SYMPOSIUM G
Thermoelectric Materials 2001–Research and Applications

November 26 – 29, 2001

Chairs

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

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

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

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*Invited paper
SESSION G1: GUIDANCE TO ADVANCED RESEARCH
Chair: George S. Nolte
Monday Morning, November 26, 2001
Room 208 (Hyenas)

10:45 AM *G1.1
OVERVIEW OF VARIOUS STRATEGIES FOR THE DEVELOPMENT OF NEW BULK MATERIALS FOR THERMOELECTRIC MATERIALS. Terry M. Trud, 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 researchers. These efforts are aimed at minimizing lattice thermal conductivity while other efforts focus on materials that exhibit large power factors. An overview of the requirements and strategies for the investigation and optimization of a new system of materials for practical 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. HfTe5), quinhydrates (e.g. Al2PdMnMn2Ga and Ga0.75Zn0.25), half-Heusler alloys (e.g. TiNi3-xSb x), skutterudites (e.g. CeGe3 and CoGe3), and chalcogenides (e.g. SnxGe2-xSb x). 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 THERMOELECTRIC MATERIALS. David J. Singh, Naval Research Laboratory, Center for Computational Materials Science, Washington, DC.

The use of density functional electronic structure calculations for identifying potential thermoelectric materials and guiding their optimization is discussed. The basic theoretical tools including band structure calculations and kinetic transport theory are briefly reviewed 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 MnCoGe.

11:45 AM *G1.3
THERMODYNAMIC CALCULATIONS IN NEW THERMOELECTRIC MATERIALS. J.C. Tiedemann, M.C. Record, Laboratoire de Physico-Chimie de la Matiere Condensee, Universite de Montpellier 2, Sciences et Techniques du Languedoc, Montpellier, FRANCE; S.G. Fries, ACCESS C.V., RWTH Aachen, Inezstrasse, GERMANY.

Performance enhancement of thermoelectric modules can be obtained by a good knowledge of the materials constitution involved in their fabrication. For this reason a thermodynamic analysis of the material is of interest. Improvement of the figure of merit in thermoelectric materials depends on multiple factors [crystalline 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 entail 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] entail points 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 free energy density 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 relying 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 or solidification consolidation. 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 (Hyenas)

1:30 PM G2.1
LATTICE VIBRATION OF YTTERBIUM FILLED SKUTTERUDITES: AN INELASTIC ELECTRON TUNNELING STUDY. Jiro Nagano, Mariumo Fuchar, Devanaj Naray, Tsutomu Uchida, Shodo Takeya, Tokyo Eihamma, Institute for Energy Utilization, National Institute of Advanced Industrial Science and Technology (AIT), Sapporo, JAPAN; Hiroshi Amo, Kakuei Matsubara, Dept of Electronics and Computer Science, Science University of Tokyo in Yamaguchi, Ono, JAPAN; Eiji Hatta, Koji Kubota, Nano-Electronic Laboratory, Graduate School of Engineering, Hokkaido University, Sapporo, JAPAN.

Inelastic electron tunneling experiments were performed on Yb2Co3Sb12+Al codoped-AI junctions measured at 4.2K. A peak observed at ~7meV for Yb-filled samples is closely related to the vibration mode of Yb ions in the cages of skutterudite structure. This gives direct evidence that the rattling effect plays a dominant role in filled skutterudites. The phonon energies contributed from optical phonons shifts to the lower energy with increasing the Yb concentration. This observation indicates that an interaction between host lattice and guest ions is strong in Yb-filled skutterudites, which seems to be related to a valence fluctuation observed in Yb-filled skutterudites.

1:45 PM G2.2
THERMOELECTRIC PROPERTIES OF EU-DOPED CoSb3. G.A. Lumiberton Jr., Terry M. Trud, Dept of Physics and Astronomy, Clemson Univ, Clemson, SC; G.S. Nolte, Dept of Physics, University of South Florida, Tampa, FL.

Resistivity and thermopower data is presented on Eu-doped CoSb3 skutterudites over the temperature range of 10 K to 700 K. Thermal conductivity is also presented from 10 K to 700 K in order to determine the figure of merit. Equ. 44CoSb11.96Co0.04Sb12.17Ge0.5 and Equ. 44CoSb11.96Co0.04Sb12.17Sn0.5 exhibit an enhanced figure of merit as compared to the CoSb3 and Eu0.4CoSb12. The room temperature value of ZT has been measured for the Eu44CoSb11.96Co0.04Sb12.17Ge0.5 skutterudite as ZT = 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 Eu44CoSb11.96Co0.04Sb12.17Sn0.5 and the Eu0.4CoSb12 samples respectively. These results will be discussed in relation to the potential of these materials for thermoelectric applications. Data on a series of Yb-filled CoSb3 is underway and will also be discussed.

2:00 PM G2.3
HIGH PRESSURE SYNTHESIS OF NEW FILLED-SKUTTERUDITES. Hirotsugu Takizawa, Ken-ichi Okuzuki, Kyota Uehda, Tadashi Endo, Tohoku Univ, Dept of Materials Chemistry, Sendai, JAPAN.

Germanium and tin atoms were inserted into the CoSb3 skutterudite host lattice under high pressure and temperature condition using belt-type high-pressure equipment. Both atoms could be inserted in the body-centered face-centered site of the host lattice, resulting in the formation of filled-skutterudites, ML4CoSb12 (M = Ge, Sn). Complete filling was achieved in both cases at 6.8 GPa. Crystal structures of the filled-skutterudites were refined by the Rietveld analysis of the powder X-ray diffraction data. The phase exhibited high 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 germainium-filled compounds exhibit n-type semiconducting behavior. A remarkable reduction in the thermal conductivity is achieved in tin-filled compounds. It is conluded that tin atom is a better ‘trailer’ in the CoSb3 host lattice.

2:30 PM G2.4
ELECTRONIC STRUCTURE AND THERMOELECTRIC PROPERTIES OF YTTERBIUM FILLED SKUTTERUDITES. Hiroshi Amo, Kinghiro Asahi, Kakuei Matsubara, Science Univ of Tokyo in Yamaguchi, Dept of Electronics and Computer Science, Ono, JAPAN; George S. Nolte, Dept of Physics, University of South Florida, Tampa, FL; Koji Aiki, Misuzu Matsuura, Yamaguchi Univ, Dept of Advanced Materials Science and Engineering, Ube, JAPAN; Jiro Nagano, National Institute of Advanced Industrial Science and Technology, Institute for Energy Utilization, Sapporo, JAPAN.
We have investigated the electronic structure and transport properties of Yb-doped Cd$_2$Yb, a valence-band structure of Yb-doped Cd$_2$Yb 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 Kα line (photocurrent: 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 fullpotential 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 Cd$_2$Yb were closely observed in both the core-level and valence-band spectra. The observed spectra agree qualitatively with results of band calculation. This result is consistent with the results of magnetic susceptibility and the inelastic electron tunneling measurements. The electronic properties (the carrier mobility, effective mass, etc.) and the thermal properties of Yb-doped Cd$_2$Yb 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 CeP$_x$, Virgil Shields, Thierry Calliat, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA.

In an effort to expand the range of operation for highly efficient, segmented thermoelectric unincoupled currents currently being developed at the Jet Propulsion Laboratory (JPL), skutterudite phosphides are being investigated in potential high temperature segments to supplement antimonide segments that limit the use of the unincoupled at a hot-side temperature of about 600-700°C. We report here on the synthesis and transport properties of one of these phosphides, CeP$_x$. Large amounts of cobalt triphosphide have been prepared by heating the metal from stoichiometric powders at temperatures ranging from 500 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 at high temperature and the 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 (Hyades)

3:30 P.M. G3.1
NOVEL THERMAL TRANSPORT IN STABLE BINARY Cd$_2$Yb QUASICRYSTALS. A. L. Pope, Terry M. Tratt, Dept. of Physics and Astronomy, Columbia, SC, J. Strong-Olsen, Dept. of Physics, McGill University, Montreal, CANADA.

Quasicrystalline materials have been investigated for applications as thermoelectric materials due to their inherently low thermal conductivity. With the discovery of a new stable binary Cd$_2$Yb quasicrystal, thermal and electrical transport measurements have been performed on these materials. It is found that the Weidmann-Franz relation is unsuitable for modeling thermal conductivity in the Cd$_2$Yb quasicrystal. The electronic contribution to the thermal conductivity is calculated from the Weidmann-Franz relationship to be comparable to or greater than the measured total thermal conductivity, thus negating the appearance of a "negligible lattice contribution". In reality, the contribution of the lattice appearance in the temperature dependence of the thermal conductivity. The thermal conductivity increases linearly with temperature above 250 K and is proportional to $\rho^{1/2}$ between 2 K and 75 K. The fine grain of the Weidmann-Franz relationship are discussed as well as the possibility of a minimum thermal conductivity.

