

SYMPOSIUM Z

Thermoelectric Materials 2000—The Next-Generation Materials for Small-Scale Refrigeration and Power-Generation Applications

April 24 – 27, 2000

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* Invited paper

SESSION Z1: SKUTTERUDITES

Chair: George S. Nolas
Monday Morning, April 24, 2000
Golden Gate A1 (Marriott)

10:15 AM OPENING REMARKS

10:30 AM *Z1.1

THE SYNTHESIS OF METASTABLE SKUTTERUDITES AND CRYSTALLINE SUPERLATTICES. Heike Sellinschegg, Joshua R. Williams, Fred Harris, David C. Johnson, Materials Science Institute and Department of Chemistry, University of Oregon, Eugene, OR; Michael Kaeser, Terry M. Tritt, Department of Physics and Astronomy, Clemson University, Clemson, SC; George Nolas, Research and Development Division, Marlow Industries, Dallas, TX.

We have used controlled crystallization of elementally modulated reactants to prepare a series of kinetically stable, crystalline skutterudites ($M_{1-x}M_4Sb_{12}$ where M' = vacancy, RE, Hf; M = Ni, Fe, Co) and crystalline superlattices containing promising thermoelectric materials. For the bulk synthesis of skutterudites, low angle diffraction data demonstrates that the elemental layers interdiffuse at temperatures below 150°C. Nucleation of the skutterudite structure occurs with a large exotherm on annealing at temperatures below 200°C regardless of the ternary metal. All of the metastable ternary compounds and the new binary compounds were found to decompose exothermically on higher temperature annealing. The decomposition temperature ranged from 250°C for the binary compound $NiSb_3$ to approximately 550°C for the rare earth containing iron compounds. The occupation of the ternary cation was found to depend on the composition of the initial reactant and was varied from 0 to 1. Full occupancy typically required an excess of the filling cation. Structural analysis of crystalline superlattices containing skutterudites and other promising thermoelectric materials will be presented. Results of electrical and thermal conductivity measurements of representative samples will be discussed.

11:00 AM Z1.2

HOW CERIUM CONCENTRATION INFLUENCES THERMAL FACTORS AND MAGNETISM IN $Ce_yFe_{4-x}Ni_xSb_{12}$ SKUTTERUDITES. L. Chapon, D. Ravot, J.C. Tedenac, F. Bouree-Vigneron, Univ of Montpellier II, Montpellier, FRANCE.

Partially filled skutterudite are promising thermoelectrics compounds specially because of very low values of thermal conductivities (glass like materials). It has been shown previously [1-3] that the insertion of rare earth inside the 2(a) site of the structure affects dramatically the propagation of phonons. This behavior belongs to the thermal vibration of rare earth pointed out by large atomic displacement parameters (ADP). Moreover the presence of vacancies inside the structure created by partial insertion adds a static disorder term and decreases again the thermal conductivity in respect with totally filled compounds. This partial insertion influences the magnetic behavior to, specially at low temperature.

We have performed neutron diffraction experiments on $Ce_yFe_{4-x}Ni_xSb_{12}$ powder in the 10K-300K temperature range ($0.16 < y < 1$). We extract by calculations based on the Housley and Hess theory the static contribution of Ce-[] to ADPs. The behavior of cerium's ADP is directly correlated to lattice thermal conductivity measurements for similar compounds [3].

In order to demonstrate that the role of vacancies affect greater the thermal conductivity of skutterudites than any substitutions, we compare those results with neutron diffraction experiments for La-Ce substitutions.

We also give a possible interpretation of the magnetic properties and the respective contribution of rare earth and transition metal to the effective moment. In the over hand, low temperature susceptibilities are discussed in the framework of highly correlated system.

[1] Nolas et al., J. App. Phys. 79(8) 1996, 4002.

[2] B.C. Sales et al., Science 272 1996, 1325.

[3] G.P. Meisner, Phys. Rev. B 80(16) 1998, 3551.

