M. Stacy, Dept of Chemistry, University of California, Berkeley, Berkeley, CA.

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 dimensionality improves their efficiency. For this reason, our studies focus on using porous alumina templates to obtain ordered arrays of thermoelectric nanowires. The best opportunity for creating commercially viable nanowire devices is to employ Sb and Se doped Bi₂Te₃ nanowires. The electrochemical behavior of those 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 G14: CLATHRATES II

Chair: Otto F. Sankey

Thursday Morning, November 29, 2001

Room 208 (Hynes)

10:15 AM G14.1

Cs-133 AND Na-23 NMR STUDIES OF Cs(8)Na(x)Ge(136) CLATHRATES. R.F. Marzke, Arizona State Univ, Dept of Physics, Tempe, AZ; G.S. Nolas, Department of Physics, University of South Florida, Tampa, FL; J. Gryko, Jacksonville State Univ, Jacksonville, AL.

Cs(8)Na(x)Ge(136) clathrate shows large paramagnetic shift for cesium in Cs-133 NMR spectrum and no paramagnetic shift for sodium in Na-23 resonance. Germanium clathrate is different from Cs(8)Na(16)Si(136) 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 G14.2

PURIFICATION AND THERMOELECTRIC STUDY OF TYPE I Ge CLATHRATE. J. Daniel Bryan, Galen D. Stucky, Dept of Chemistry, University of California, Santa Barbara, CA; Bo B. Iversen, Dept of Chemistry, University of Aarhus, Aarhus C, DENMARK.

Impurity concentrations in the synthesized inorganic clathrate compounds M₈Ga₁₆Ge₃₀ (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 Ba₈Ga₁₆Ge₃₀ 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 G14.3

MAXIMUM ENTROPY METHOD ANALYSIS OF THERMAL MOTION AND DISORDER IN THERMOELECTRIC CLATHRATE Ba₈Ga₁₆Si₃₀. Bo B. Iversen, Anders Bentien, Department of Chemistry, University of Aarhus, 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 (Uiso) 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 analysed with probability density function models. For the present study of Ba₈Ga₁₆Si₃₀ 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 Gram-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

is quite limited on the guest atom positions, and thus probably not a main scattering mechanism for the phonons. [1] Sales, B.C., Mandrus, D., Chakoumakos, B.C. Semiconductors and semimetals 70, 1-36 (2000) [2] Kuhs, W.F. Acta Crystallogr. Sect. A 48, 80 (1992) [3] Iversen, B.B., Nielsen, S.K., Larsen, F.K. Philos. Mag. A 72, 1357 (1995).

11:00 AM G14.4

MULTINUCLEAR NMR AND POWDER X-RAY DIFFRACTION STUDIES OF Si, Ge AND Sn CLATHRATES OF ALKALI METALS: VACANCIES, DISORDER AND KNIGHT SHIFTS. Michael J. Ferguson, Christopher I. Ratcliffe, John S. Tse, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, CANADA.

Clathrates consisting of 4-coordinate tetrel atom frameworks with metal atom guests in the cages are now well known as potential thermoelectric materials. One of their attractive features is the possibility of property-tuning by varying the components and also the stoichiometry. Numerous techniques have been applied to study thermal and electrical properties. Most NMR work to date has focussed on the Knight shifts as a source of information about the conduction electrons. NMR, however, can also be used as a probe of local structure, and is more sensitive in some aspects than X-ray diffraction. Here we present studies of the synthesis, PXRD and NMR (²³Na, ³⁹K, ⁸⁷Rb, ¹³³Cs, ²⁹Si and ¹¹⁹Sn) of clathrates of types Str.I and Str.II with frameworks of Si, Ge or Sn, with either one or two types of alkali metal in the cages, and including the Rb/Sn and Cs/Sn Zintl phases. Emphasis is placed on the complementary use of the two techniques for structural information, in addition to the determination of Knight shifts. It will be shown that defect structures are commonplace in many of the clathrate samples produced, because of vacancies in both the framework and more often in the cages. Ultimately one must ask, therefore, what the consequences are for the overall properties, and how much control do we actually have over the stoichiometry?