4:00 P.M. G3.3
NANOCLASSES MATERIALS AND DEVICES IN PbSnTe-BASED QUANTUM DOT SUPERLATTICES. C.C. Harman, Patrick Taylor, M.P. Walsh, B.J. Lofane and G.W. Turner, Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, MA.

High-quality PbSnTe-based QDSSL quantum-dot superlattices (QDSLs) 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 PbSnTe-based materials (in which the 300 K energy gap can be varied) is presented. Our initial objective of demonstrating growth with QDSL materials (conseratively estimated at 0.8 as 300 K) and 2.0 as 550 K has been achieved. We have demonstrated QDSL thermoelectric unincoupled devices with greater than 15 K cooling below room temperature in highly optimized 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/cm$^2$ over a 20 to 50 K temperature difference.

4:30 P.M. G3.4
DOPING AND ALLOYING TRENDS IN NEW THERMO-ELECTRIC MATERIALS. Sim Loo, Sangeet Lal, Duc-Yung Chung, Kwei-Fang Hsu, Doreeta Kyras, Mercouri K. Kanatzidis, Timothy P. Hogan, Department of Electrical and Computer Engineering, Michigan State University, East Lansing, MI.

Chemistry Department, Michigan State University, East Lansing, MI.

New thermoelectric bulk materials such as Cd$_4$Te$_5$, 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 for measuring the temperature and voltage drops across the sample. A sample probe attached to the end of the sample provides a heater and current the sample both thermally and electrically. The sample's response to cyclic heat pulses is measured in real time using a small probe. A nonlinear $\kappa$-square fit is used, essential to use a two-probe temperature measurement to determine the thermal conductivity and the Seebeck coefficient for the material. Data acquisition using these techniques is expedited since we can sweep the 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.

8:30 AM G4.1
RESONANT ULTRASONIC SPECTROSCOPY STUDIES OF...
SESSION G5: CHALCOCOINIDES
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, Bi, and Hg) 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 high Seebeck coefficients and 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 CdBiTe 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
Nadine D. Loehr, 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$_5$, ZrTe$_5$, and HfS$_5$ 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 ZrTe$_5$ and HfTe$_5$

The resistivity anomaly and the corresponding thermopower in ZrTe$_5$ are sensitive to doping with Sb[1]. A series of doped ZrTe$_5-x$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 ZrTe$_5-x$Sb$_x$ in the 96-3300 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, 129, 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 ZrTe$_5-x$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/SbQ$_x$(A = K, Rb, Cs, Q = Se, S) SYSTEM AND COMPOSITIONAL MANIPULATIONS FOR GOOD THERMOELECTRIC PROPERTIES
S. Duck-Yong Chung, Theodor Kyratsis, Mercouri G. Kanatzidis, Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, MI; John Ireland, Carl R. Kannwurf, 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

We have explored the electronic and vibrational properties of type-I and type-II semiconductor (Si, Ge, and Sn) chalcogenides using theoretical DFT electronic structure methods. These framework materials have open cages which harbor guest impurities, and produce localized vibrational modes 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 guest on the lattice thermal conductivity by using a linear response theory based on correlation functions using molecular dynamics. We compare these results to results of guest-free crystals, and to amorphous materials. Our results are consistent with experiments, and have impact as a theoretical test of the "rattler" concept.

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

We measured the temperature dependence of electrical conductivity ($\sigma$) and thermopower ($S$) of Cs$_x$Sn$_{1-x}$Te$_4$ under high pressure up to 1.2 GPa. We observed the reversible gap widening, irreversible $S$ increasing under high pressure, which were similar to the behaviors of Cs$_x$Sn$_{1-x}$Se. However, the relaxation effect of $\sigma$ for Cs$_x$Sn$_{1-x}$Te$_4$ was negligible in contrast with that of Cs$_x$Sn$_{1-x}$Se. We will also present the result of Cs$_x$Sn$_{1-x}$Te$_4$ for further comparison. The results suggest that the vacancy pressure is important role in transport properties for tin clathrulates under high pressure.

9:45 AM G4.5
Abstract WE.5

CLATHRATE THERMOELECTRICS, Veerle Kepplgen, Michael McGurk, and Alen Tekei, 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 Ultrasonic Spectroscopy (RUS) measurements have been carried out for 3 cubic clathrate materials, Ba$_4$Ga$_2$Ge$_3$$_{30}$, Sr$_2$Ga$_2$Ge$_3$$_{30}$, and Eu$_2$Ga$_2$Ge$_3$$_{30}$. In these materials, the Ba, Sr and Eu ions are in oversized atomic cages. They have attracted attention as promising thermoelectric materials, having high electrical conductivities comparable to glasses while maintaining crystalline electronic properties. RUS has proven to be useful for the study of similar cage-like materials [1]. Identifying 2 local modes in the filled skutterudite $La_2$Bi$_2$Sb$_3$ is the RUS measurements we present here were carried out as a function of temperature (2-300K) on single crystals, and allow the determination of the 3 elastic moduli. The results are compared to ultrasonic attenuation measurements on Sr$_2$Ga$_2$Ge$_3$$_{30}$ and RUS measurements on filled and unfilled skutterudites. This work is supported in part by the Office of Naval Research, Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725.


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

Materials with both low thermal conductivity due to efficient phonon coupling and high electrical conductivity (Shack's so-called phonon glass/electron crystal, or PGEF) offer promise as thermoelectric materials. Here we report thermal properties of several semiconductor clathrates: SrGa$_4$Ge$_3$$_{30}$, Sr$_2$Ga$_2$Ge$_3$$_{30}$, Cs$_x$Ga$_2$Sb$_3$$_{30}$ and Ba$_4$Ga$_2$Sb$_3$$_{30}$. In these structures, generalized as $M_xN_yV_{6-x-y}$, M is a guest host lattice formed by X and Y. In principle, melting M within the cage 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 THERMAL INFLUENCE ON THE LATENT THERMAL CONDUCTIVITY IN CLATHRATE-FRAMEWORK SEMICONDUCTORS: Otto F. Sankey, Jianjun Dong, and Charles W. Myles, "Arizona State University, Tempe, AZ; Auburn University, Auburn, AL; Texas Tech University, Lubbock TX.

We have explored the electronic and vibrational properties of type-I and type-II semiconductor (Si, Ge, and Sn) chalcogenides using theoretical DFT electronic structure methods. These framework materials have open cages which harbor guest impurities, and produce localized vibrational modes 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 guest on the lattice thermal conductivity by using a linear response theory based on 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.
is practically based on Sb$_2$Te$_3$. It also has the tendency to replace Bi in many compounds forming a series of solid solutions. Since the electrical properties of solids depend directly on their crystallographic and electronic structure, we are looking for new materials and new compositions involving antimony. We have discovered several new ternary compounds in the A/Bi$_3$/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. IBM T.J. Watson Research Center, Yorktown Heights, NY; GE Global Research, Niskayuna, NY. We have been using the approach of incorporating quantum dot heterostructures in order to reduce lattice mismatch strain in thermoelectric materials. The basic concept of quantum dot heterostructures is to create mismatch strain energy in a material, and then to reduce this strain energy by incorporating quantum dot heterostructures in order to reduce lattice mismatch strain in thermoelectric materials. The basic concept of quantum dot heterostructures is to create mismatch strain energy in a material, and then to reduce this strain energy by incorporating quantum dot heterostructures in order to reduce lattice mismatch strain in thermoelectric materials. 

SESSION G6 DEVICES I
Chair: Thierry Callis
Tuesday Afternoon, November 27, 2001
Room 208 (Hyenas)

1:30 PM G6.1
SUPERLATTICE THIN-FILM THERMOELECTRIC DEVICES FOR ANYWHERE, ANY TIME COOLING AND HEATING.
Hanan Venkataraman, Edward Sicola, Brooks Quinn, Thomas Cogdill. Research Triangle Institute, Research Triangle Park, NC. A major goal of our Thermoelectric program is to demonstrate significant enhancement in figures-of-merit (ZT) at 300K using the concept of phonon-blocking electro-magnetic superlattices. 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 heterostructures. Another goal of our development is to improve both of the materials to high coefficient of performance (COP) in cooling devices and demonstrate ZT=1000 W/cm$^2$ cooling power densities in thin-film thermoelectric devices. The high-performance superlattices materials and the extremely low specific heat resistance at high ZT=1.2 to 1.4 in n-type superlattice thermoelectrics at 300K. In addition, we have obtained 32K and 48K sub-ambient cooling at 298K and 33K, respectively, in p-type superlattice micro-thermoelements. We have utilized a simple heat sink design to achieve the coefficient of performance (COP) of thermoelements; a COP of 0.06 was achieved for 17.5K cooling at 300K with an estimated heat load of 30W/cm$^2$ for the p-type micro-thermoelements and 19W/cm$^2$ for the n-type micro-thermoelements. We have fabricated p-n couples using these micro-thermoelements, obtaining sub-ambient cooling of 15K 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 25 faster than bulk thermoelectric technology. The results have allowed into the concept of high-performance anywhere, any time active cooling and heating. We will present results to demonstrate this concept with IR-imaging of superlattice micro-thermoelements.