11:15 AM Z1.3

PULSED LASER DEPOSITION OF THIN FILM SKUTTERUDITE THERMOELECTRICS. J.C. Caylor, A.M. Stacy, University of California, Department of Chemistry, Berkeley, CA; R. Gronsky, T. Sands, University of California, Department of Materials Science and Mineral Engineering, Berkeley, CA.

Contemporary research in thermoelectric (TE) materials seeks confirmation of promising theoretical predictions that reduced dimensionality enhances TE performance, attributed at least in part to quantum confinement. In this program, a systematic investigation of the effects of dimensionally-restricted skutterudites, known to behave as bulk thermoelectrics, is underway. Pulsed laser deposition is used to deposit thin films of two binary skutterudite compounds, $CoSb_3$ and $IrSb_3$, in multilayer arrays assess their microstructural

integrity, stability, and thermoelectric performance. Results of detailed x-ray diffraction and electron microscopy studies confirm several expectations, but also reveal the formation of an unexpected 1:1 metastable alloy of the two terminal components. These structures are correlated with thermoelectric properties. Also, an unprecedented epitaxial growth of these binary skutterudites and other "filled" skutterudites will be described.

11:30 AM Z1.4

THERMOELECTRIC PROPERTIES OF SOME PHOSPHORUS-BASED SKUTTERUDITE COMPOUNDS.

Anucha Watcharapasorn*, Robert S. Feigelson**. *Stanford Univ, Dept of Materials Science and Engineering, Stanford, CA; Robert C. DeMattei**, **Stanford Univ, Center for Materials Research, Stanford, CA; Thierry Caillat, Alex Borschevsky, G. Jeffrey Snyder, Jean-Pierre Fleurial, Jet Propulsion Laboratory, Pasadena, CA.

Several phosphide skutterudite compounds were synthesized by the flux technique using tin as the solvent. Thermoelectric measurements showed that $CeFe_4P_{12}$ gave the best ZT value among these compounds. This is due to the increasing values of Seebeck coefficient as well as the decreasing values of electrical resistivity and thermal conductivity at higher temperatures. From these data, we were able to deduce the influence of cage size (and, therefore, the rattling amplitude) on the thermal conductivity of phosphide, arsenide and antimonide skutterudite compounds as a function of anion radius. The rather high thermal conductivity of the phosphorus-based skutterudites is believed to be due to the small rattling amplitude of Ce inside the cage whose volume is defined by twelve phosphorus atoms. Cation and/or anion substitution in order to increase the cage size and/or the lattice should lead to reduced thermal conductivity and improved ZT. On this basis, solid solutions between CoP_3 and $CoAs_3$ as well as $CeFe_4P_{12}$ and $CeFe_4As_{12}$ have been investigated. Other compounds with starting compositions of $Ce_{0.3}Co_4Ge_{1.2}P_{10.8}$ and $CeCo_4Si_3P_9$ have also been made by direct reaction of pure elements and their thermoelectric properties measured.

11:45 AM Z1.5

PREPARATION OF SKUTTERUDITES THIN FILMS FOR THERMOELECTRIC APPLICATIONS BY EXCIMER LASER EVAPORATION. H.-A. Durand, K. Nishimoto, K. Ito, I. Kataoka, JAE Ltd., Tokyo, JAPAN.

The extra-ordinary electrical and thermal transport properties of the family of materials having the skutterudite structure have attracted a lot interests. Particularly, the group of cobalt antimonide skutterudites has been referred to as electron crystals and phonon glasses, a concept underlying the development of new thermoelectric materials. Meanwhile, excimer laser ablation is a unique method to evaporate complex compositions as deposition of thin films in leaves the stoichiometry of targets untouched. The additional energy provided by the plasma plume expansion confers extra-ordinary properties to the thin film growth. Excimer Laser Ablated Molecular Beam Evaporation (ELA-MBE) provides an hyperthermal beam of particles and enables the subsequent deposition and growth of a thin film out of thermodynamic equilibrium. In our investigations, we use a pulsed excimer laser at the wavelength of 193 nm to evaporate sintered and quenched targets of cobalt antimonide skutterudites in ultra-high vacuum. We have deposited thin films on silicon wafers and fused silica substrate. We have studied the composition and crystallographic structure of the deposits as a function of substrate's temperature, target to substrate distance and annealing. Deposits are skutterudite polycrystals with size several hundreds of nanometers. We investigated the electrical as well as the thermal transport properties of thin films having the desired phase. These compare well with values reported for bulk mono-crystals. The scattering that may happen at the boundaries of grains appears to be balanced by the intrinsic high quality of the mono-crystalline grains. Our results opens new ways to Peltier cooling and electric thermo-generation using thin films for a large number of applications.