1:45 PM G6.2
THERMOELECTRIC MODULE FOR LOW TEMPERATURE APPLICATIONS.
Timothy P. Hogan, Sangeeta Lat, Sin Loo, Duck-Young Chung, Theodore Kyriakos, Michael C. Crossley. "Electrical and Computer Engineering Department, University of Houston, Houston, TX; Chemistry Department, Michigan State University, East Lansing, MI; Telmax Corporation, Traverse City, MI.

The possibility of a prototype thermoelectric cooling device for operation near liquid nitrogen temperatures has been explored. In these devices, the figure of merit is a combination of the properties of the two branches of the module. Here, we investigate the fabrication of a module with a new low temperature material, Bi$_2$Te$_3$ (p-type), and the best known low temperature n-type material Bi$_2$Sb$_3$. Transport measurements for each of these materials show high performance at low temperatures. Known values for the figure of merit of Bi$_2$Te$_3$ is 3.5x10$^3$ K$^{-1}$/W at 25K and for Bi$_2$Sb$_3$, is 6.5x10$^3$ K$^{-1}$/W at 7K. At 100K these values drop to 2.5x10$^3$ K$^{-1}$/W for Bi$_2$Te$_3$ and 6.0x10$^3$ K$^{-1}$/W for Bi$_2$Sb$_3$. Theoretical simulations based on these data place a cooling power of about 900μW at 100K, which is almost three times the efficiency of a Bi$_2$Te$_3$ 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 Frechet, Jennifer A. Herman, Nick Stoltz, G. Jeffrey Snyder, Ching-Kuei Hung 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 interest is in p-type Bi$_2$Te$_3$ and n-type Bi$_2$Sb$_3$ and Bi$_2$Sb$_3$, respectively, and new materials such as Bi$_2$Te$_3$-xS$_x$ and CoSb$_3$. Room temperature electronic 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 electrodeposits films as a function of temperature, film composition and post-deposition heat treatments, in particular for Bi$_2$Te$_3$, Bi$_2$Sb$_3$ and n-type Bi$_2$Sb$_3$, respectively.

2:15 PM G6.4
THERMIONIC REFRIGERATION WITH AN IMPROVED EMITTER.
Yoshikiro Ishimaru, Boni Y. Moyaes, Theodore H. Geballe. Stanford University, Applied Physics Dept., Stanford, CA; Stanford University, Dept. of Mechanical Engineering, Stanford, CA. We consider new possibilities for cooling by vacuum tunneling of electrons. Vacuum electron emission is attractive for cooling because of the absence of lattice thermal conduction and absence of ohmic resistance. We investigate a layer of low electron affinity semiconductor which overcomes the metallic emitter. The thermionic surface eliminates emission of electrons below the Fermi level and thus improves the current with a higher Peltier coefficient. Under the influence of an strong electric field (10$^9$ - 10$^{12}$ 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, electric constant, and electron affinities of the semiconductor. We find that these cooling currents can be obtained by a combination of energy selective tunneling and thermionic emission. Numerical calculations show that emiters covered with 30A of semiconductor with electron affinity of 0.5 eV can produce a cooling power of 10 W/m$^2$ with a Peltier coefficient of 10$^4$ V/A for electric field of 10$^{12}$ V/cm.

2:30 PM G6.5
CONSERVATION OF LATERAL MOMENTUM IN HETERO-STRUCTURE INTEGRATED THERMIONIC COOLERS.
Dongwook Vahid, Ali Shikouri, 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 hot side 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 electron transport in a range of 435 K 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 translational energy contribute in thermionic emission thereby resulting in a higher cooling efficiency.

2:45 PM G7.6 HIGH COOLING POWER DENSITY SiGe/Si THIN FILM COOLERS. Gehong Zeng, Xiaofeng Fan, Edward Croyle*, Chris Labounty, Daryosh Vazhieh, Ali Shokouhi, and John E. Bowers, Department of Electrical and Computer Engineering, University of California, Santa Barbara, CA; *HRL Laboratories, LLC, Malibu, CA; #Haskin School of Engineering, University of California, Santa Cruz, CA.

For the thermal management of micro-electronic 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. Thin film coolers have the advantage of high cooling power density. SiGe-based device structure was fabricated on silicon substrates by molecular beam epitaxy. This thick film SiGe/Si micro coolers integrated with resistive heater on top of them were fabricated using standard IC processing technology. The resistive heater was used as a thermal source and the temperature control was achieved by adjusting the bias current. 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 HEREDIT program and the Army Research Office.

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

3:30 PM G7.1 REDUCTION OF LATTICE THERMAL CONDUCTIVITY IN BALL-MILLED AND SHOCK-COMPACTION TIN/Sn HALF-HEUSLER ALLOYS. B. Bhattacharya, Tery M. Tris, Dept. of Physics and Astronomy, Temple University, Philadelphia, PA; V. V. Ivanov, Y. V. Popovnshchik, S.J. Poon, Dept. of Physics, Univ. of Virginia, Charlottesville, VA; N. Thandhli, Dept. of MSE, Georgia Institute of Technology, Atlanta, GA.

Half-Heusler alloys are currently being investigated for their potential as thermoelectric materials. They exhibit high negative thermopower (40–250 μV/K) and favorable electrical resistivity (0.18 mΩ cm) at room temperature. Attractive power factors (~2 T) of about (0.2 ± 0.1 W/mK) at room temperature and about 4.5 W/mK 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 (~1.0 W/mK) 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/mK) in some Sn-based half-Heusler alloys which have been prepared by ball milling and followed by shock-compaction. This process resulted in 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, Reggying Jin, Jim Thompson, Solid State Division, ORNL, Oak Ridge, Tennessee; Theodore Kippeners, 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 Tl2S SINGLE CRYSTAL. Hitode Imai, Yichi Shimakawa, and Yoshimi Kubo, NEC Corporation, Fundamental Research Laboratories, Tsukuba, JAPAN.

A Tl2S 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 (p, T), 0.37 W/mK at 300 K with p = 1.7 mΩ cm and T = 651 mK/v, its high electrical and highly anisotropic behavior, suggesting that the electronic structure of this compound has a quasi-two-dimensional nature. The carrier density was 2.8 x 10¹⁹ cm⁻³, which is an order of magnitude larger than that of optimally doped (Bi, Sb)₂Te₃. It is notable 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 Tl₂S 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 COCHRALSKI GROWN GeSi SINGLE CRYSTALS. Ichiro Yonenaga, Tatsuya Aoki, Toshihide 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 single crystals of Ge0.55-Si0.45 alloys in the various composition 0.8 < x < 1 were investigated in the temperature range 300–1000 K. Based on these results, 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 measured 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 Ge0.45Si0.55 alloys. The dependence of the Seebeck coefficient on the electrical conductivity was revealed. The dimension-less figure of merit 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. Hiroshi Naka, Yoshinori Honda, Naoyuki Shimizu, Masahito Komai, Mingawa, Nousaku Sawamoto, Toshiaki Ohnishi, 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, heavily 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. Amelting medium was mixture of Si rich phase and Ge rich phase. The starting material and Ge melt was kept in 1.2 macrogravity using 1 l/h drop tower and dropped...
from aminol in a 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-melted one. The electric conductivity of the sintered sample was similar to that of as-melted one. Other thermoelectric property will be presented at this meeting.

SESSION GS-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. Sharpe.

Tuesday Evening, November 27, 2001
8:00 PM
Exhibition Hall D (Hyatt)

GS1 Non-Equilibrium Electrons and Phonons in Heterostructure Integrated Thermoelectric Coolers.

Daryosh Vashapeh, Ali Shokouri, 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 identified. 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 description of the device. 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 certain SiGe thin film coolers are not limited by hot carrier effects.

GS2 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.

Polymers-matrix composites containing continuous carbon fibers are important for lightweight structures. This paper is aimed at developing thermoelectric properties 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 interfacial 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.

GS3 Microstructure Effects on the Thermoelectric Properties of Based PtTe Films Prepared by Pulsed Laser Deposition.

Anne Dauscher, Bertrand Lenoir, Alexandre Jacquod, L.P.M., Ecole des Mines, Parc de Staurupt, Nancy, FRANCE; Marin Danescu, NILPRP, Laser Department, Bucharest, ROMANIA

Lead telluride (PbTe) thin films, as well as Pb/Te and Bi/Te multilayers, were prepared by pulsed deposition from a Nd:YAG laser working at a wavelength of 522 nm. The films were deposited under vacuum onto silicon/silicon (111) and baryum fluoride (111) at 150°C, temperature at which congruent transfer from target to substrate occurs. Strong influence of substrate nature and annealing on the structure and morphology of the PbTe films was observed. The effect of these microstructure changes as well as the presence of additional thin Bi or Te layers on the transport properties of PbTe will be presented and discussed.

GS4 Microstructural and Thermoelectric Properties of \( \text{Pb}_2\text{Bi}_8\text{Sb}_3\text{Te}_3 \) and \( \text{Pb}_2\text{Te}_7\text{Sn}_3 \) Films Deposited by Pulsed Laser Ablation.

M.S. Bhasker, M. Jagannadh, North Carolina State University, Department of Materials Science and Engineering, Raleigh, NC; R.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 \( \text{Pb}_2\text{Bi}_8\text{Sb}_3\text{Te}_3 \), n-type \( \text{Bi}_2\text{Te}_3 \), and n-type \( \text{Bi}_2\text{Te}_2\text{Se}_3 \) with Sn doping were deposited on mica substrates using Nd:YAG pulsed laser ablation at temperatures ranging from 300°C to 500°C. The films were characterized using X-ray diffraction, SEM and TEM. X-ray mapping and EDS were used to determine the stoichiometry. The films showed uniform thickness and high crystalline quality with a preferred (001) alignment with the substrates. The film quality in terms of stoichiometry and residual 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.

GS5 Discrete State Simulation of the Pellet Effect for Interfaces between Arbitrary Band Structures.

Peter F. Radzicki III, Timothy D. Sands, Graduate Group in Applied Science and Technology, University of California, Berkeley, CA.

The Pellet Heating and Cooling Effects are generated by external electric potentials applied across junctions between two materials characterized by different electronic conduction band structures. At these interfaces, there are significant changes in the band structure. The increase of charge density across an isothermal junction is accompanied by the exchange of heat with the lattice. The direction of the charge carriers and the details of the band structure determine whether phonons are absorbed or emitted. The magnitude of Pellet Cooling is further influenced by the lattice heat conduction within the separate materials and by the transport of phonons across the interface. Analytic treatments of these processes are often restricted to 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 (tablular) 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 phonon quantum mechanical scattering and occurs in both real and reciprocal lattice spaces. The electron and phonon conduction and relaxation-time approximations of Boltzmann's equations. The extension of this method to more complicated band structures is presented.


Jin Weng, Daniel Marshall, Motorola Labs, Physical Sciences Research Labs, Tempe, AZ; Nikolay Zein, Gregory Krenov, Sci-Tec, Moscow, RUSSIA

The crystal structure of a crystalline boron carbide has an energy forbidden gap of ~3 eV 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 bipolarons through localized defects were developed, accordingly. Although the bipolaron model is attracting a lot of interest, it does not rely on any specific types of defect, the bipolaron formation in boron carbide is believed to be a defect of CB-B intralattice chain in connection with a B\(_2\)C isochadron. The current study examined the existing theory and compared it by performing a systematical study on the formation energies of defects in boron carbide using a state-of-the-art ab initio electronic structure method. The studied defects cover a) stoichiometric vacancies of carbon concentration, b) moving 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 B12Cicosahedra connected by C6B1 internodal chains, i.e. consistent with the reported structural model of B12C. When carbon concentration is reduced, however, the population of C-B-C chain is found to be intact, while the population of B12Cicosahedra is reduced by the replacement of B12Cicosahedra. This observation is fundamentally different from the earlier model of boron-rich boron carbide. The localized states associated with missing boron atoms are identified and the electrical conductivity of these localized defects states is studied.

GS.7 SYNTHESIS OF BORON-RICH METAL BORIDES AND THEIR THERMOELECTRIC PROPERTIES. Masahiko Takada, Ferre Dominger, Takahiro Mura, Takahiro Fukuda, Nagoya University of Technology, Dept of Mechanical Engineering, Nigata, JAPAN.

Polycrystalline metal borides AlMgB2, MVB (M = Ca and rare earth metals), and MgB2 (M = transition metals) were prepared by using PECS (Pulse Electric Current Sintering) technique. Single phase of orthorhombic AlMgB2, which contains B12icosahedral clusters as building blocks, was obtained at sintering temperatures between 1573 K and 1852 K, while higher sintering temperatures lead to the appearance of γ-Al2B12-type phase. Seebeck coefficient (α) and electrical conductivity (σ) of the AlMgB2 at room temperature was about 600 [μV/K] and 104 [S/m], respectively. Such large α and low σ are comparable to those of typical ceramic boron. MgB2-type materials such as TiB2 and VB2, which have layered structure comprising interleaved two-dimensional boron and metal layers, were also synthesized. These have metallic property with large σ (more than 103 [S/m]), and their α was enhanced up to 20 [μV/K] by substituting metal atoms with other metals. Further increase is expected.

MgB2 hexaborides are cubic phase whose structure is a three-dimensional skeleton constituted of B6icosahedral clusters, and the interstice of which are filled by metal atoms. The α and the σ of the synthesized CaB6 were about 200 [μV/K] and 104 [S/m] at room temperature, respectively. Substituting Ca atoms with rare earth metals enabled us to improve these thermoelectric properties. Details of the results and discussion will be presented at the meeting.

GS.8 FORMATION OF BISMUTH-SILICA NANOCOMPOSITE VIA HIGH-Energy BALL MILLING. Matthew A. Metl, Timothy M. Dollinger, 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 Mincer MILL. As determined by transmission electron microscopy (TEM), the average diameter of the bismuth particles decreased to 10 nm after 20 hours of milling. By 40 hours, the Cr−Kα x-ray diffraction peaks vanish, and finally, after 62 hours, the Bi nanoparticles are not observed in TEM samples due to the formation of a Bi-silica solid solution or the oxidation of Bi metal to bismuth oxide. The 10 nm Bi nanoparticles after 19 hours of milling should be sufficiently small to exhibit quantum confinement. Measurements of the electronic properties of these nanophase Bismuth-silica composite materials in function of milling time and Bi volume fraction are currently underway.

GS.9 THE FABRICATION AND THERMOELECTRIC PROPERTIES OF AMORPHOUS Si/Ge BULK SAMPLES. Sangmin Lee, Yoichi Okamoto, Toshik Amano, Jun Morimoto National Defense Academy, Dept of MSE, Yokosuka, JAPAN.

We have already reported that the Si/Ge amorphous superlattine 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.

GS.10 HIGH TEMPERATURE ELECTRICAL TRANSPORT PROPERTIES OF Eu AND Yb-DOPED SKUTTERUDITES. R.H. Tiedtke, R.A. Lambertson Jr., Terry M. Trit, 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, the power factor and resistivity is measured and presented on a series of Eu and Yb-doped skutterudites over a temperature range of approximately 100 K to 700 K using our high temperature thermoelectric probe. Simple measurement techniques are briefly discussed. Data from various levels of Eu and Yb dopings will be presented and compared in order to show trends that point towards improvements in these skutterudites for potential thermoelectric applications.


Quasicrystals have properties connected 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 quasicrystals were prepared with various levels of Pd substitution for 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, 1 K < T < 300 K. The relationship between the electrical and thermal transport properties and microstructure will be presented and discussed.

GS.12 THERMOELECTRIC PROPERTIES OF AlFeSi QUASICRYSTALS AND THEIR APPROXIMANTS. P.N. Aloni, A.L. Pope, Terry M. Tritt, Clemson Univ, Clemson, SC. A. Ross, C. Jenkins, 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 quasicrystal, however, have largely been ignored. These relatively high thermal conductivities suggest there are similar structures, yet the periodicity of a crystal. In this paper, we have investigated an icosahedral AlFeSi quasicrystalline phase as well as two of its corresponding approximant phases (α and β). Electrical and thermal transport properties of these materials are presented. The visibility of the AlFeSi quasicrystalline system and the α and β approximate phases as thermoelectric materials is discussed.


SiB6 has proved to a potentially useful material because of its excellent thermoelectrical properties above 700°C, low specific gravity, high degree of hardness, and moderate melting point. SiB6, which has a poor sintering quality of the sintering temperature, was successfully doped fully using an spark plasma sintering (SPS) method. The SPS-processed specimens consisted of SiB6, SiC and SiB6 phases. Pure SiB6 powder were doped after 10 kbar at the sintering temperature of 1600°C. In particular, it was formed that the rare earth element was very effective in evoking the microstructure of SiB6 phase, resulting in reducing the sintering temperature and controlling grain growth. These effects were discussed in detail in terms of microstructure evolution during the SPS process.