SESSION Z2: SUPERLATTICE

Chair: Mildred S. Dresselhaus
Monday Afternoon, April 24, 2000
Golden Gate A1 (Marriott)

1:30 PM *Z2.1

THERMOELECTRIC PROPERTIES OF Bi_2Te_3 -BASED LOW DIMENSIONAL STRUCTURES. Joachim Nurnus, Harald Beyer, Harald Böttner, Armin Lambrecht, Fraunhofer Institut Physikalische Messtechnik (IPM), Freiburg, GERMANY.

Bi_2Te_3 -based low dimensional structures are a new material system to increase the thermoelectric figure of merit ZT by a reduction of the thermal conductivity and by a power factor enhancement due to

quantum confinement. Due to low lattice mismatch Pb(Sr)Se, Pb(Sr)Te, SrTe and BaF₂ are suitable materials for Bi₂Te₃ based superlattice structures. Because of the significantly enhanced bandgap the ternary lead salt compounds PbSrSe and PbSrTe (Pb_{0.87}Sr_{0.13}Te: 0.6 eV) are also well-suited barrier materials for MQW structures. Alternatively the insulators SrTe and BaF₂ can be used as barrier materials.

We report on first results of these superlattice structures grown by molecular beam epitaxy (MBE) on BaF₂(111). The structural properties of these layers were investigated by X-ray diffractometry (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and secondary ion mass spectroscopy (SIMS). The thermoelectric properties of different Bi₂Te₃-based superlattices were compared with regard to superlattice parameters, e.g. barrier material and Bi₂Te₃ layer thickness in relation to barrier thickness. Additionally temperature dependent measurements of electrical conductivity $\sigma(T)$ and thermopower $S(T)$ are reported.

*This work was supported by the BMBF, Grant-No. 03N2014A.

2:00 PM Z2.2

THIN-FILM SUPERLATTICE STRUCTURES AND THEIR PROTOTYPAL DEVICE MEASUREMENTS.

Rama Venkatasubramanian, Edward Siivola, Thomas Colpitts and Brooks O'Quinn, Research Triangle Institute, Research Triangle Park, NC.

The thermoelectric performance of Bi₂Te₃/Sb₂Te₃ superlattice structures in device formats will be presented. These superlattice structures are useful in optimizing the transport of electrons and phonons [1, 2]. A brief summary of the status of these measurements and an understanding of the thermal conductivities in these short-period superlattices would be presented. We estimate an intrinsic figure of merit (ZT) in the range of 1.6 to 3 at 300K in the optimal Bi₂Te₃/Sb₂Te₃ superlattice structures from isothermal cross-plane electrical resistivities and adiabatic Peltier voltages measured across thermoelements during quasi-steady state current flow. We have worked on the various parasitic elements, such as contact resistances and heat losses that are inevitable especially in the operation of these thin-film thermoelements. In so doing, we have been able to improve the extrinsic figure-of-merit from 0.03 to about 1.1, using the same material with an intrinsic figure-of-merit of about 3, that would be relevant for device performance. The extrinsic ZT of 1.1 measured by the classical Harman method for a thin-film superlattice thermoelement exceeds that of an extrinsic ZT of 0.7 measured for a bulk thermoelement with an intrinsic ZT of 1. Work is in progress to demonstrate improved extrinsic ZT at 300K. We have also made prototypal device couples utilizing p- and n-type superlattice thin-films. Initial measurements on these couples have focussed on their operation as a power conversion device. Open-circuit voltage measurements with these couples are apparently consistent with the reduced thermal conductivities in these superlattices and these early device results even on extremely thin-films point to a considerable potential for a wide range of thin-film thermoelectric device applications utilizing superlattice structures.