Thermoelectric oxide semiconductors have recently been paid much attention in the literature. In this paper, Ni and La-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 pallets. The chemical processing greatly shortened the overall preparation time period. We carried out x-ray diffraction and electron microscopy analysis, and measured their electrical conductivity, Seebeck coefficient and thermal Seebeck coefficient. The influence of various dopants and processing routes on their microstructure and thermoelectric properties were investigated in high temperature region. The novel chemical processing is effective to prepare the oxide ceramics.

GS.15 CRYSTAL SYNTHESIS OF Ca2Co12O28 AND THERMOELECTRIC PROPERTIES. Shengli Chen, Jun Nan, and Co Wen Nan, Tsinghua Univ, Dept of Materials Sci & Eng, Beijing,
behavior were observed in the dependences of the thermoelectric properties 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.

GS. 10

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

110


A significant increase in the thermoelectric power factor upon decreasing the PbSe well width in PbSe/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 PbSe buffer layer in determining the kinetic properties of the superlattices. In the present work, the influence of the PbSe thickness d (varying between 2 and 200 nm) with a fixed thickness of the EuS layer (about 30 nm) on the thermoelectric properties of PbSe/EuS bilayers grown by thermal evaporation and vacuum deposition on [100] 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 microscope studies showed that PbSe grows on the 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 ≤ 5 nm, and the extremum 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 characteristic of the temperature dependences of the thermoelectric properties changes qualitatively with increasing d. At d < 10 nm, PbSe/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 extremum in the thermoelectric parameters, the non-monotonic behavior in the form of steps and oscillations is observed, indicative of system instability.

GS. 20

THERMOELECTRIC NANOBIRES BY ELECTROCHEMICAL DEPOSITION. Qidil Rubin*, Yu-Ming Lee*, Stephen B. Cross†, Miklised S. Dresselhaus*, Massachusetts Institute of Technology, MA; †Dept. of Chemistry; ‡Dept. of Electrical Engineering and Computer Science; †Dept. of Physics, Cambridge, MA.

Nano-bires 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 nano-bires 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 nano-bires synthesized by other techniques.

GS. 21

Abstract Withdrawn.

GS. 22

Abstract Withdrawn.

GS. 23

THERMOELECTRIC PROPERTIES AND CRYSTAL AND ELECTRONIC STRUCTURES OF A LAYERED STRUCTURE MATERIAL InGaZnO4, Hideo Ima, Hidekazu Kimura, Yuichi Shimakawa, and Yoshihiko Kubo, NEC Corporation, Fundamental Research Laboratories, Tuskuba, JAPAN.

A layered structure material can be a good thermoelectric, because the thermopower, S, is enhanced with the two-dimensional (2D) electronic state. An InGaO2 type layered InGaZnO4, which consists of InO2 and GaZnO2 layers, was expected to show such 2D characteristics. A small amount of highly conductive carriers in the 2D InO2 layers. The insulting nature of the GaZnO4 layer, on the other hand, is thought to come from the small overlapping between the 3-d orbitals of Ga and Zn due to the difference of the 3-coordinates of Ga and Zn in the GaZnO4 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 (InₓGa₁₋ₓZnO₄) (GaZnO₄) with the highest figures-of-merit, ζT, 0.04 at 300 K with ρ of 5 mΩcm, of 0.08 µV/K, of 42 mW/Kcm, and of 6 × 10⁴ cm²/Vs. Both magnitude and T-dependence of η are well explained in terms of the 3D effective-mass approximation carrier density, and no enhancement of η was observed; that is, the result of transport measurements suggests 3D 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 Å – 2 Å as speculated by Ori in et al. [1] However, the band-structure calculation using the obtained structural parameters predicted a considerable 3D conduction due to the overlapping of the In 3s and Ga 4s orbitals. This result is consistent with our transport results, but it is in sharp contrast with the previous speculation of 2D electronic structure from chalcogenide calculation [1].

GS.24 THERMOELECTRIC PROPERTIES OF Bi₂Sb₃Te₅ COMPOUNDS PREPARED BY MA-PDS METHOD. Yang-Chao 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 Bi₂Sb₃Te₅ doped with Ag, Ag₃Bi and Ag₃Bi₃N. The electrical, thermal and thermoelectric properties of the doped samples were systematically investigated as a function of the doping content and temperature. Based on these studies, we identified a unique potential for further improving the thermoelectric performance of the mother 25%Bi₂Te₅-75%Bi₂Sb₃Te₅ alloy by doping a small amount of Ag. The doping content was optimized at 0.01-0.02 mol%, which corresponds to the maximum improvement of 3% in the ZT at 823 K. Ag₃Bi and Ag₃Bi₃N, however, yields extremely low values of Seebeck coefficient, finally resulting in a low figures-of-merit.

GS.25 STRUCTURE AND THERMOELECTRIC PROPERTIES OF NEW LAYERED COMPOUNDS IN THE QUATERNARY SYSTEM Ca₇Pr-Bi₂Te₅. Kuo-Hsuan Hsu, Nuo-Chieh Wang, An-te Mou, University of Michigan, Michigan State University, Dept. of Chemistry and Center for Fundamental Materials Research, East Lansing, MI; Sangeeta Lal, Tim Hogan, Michigan State University, 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 Ca₀.₃Bi₂Te₅ exhibits promising thermoelectric properties. In an effort to explore the ultimate performance of this compound, we introduce Pr₆ metal into its layered framework. Consequently, the four new compounds of CaₓPr₁₋ₓBi₂Te₅ (1), CaₓPr₁₋ₓBi₂Te₇ (2), CaₓPr₁₋ₓBi₂Te₃ (3) and CaₓPr₁₋ₓBi₂Te₉ (4) were obtained by the reactions of CaₓBi₂Te₅ with increasing content of Prₓ. The formed layered structures lay up of mica-like slabs with progressively increasing thickness. We will present the four compounds as members of the brand-new homologous series CaₓPr₆Bi₂Te₅νm (m = 1 to 4).

GS.26 HALL CARRIER MOBILITY OF THERMOELECTRIC Ag₃Bi₂Te₅-Ag₃Te³ COMPOSITES. T. Nakajima, A. Sugi, K. Nakamura, Y. Takigawa, Osaka Electric Communication Univ., Dept. of Electronics Engineering, Osaka, JAPAN; K. Kurosawa, Univ. of Myazaki, Myazaki, 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 merit are increasing the effective mass or mobility of carriers or decreasing the thermal conductivity. [1] In the present study, we propose a novel way to increase the carrier mobility by forming composites. We prepared a series of (Ag₃Bi₂Te₅ – Ag₃Te³) (0 ≤ x ≤ 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 range from 293 to 383K, and then Hall carrier mobility were calculated from these data. The mobility of Ag₃Bi₂Te₅ was much higher than that of Ag₃Te³. A composite (Ag₃Bi₂Te₅)x(1-x)-(Ag₃Te³)y, with x = 0.5, y = 0.5 showed the higher value than Ag₃Te³ below 383K. Around 183K, at which the carrier type changes from p-type to n-type with increasing the temperature in Ag₃Te³, there is a competition between the negative and positive carriers in both phases, resulting in an enhancement of the Hall mobility.

GS.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. Fleury, 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 the pulse laser firing time that is supported by DARPA HERETIC Project. Reference: 1. H.J. Goldman, Electronic Refrigeration, Pion Limited, London, 1986. 2. K. Landecker and A.W. Findlay, Study of the Fast Transit Behavior of Polite Junctions, Solid State Electronics, Vol. 3 pp.291-290, 1961. 3. G.E. Hoyes, K.R. Rao and D. Jerger, Fast Transit Response of novel Polite Junction, Energy Conversion, 17, pp.45-54, 1977.

GS.28 CLASSICAL SIZE EFFECT ON IN-PLANE THERMOELECTRIC PERFORMANCE 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 figures-of-merit enhancement. However, the classical size effect may still exist and have effects on transport properties. In this paper, we report a theoretical approach to investigate the classical size effect on in-plane thermoelectric transport properties. An ab initio Boltzmann transport model at in-plane superlattice is established in superlattice system. Partial specular and partial diffuse interface scattering boundary condition are included in the solution. By incorporating the superlattice property and that of Si/Ge, the result obtained are compared with p-type Ge/CdTe/Ge/Si/SiGe superlattice 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

GS.29 A METHOD FOR FINE TUNING OF THERMOELECTRIC PERFORMANCE. C. Grimald, E. Heikkenen, Dept. of Physics, Aristotle University of Thessaloniki, Thessaloniki, GREECE; P. Lhost, L. Kudelski, University of Padurice, Padurice, 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 immersion 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 this method is that it is performed on one and single sample, as charge transfer can gradually change it from p-type to n-type. The method has been applied to a series of bismuth or 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 lithium) to by exposure to hydrazine hydride. As charge transfer gradually changes p-type to n-type, the peak on power factor is clearly observed experimentally both for p and n-type of material.
In this work we present results on a series bismuth or antimony tellurides and solid solutions, estimate ZT performance in each case and compare with known optimized compositions.

**GS.30**

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

E. Harkonen, C. Granaklis, Dept. of Physics, Aristotle University of Thessaloniki, Thessaloniki, GREECE.

In this way we present a simple, yet accurate method that allows a direct evaluation of thermoelectric properties from a minimum set of experimental data. The method, a numerical algorithm, uses experimentally measured values of electrical conductivity in a p-type 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 the p and 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-type transition is in a very good agreement with separately measured ones.

**GS.31**

**PELTIER JUNCTION USING A YBCO HIGH T, SUPERCONDUCTOR.**

J.E. Rodriguez and A. Marín, Department of Physics, Universidad Nacional de Colombia, Bogota, COLOMBIA.

A junction between bismuth-antimony alloy as active leg and YBa$_2$Cu$_3$O$_7$-y as passive leg, which operate at around liquid nitrogen temperature, has been built. Measurements of electrical conductivity, thermoelectric power and thermal conductivity of YBCO and Bi-Sn were carried out and their influence on the thermoelectric merit figure (ZT) were analyzed. The effect of the applied magnetic field (up to 1 T) on these transport parameters are discussed.

**GS.32**

**GROWTH OF PbTe FILMS BY MAGNETRON SPUTTERING.**

A. Jiménez, J. Pinto, J. Dzhokharov, and R. Sineck, Department of Materials Engineering, Ben Gurion University of the Negev, Beer Sheva, ISRAEL.

The monolithic integration of a narrow gap IV-VI semiconductors and Si devices is highly attractive for IR optoelectronic and thermoelectric applications. The growth of epitaxial PbTe is constrained by the large difference of ~19% between the lattice parameters of PbTe and the Si substrate and the considerable difference in their thermal expansion coefficient. In recent years, the epitaxial growth of IV-VI semiconductors on Si substrates has been successfully realized using fluoride buffer layers and bilinear IR sensors have been fabricated. However, epitaxial growth of PbTe films directly on Si wafer is desirable for simplification of the process. In our research we used RF magnetron sputtering for thin film preparation. Si (111) wafers were used as substrates and PbTe films were deposited at constant power for different times at various power levels. The growth of PbTe films with thickness 80-280 nm was performed at substrate temperature ~400°C with a deposition rate of about 0.1 nm/s. Films were studied by x-ray diffraction (XRD) using a Rigaku diffractometer. A combination of 400W and 30min sputtering time and heating the substrate at ~400°C provided a highly textured film. The peak was that of (200) thus indicating the possibility of obtaining epitaxial growth of lead telluride under the above conditions by magnetron sputtering. The results were reproducible. Other power/time combination is presently under investigation in order to test other possibilities of obtaining epitaxial films. The films were characterized also by scanning electron microscopy (SEM) and Auger spectroscopy.

**GS.33**

**SYNTHESIS OF NONSTRUCTURED BISMUTH COMPOUNDS IN LIQUIDOTHIC LIQUID CRYSTALS.**

T. M. Dollinger, Paul V. Braun, University of Illinois at Urbana-Champaign, Dept. of Materials Science and Engineering, Urbana, IL.

Lytotropic liquid crystals selforganize 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 resultant 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) oligomer 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 enhance thermoelectric figure of merit (ZT) due to quantum confinement within these nanostructures.

**GS.34**

**EXPERIMENTAL THERMOPOWER OF QUANTUM WIRES.**

M.V. Vedernikov, O.N. Orygin, B.M. Golubskiy, Yu. V. Ivanov, Yu. A. Komarov, Y.P. Ioffe Technical-Physical Institute, St. Petersburg, RUSSIA.


**GS.35**

**SE$_2$S$_4$: A PROMISING NEW THERMOELECTRIC MATERIAL: ELABORATION AND CHARACTERIZATION.**

Veronique Israil, Marie-Christine Record, Julien Haines, Jean-Claude Tedeschi, UMI, Laboratoire de Physico-chimie de la Matière Condensée, Montpellier, FRANCE.


**GS.36**

**FORMATION, CRYSTAL STRUCTURE AND PHYSICAL PROPERTIES OF NOVEL THERMOELECTRIC SKUTTERUDITE $\text{Eu,Fe}_{2+x}\text{Ni}_2$**

A. Grytsay, Peter Rogl, University Wien, Institut für Physikalische Chemie, AUSTRIA, Stefan Berger, Christoph Paul, Ernst Bauer, T.U. Vienna, Institut für Experimentalphysik, AUSTRIA; Claude Godart, CNRS-UPR269, Thiais, FRANCE; Bingfan Ni, M.olsen Abé-Elmeguid, University Köl, Physikalisches Institut, GERMANY; Andreas Sgrenne, Rico Ferro, Université de Genova, Dipartimento di Chimica e Chimica Industriale, ITALY; Derek Kaczorowski, W. Trzebinski, Institute For Low Temperature and Structure Research Polish Academy Of Sciences, Wroclaw, POLAND.

Alloys from the solid solution $\text{Eu,Fe}_{2+x}\text{Ni}_2$ were synthesized by argon arc-melting following by long term annealing. From quantitative X-ray powder Rüdiger refinements nctypism was established in all
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 1.10 eV, 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 parabolic valence and conduction bands and two parabolic conduction bands.

Using the simple band model, the 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.

9:00 AM *G9.2* SKUTTERUDITE AND SEGMENTED THERMOELECTRIC UNICOUPLES FOR POWER GENERATION APPLICATIONS. Thierry Cailler, Alex Borschchevsky, Jeff Snyder, and Jean-Pierre Fleurl. Jet Propulsion Laboratory/California Institute of Technology, Pasadena, CA.

Highly efficient, segmented thermoelectric unicouples incorporating advanced thermoelectric materials with superior thermoelectric figures of merit are currently being developed at the Jet Propulsion Laboratory (JPL). Both segmented unicouples (including a combination of state-of-the-art thermoelectric materials based on Bi$_2$Te$_3$ and novel p-type Zn$_2$Sb$_3$-type CeFe$_4$Sb$_2$-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 unicouples 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. IV curves have been generated for selected unicouples and are presented and discussed. Several potential applications for these advanced unicouples are reviewed.

9:15 AM *G9.3* ELECTRONIC STRUCTURE AND THERMOELECTRIC PROPERTY OF SKUTTERUDITE CoSb$_3$. K. Koga, K. Akai, K. Osahi, and M. Masauei. Faculty of Engineering, Yamaguchi University, Takamatsu, Ube City, JAPAN.

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 skutterudite structure. It has been shown that two-dimensional electronic quantum confinement can enhance the 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 electrochemical 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 in situ concentration, deposition time, and potential were adjusted to achieve the stoichiometric CoSb$_3$ composition both through the codoping 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


Alloying Bi with Sb provides another important variable in controlling the band structure of Bi$_{2-x}$Sb$_x$ nanowires and their transport properties. By varying the Bi concentration and the wire diameter, the thermoelectric figure of merit ZT can be optimized. Theoretical calculations have predicted encouraging ZT values (> 1) at 77K for Bi$_{2-x}$Sb$_x$ nanowires of easily achievable wire diameters (≈ 40nm) and x in the range 0.11 < x < 0.15. Theoretical predictions for optimizing ZT for n-type and p-type Bi$_{2-x}$Sb$_x$ nanowires are presented, emphasizing the unusual situation where the extremes of 10 hole pockets at the L-points, 8-points and T-points are simultaneously degenerate. Experimentally, Bi$_{2-x}$Sb$_x$ nanowire arrays are fabricated by a template-assisted process in smooth alumina membranes. Measurements of the Seebeck coefficient and of the resistance of Bi$_{2-x}$Sb$_x$ nanowire arrays over a wide range of temperatures (4K < T < 300K) and magnetic fields (0 T < B < 6T) are briefly reviewed within the context of the theoretical model. Characterization measurements using optical spectroscopy and other techniques are summarized. The potential of the Bi$_{2-x}$Sb$_x$ nanowire system for thermoelectric applications is assessed.