[1] R. Venkatasubramanian et. al, Appl. Phys. Lett, 75, 1104 (1999).

[2] R. Venkatasubramanian, Phys. Rev. B, To be Published (1999).

2:15 PM Z2.3

SYNTHESIS AND PHYSICAL PROPERTIES OF BULK SKUTTERUDITE SUPERLATTICES. Joshua R. Williams, David C. Johnson, University of Oregon, Dept. of Chemistry and Materials Science Institute, Eugene, OR; Michael Kaeser, Terry Tritt, Clemson University, Dept. of Physics and Astronomy, Clemson, SC; George Nolas, Marlow Industries, Research and Development Division, Dallas, TX.

Predicted and observed decreases in thermal conductivity of materials with superlattice structure have prompted interesting research into the possibility of using superlattice materials as higher efficiency thermoelectrics. Transport property measurements as well as other physical characterization of bulk unfilled skutterudite superlattices will be presented. The properties are expected to change with period, and these results will be discussed as well as the potential for decreasing the thermal conductivity of the materials by "filling" the skutterudite structure.

2:30 PM Z2.4

ARTIFICIALLY ATOMIC-SCALE ORDERED SUPERLATTICE ALLOYS FOR THERMOELECTRIC APPLICATIONS. S. Cho, Y. Kim, A. DiVenere, G.K.L. Wong, A.J. Freeman, J.B. Ketterson, Dept of Physics & Astronomy, Northwestern Univ.; L.J. Olafsen, I. Vurgaftman, J.R. Meyer, C.A. Hoffman, Naval Research Lab; Gang Chen, Mechanical & Aerospace Engineering Dept, Univ. of California, Los Angeles, CA.

Currently, much effort is being devoted to achieving a high thermoelectric figure of merit (ZT) involving: i) exploring new

materials with a higher power factor and/or a lower thermal conductivity and ii) quantum well superlattices or superlattice structures, etc. In a conventional quantum well superlattice, enhanced ZT values due to quantum confinement have been reported. However, one disadvantage of the quantum well structure is the thermal back-flow through the barrier layers, resulting in a lower effective ZT. We will present a new approach for achieving high ZT materials: atomic-scale ordered superlattice alloys. The advantage of this structure is that it allows one to "engineer" the electronic band structure by forming an ordered alloy with the goal of achieving better thermoelectric properties and/or reducing the lattice thermal conductivity because of boundary scattering from the layers. We have fabricated Bi/Sb superlattice alloys using MBE that are artificially-ordered on the atomic scale. We can tune the electronic band structure from a semimetal, through zero-gap, to a narrow-gap semiconductor by changing the thicknesses of the Bi and Sb layers. We will discuss the preparation and thermoelectric properties of atomic-scale ordered superlattices such as Bi/Sb, InSb/Sb, etc. This work was supported by DARPA under Grant No. DAAG55-97-1-0130.

2:45 PM Z2.5

THERMOELECTRIC PROPERTIES OF PbSr(Se,Te)-BASED LOW DIMENSIONAL STRUCTURES. Harald Beyer, Joachim Nurnus, Harald Böttner, Armin Lambrecht, Fraunhofer Institut Physikalische Messtechnik (IPM), Freiburg, GERMANY.

In 2D PbTe-based structures an enhancement of the 2D figure of merit ZT can be observed. Recently Harman et al.¹ observed an increase of the 3D figure of merit in PbTe/PbSe quantum dot systems. Thermoelectric and structural properties of low dimensional structures based on PbTe/PbSrTe-MQW's with regard to the structural dimensions and doping profiles are presented. N-type doping is performed by pure Bi, whereas BaF₂ is used as p-type dopant. XRD and AFM measurements show a high structural perfection of these layers. Energy levels and barrier bandgap were determined from IR-transmission spectra. The results are compared with a Kronig-Penney model for superlattices. The influence of the data evaluation method to obtain the 2D power factor will be discussed. Additionally first experiments on the mixed system PbSe/PbSrTe are compared with the results of PbTe/PbSrTe-MQW structures.