10:45 AM *G10.2* SYNTHESIS AND PROPERTIES OF LEAD SELENIDE NANOCRYSTALS. L.S. Solodov, K. Lozovik, Y. Peng, and C. Zhou, 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 selenium (PbSe) nanocrystalline films. Stable colloidal suspensions of monodispersed PbSe nanoparticles with sizes on the order of 5-10 nm were synthesized using an organosol microemulsion method in high-temperature organic solvents (110°C - 200°C). The nanocrystalline powder was then characterized by X-ray scattering (WAXS), electron microscopy and optical absorption. Thin films were formed by precipitation of the nanoparticles from solution onto insulating substrates. Depending on the deposition conditions, meso- or microcrystalline structures were 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 Bi$_2$Sb$_3$: NANOCRYSTALLITES
Jie Fang, Kevin L. Stokes, Jibao He and Charles J. O'Connor, Advanced Materials Research Institute, University of New Orleans, LA.

Binary-metal tellurium-antimony is a very important thermoelectric material. In this work, nanocrystalline Bi$_2$Sb$_3$ has been prepared using a high-temperature organic solution reduction method by presence of proper capping/stabilizing agents. By using this technique, we are able to produce Bi$_2$Sb$_3$ nanocrystals as small as 10 nm in size with monodispersion through a size-selection post-treatment. TEM characterization reveals that the prepared particles possess a high crystallinity in single rhombohedral phase as well. Followed on this preparation, self-assembled patterns of Bi$_2$Sb$_3$ were also achieved in our laboratory. To further engineer the devices toward the application in thermoelectric devices, we have, for the first time, also demonstrated that we are able to control the pattern-shape of Bi$_2$Sb$_3$, self-assembly from 2D to 3D by employing different solvent systems with variation of the ratio between polar and non-polar components.

11:15 AM G10.4
THERMOELECTRIC TRANSPORT PROPERTIES OF INDIVIDUAL BISMUTH NANOWIRES
*Department of Physics, **Department of Electrical and Computer Engineering, ***Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA.

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 pyrolysis of SnO$_2$-Sn metal catalyst during metal evaporation using a pressure injection method. Nanowires with diameters between 10 and 200 nm have been fabricated using this scheme. In order to assess the thermal transport properties accurately, the nanowires are removed from the substrate 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 nanowire arrays by electrolysis filling alumina templates. The thermoelectric transport properties are also reported for the Bi nanowire array system.

We gratefully acknowledge the support of MURI subcontract 60295-G-ZA114-01, NSF grants CTS-9525223 and DMR-98-04374, and the US Navy contract N00167-95-K-0052.

11:30 AM G10.5
PREPARATION AND CHARACTERIZATION OF Bi$_2$Sb$_3$: NANOWIRE ARRAYS
Shan Ren, Lin Hong, Zhongshun, Dept. of Physics, Guangzhou, PR. CHINA; Li Sun, P.C. Semporn, Johns Hopkins Univ, Dept of Materials Sci and Eng, Baltimore, MD.

The Bi$_2$Sb$_3$ nanowire arrays were synthesized by electrodeposition in anodic alumina templates. The electrolytes consisted of BiCl$_3$, SnCl$_2$, and HCl. The deposition process was carried out at 30°C in aqueous medium, with the expected molar ratio of bismuth to antimony. Three bath compositions were used to synthesize nanowire arrays, that is 5% SnCl$_2$ at 50% SnCl$_2$. The composition of the wires, their crystal structure and microstructure were characterized using XRD, SEM and TEM. The results were compared with the Bi-Sb film electroplated with the same electrochemical parameters and bath composition. The volumetric analysis study was carried out about the Bi-Sb film systematically. It is shown that the structure of the obtained nanowires is different from the thin films. The films have a (012) preferred orientation when the concentration of antimony between 23%at and 100%at in both solution.

11:45 AM G10.6
THERMOELECTRIC PROPERTIES OF Bi$_2$Sb$_3$: NANOWIRE ARRAYS
Xi-Ming Liu, 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.

Bi$_2$Sb$_3$ 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-cookers 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 Bi$_2$Sb$_3$ nanowires and their transport properties can be varied by varying the Sb concentration and the wire diameter to optimize ZT. Theoretical calculations have predicted encouraging ZT values (> 1) at 77K for Bi$_2$Sb$_3$ nanowires of attainable wire diameters (> 40nm). The Bi$_2$Sb$_3$ nanowire arrays are fabricated by a template-assisted approach in anodic alumina membranes. Experimental measurements of the Seebeck coefficient and of the thermoelectric power factor of Bi$_2$Sb$_3$ nanowire arrays will be presented for a wide range of temperatures (4K < T < 300K) and diameters, with 0T < B < 6T. The T-dependent resistance shows an unusual trend as the Sb concentration varies. These results will be discussed and compared with our modeling calculations.

SESSION G11: DEVICES II
Chair: Ali Shokrollahi
Wednesday, November 28, 2001
Room 208 (Hyatt)

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

In a thermoelectric cooler, the Peltier effect is the heat generated by Joule heating in the thermoelectric elements, such that a maximum temperature difference, $\Delta T$, 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 effect, resulting in a net decrease of $\Delta T$. However, since Peltier cooling occurs instantaneously at the cold junction, while Joule heating occurs throughout the device, there will be a period during which the cold junction is supercooled before the hot junction reaches the cold end. In this way, a current pulse applied to a cooler running at maximum $\Delta T$ can temporarily achieve an additional $\Delta T_{pulsed}$, due to the current pulse. Such a cooler has been built using (Bi$_2$Sb$_3$)$_2$Te$_3$ materials and tested for its pulse cooling properties. A pulse cooling of 1.5K has been achieved. The response time and the important material and geometric parameters will be discussed and compared to theoretical predictions. Applications include cooling of a gas laser for laser cooling.

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

The integrated thin film heater and thin film thermocouple have potential MEMS applications, such as miniaturized pressure sensor, flow meter, medical surgery, inkjet printer head, and so on. Thus, much research has been performed on this topic. Metal-silicide (TiSb$_2$ and TaSb$_2$) 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 radiation side effect caused by repeatedly applied voltage pulses. To measure accurate temperature, the silicon 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
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 applications.

3:15 PM G12.2

EFFECTS OF CATION DOPING ON THE THERMOELECTRIC PROPERTIES IN Cu2O–In–In2O3: Ichiro Masahara, 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 Na3Co2O4, 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 Cu2O-CoO 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 the metallic layers and a single CuO-type interlayer are stacked alternately. Due to the high ZT value of the whisker, this type of material is expected to be applied to thermoelectric power generators. In this study, we have investigated the effects of cation doping on the thermoelectric properties of the BC-222 system. We have adopted a combinatorial approach to synthesize the cation doped Cu2O-CoO thin films rapidly and evaluated the solid solution range. In the compounds of (Cu1−x−yMxMyA2/3B1/3O4, A = Mg, Sr, Ba, and Bi; y = 0, 0.1, 0.2, 0.3, and x ≤ 0.4) on the other hand, no solid solution 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 co-doped Cu2O-CoO sample shows the highest power factor.

3:30 PM G12.3

THERMOELECTRIC PROPERTIES OF Cd2-xA2xTeO4 (A = In3+, Ln3+ and Bi3+): CERAMICS. Weiling Luan, Yu Jin Shan, Meishu Xie, Hisao Inoue, Department of Applied Chemistry, Faculty of Engineering, University of Tsukuba, JAPAN; Materials and Structure Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN.

CdTeO4 is a perovskite-type oxide with 1:1 Baite ordered structure. Pure CdTeO4 is commonly regarded as a good insulator because its crystalline lattices, Cd2+ and Te4+, possess the same closest-packed electronic configurations as 4f0. It is accidentally found 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 have tried to dope electrons into CdTeO4 by way of introducing oxygen vacancies and substituting Gd2+ by transition metals, such as In3+, Ln3+ and Bi3+. Polycrystalline samples of Cd2-xA2xTeO4 (A = In3+, Ln3+ and Bi3+) were synthesized by a solid state reaction method. The element constitutions of samples were determined by ICP and investigated and compared with that of pure CdTeO4. The conductivities of Cd2-xA2xTeO4 (A = In3+, Ln3+ and Bi3+) showed a metallic behavior with very slight temperature dependence and were higher than those of pure CdTeO4, 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 Cd2-xA2xTeO4 (A = In3+, Ln3+ and Bi3+) decreased in nitrogen at 800°C were at the order of mΩcm at room temperature. The negative Seebeck coefficients obtained from all samples indicate that electrons are the charge carriers. The absolute values of these Seebeck coefficients are less than 10 mV/K. Unfortunately, their conductivites are high enough to provide good thermoelectric conversion factor, which is described as S/σ (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 Bi2O3:Sb2O3:Bi2O3. In conclusion, Cd2-xA2xTeO4 (A = In3+, Ln3+ and Bi3+) ceramics are excellent new n-type thermoelectric materials.

3:45 PM G12.4

SYNTHESIS AND CHARACTERIZATION OF SINGLE CRYSTAL ELECTRODE S NANO W IRES OF SILVER SEL ENIDE THROUGH A SOLID TOPOTACTIC REACTION. Byron Gross, Xunmin Xin, Univ of Washington, Dept of Chemistry, Seattle, WA; Yujing Wu, Peiking 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 dimensions of the starting nanowires. In this contribution, 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. ERGIS, S. H. HOBERT, A. MAUNER, M. HENVRIE AND B. RAVEN, Laboratoire CRISMAT, UMR CNRS 1594, 65086, Cen, FRANCE.

The misfit cobalt oxides crystallize in composite structures built of Co$_2$O$_2$ layers of the CdI$_2$ type stacked with rock salt (RS) type layers. Although these cobalt oxides exhibit metallic behavior, their room-temperature thermoelectric TEP is large (typically 10$^{-1}$ $\text{K}^{-1}$) and their thermoelectric power $Z$ is low (typically $\sim 2\text{W/K.m}$ at 300K). Among this class of layered oxides, physical properties of the Bi$_2$Pb/Se$_{1-x}$Co$_x$/O and Ca$_{3-x}$Cu$_x$O$_{2-x}$ misfits have been mainly studied. More recently, we have studied the Tl/Se$_{1-x}$Co$_x$/O misfit. Interestingly, the transport and magnetic properties of this oxide are remarkable. This oxide is metallic and paramagnetic down to 2K and its magnetoresistance is positive whereas, at low temperature, all the other misfits exhibit reentrant resistivities and large negative magnetoresistance. The high temperature thermoelectricity 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/Se$_{1-x}$Co$_x$/O and Co$_2$O$_2$ [Co/Cu] layers have been attempted.

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 Co$^{2+}$/Co$^{3+}$ which are stabilized in the Co$_2$O$_2$ layer. On the other hand, changes in the $a_0$ and $e_g$ bands 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/Se$_{1-x}$Co$_x$/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 K$_2$Bi$_4$Se$_7$. P. Larson, D. Bile, S.D. Mahanty, Michigan State University, Department of Physics and Astronomy, East Lansing, MI; M.G. Kanatzidis, Michigan State University, Department of Chemistry, East Lansing, MI.

K$_2$Bi$_4$Se$_7$ belongs to a class of complex Bi$_2$Te$_6$Se$_4$ systems which have great potential for thermoelectric performance. This compound forms in two distinct crystal structures, orthorhombic Bi$_4$Se$_3$ type triclinic with space group P$\bar{1}$ and $\beta$-K$_2$Bi$_4$Se$_7$ (monochinic with space group P$\bar{2}$,/m). To understand their thermoelectric properties we have carried out band structure calculations within ab initio density functional theory (DFT) based plane wave method implemented in WIEN97 code. Both scalar relativistic correction and spin-orbit interaction (SOI) were included. For exchange and correlation, we used Perdew-Burke-Ernzerhof potential which incorporates generalized gradient approximation (GGA). The effect of the SOI on the band structure of $\alpha$-K$_2$Bi$_4$Se$_7$ is to shift the conduction band down relative to the valence band and thereby decrease the gap from 0.57 eV to 0.47 eV, which is smaller than the experimental one (0.76 eV). There are however direct gaps at the X point (0.72 eV) and at the V point (0.72 eV) in the Brillouin zone. The low electrical conductivity and high thermopower are consistent with the gap found in this system. The effective mass calculations show a highly anisotropic (2D) electron transport and small anisotropy in the hole transport. This suggests better thermoelectric properties for the electron-doped systems, $\beta$-K$_2$Bi$_4$Se$_7$ has a mixed occupancy of Bi and K atoms within tetrahedra of the crystal structure. The measured gap in this compound is 0.56eV. 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 assumptions will be discussed in detail. While the Bi-K disorder has been suspected to reduce thermal conductivity, this disorder also can have a profound effect on the electronic structure near the Fermi energy.

Work supported by ONR/DARPA.

8:45 AM G13.2

CRYSTAL GROWTH, STRUCTURAL CHARACTERIZATION AND THERMOELECTRIC PROPERTIES OF K$_2$Bi$_4$Se$_7$, Sl$_x$, Se$_{3-x}$ SOLID SOLUTIONS. Theodora Kyra, Duck-Young Chung, Mercouri G. Kanatzidis, Dept of Chemistry, Michigan State University, Lansing, MI; Jeffrey S. Dyck, Crista 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 $\beta$-K$_2$Bi$_4$Se$_7$, led to systematic studies of solid solutions of the type $\beta$-K$_2$Bi$_4$Se$_{7-x}$Sl$_x$. Crystallographic data of selected members of the solid solutions were collected in order to determine the distribution of Sl substitutions in the lattice of K$_2$Bi$_4$Se$_7$. The homogenous Sl-Bi distribution in the structure. The charge transport, semiconducting band gaps, melting points and thermoelectric power $Z$ were studied as a function of temperature and used to optimize 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

THREE-MECHANICAL CHARACTERIZATION OF BISMUTH TELLURIDE BASED THERMOELECTRIC MATERIALS. Woold Bristow, Kevin P. Menard, Univ of North Texas, Laboratory of Advanced Polymers & Optimized Materials, Dept of Materials Science, Denton, TX; John B. White, Marlboro 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 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 flexural conditions. Flexural 3-point bending results for one p-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 micro-crystalline structure of bismuth. 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 Bi$_x$K$_{1-x}$Bi$_4$Se$_7$. John R. Ireland, C.R. Krannawer, Dept of Electrical and Computer Engineering, Northwestern University, Evanston, IL; Theodora Kyra, Mercouri G. Kanatzidis, Dept of Chemistry and Center for Materials Research, Michigan State University, East Lansing, MI.

Previous studies of the K-Bi$_2$Se$_3$-based compounds with various dopants have resulted in several compositions with promising transport characteristics for thermoelectric applications. The specific system $\beta$-K$_2$Bi$_4$Se$_7$ 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 this, we have studied this system with the solid solutions of Bi$_{2-x}$xK$_x$Bi$_4$Se$_7$, (0 \leq x \leq 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 ingots 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 (N00014-98-1-0431) and by DARPA through ARO (DAAG55-05-1-0184). Work at NU made use of Central Facilities supported by the NSF through the Materials Research Center (DMR-0167697).

9:30 AM G13.5


There is a promising future for the application of thermoelectric materials in energy conversion devices because they offer cooling and electricity generation capabilities in compact, solid-state devices.
Nevertheless, their applications are limited because they can achieve only 10% of the Carnot efficiency. However, it has been demonstrated that reduced operation requirements allow the improvement of 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 nanowires is to employ $Sb$ and $Se$ doped $Bi_2Te_3$ nanowires. The electrochemical behavior of these materials will be presented as well as their characterization using X-Ray diffraction (XRD), scanning electron microscopy (SEM) in conjunction with energy dispersive spectroscopy (EDS).

SESSION G14 - CLATHRATES II
Chair: Otto F. Staley
Thursday Morning, November 29, 2001
Room 208 (Hynes)

10:15 AM G14.1
CsI3 AND Na2Zr NaBr STUDIES OF CsI(NaI)2(Zr) (136)
CLATHRATES. R.F. Morse, 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

CsI(NaI)2(Zr) clathrate shows large paramagnetic shift for cesium in CsI3 NaBr NaI spectrum and no paramagnetic shift for sodium in NaI Zr resonance. Germanium clathrate is different from CsI(NaI)2(Zr) clathrate 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 $Mg_xCa_{1-x}Ge_{30}$ ($M = Ln$, $Sr$) have been largely dictated by the parts per thousand and 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 thermostic properties, we have prepared purified samples of $Ba_2Ca_{1-x}Ge_{30}$ by zone melting. This technique brings the impurity levels down to parts per million. We present a thermostic 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 $BaSrGaAlSiP$ 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 (Uno) can provide a quite accurate estimate of the lattice thermal conductivity as well as the Einstein temperature for the rattler. However, while standard macroscopic atomic displacement parameters (ADPs) are obtained in every crystallographic study, no study has attempted a detailed experimental analysis of the thermal motion of a thermoelectric framework material. Accurate crystallographic data allow evaluation of not only the harmonic components of the atomic motion, but also the anharmonic effects [2]. The conventional approach to thermal motion analysis is reciprocal space structure factor fitting, where parameters describing harmonic as well as anharmonic components of the atomic motion are introduced in the structure factor expression. The maximum entropy method (MEM) provides an alternative approach [3]. MEM analysis of neutron diffraction data yields the direct space nuclear density distribution (NDD), which can be analyzed with probability density function models. For the present study of $BaSrGaAlSiP$ 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 Gruen-Cutler 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 anharmone