¹T.C. Harman et al., 18th International Conference on Thermoelectrics, Baltimore, MD, 1999.

²This work was supported by the BMBF, Grant-No. 03N2014A.

SESSION Z3: NEW MATERIALS I

Chair: David G. Mandrus
Monday Afternoon, April 24, 2000
Golden Gate A1 (Marriott)

3:30 PM Z3.1

ELECTRICAL TRANSPORT PROPERTIES OF TRANSITION METAL PENTATELLURIDE MATERIALS: Hf_{1-x}A_xTe_{5-y}B_y; A = Zr, Ti, Nb, Ta; B=Sb, Se. R.T. Littleton IV, Dept of Materials Science and Engineering; B.M. Zawilski, Dept of Physics and Astronomy; D.R. Ketchum, Dept of Chemistry; J.W. Kolis, Materials Science and Engineering Dept and Dept of Chemistry; Terry M. Tritt, Dept of Physics and Astronomy and Materials Science and Engineering Dept, Clemson Univ, Clemson, SC.

The thermoelectric properties (resistivity and thermopower) of single crystals of the low-dimensional pentatelluride materials, Hf_{1-x}A_xTe_{5-y}B_y; A = Zr, Ti, Nb, Ta; B= Sb, Se, have been measured as a function of temperature from 10 K < T < 310 K. The parent materials HfTe₅ and ZrTe₅ exhibit an anomalous resistive peak, T_p ≈ 80 K for HfTe₅ and T_p ≈ 145 K for ZrTe₅. Each display a large positive (p-type) thermopower (≥ 150 μV/K) just above the peak temperature, which undergoes a change to a large negative (n-type) thermopower (≤ 150 μV/K) below the peak temperature. At T_p, the resistivity values are typically 3-7 times their room temperature value of < 1 mΩ-cm. The pentatelluride materials exhibit large thermopower values (≥ 100 μV/K) up to the highest temperatures measured (310K), while the resistivity remains below 1 mΩ-cm. Substitutions on both the transition metal and Te sites enhances the potential of these materials as candidates for low temperature thermoelectric applications. Results on the extensive doping studies of these materials will be presented.

3:45 PM Z3.2

THE TEMPERATURE DEPENDENT ELECTRONIC STRUCTURE OF PENTATELLURIDES. Bradley Kempton, Daqing Zhang, D.N. McIlroy, University of Idaho, Dept. of Physics, Moscow, ID; T.M. Tritt, R.T. Littleton, Clemson University, Dept. of Physics, Clemson, SC; C.G. Olson, Ames National Laboratory, Ames, IA.

The technique of high resolution angle-resolved photoemission has been used to probe the temperature dependent microscopic electronic structure of the pentatelluride ($A\text{Te}_5$, $A = \text{Zr, Hf}$) family of thermoelectrics. Undoped and doped pentatellurides were examined. Band shifts and band distortions were observed, which coincided with temperature dependent resistivity and thermopower measurements. Analysis of the photoemission data indicates that the pentatellurides are semimetallic/semiconducting at low temperatures ($T < T_c$) and semiconducting at elevated temperatures ($T > T_c$). The temperature dependent band shifts suggest that the pentatellurides evolve from an n-type semiconductor to a p-type semiconductor across the transition. Furthermore, the band shifts are absent in samples with Sb substitution of Zr, which is consistent with the absence of a transition in the corresponding resistivity and thermopower measurements.

4:00 PM *Z3.3

PROGRESS IN NEW THERMOELECTRIC MATERIALS AT JPL: CLUSTER AND LAYER COMPOUNDS. G. Jeffrey Snyder,

Jean-Pierre Fleurial, Thierry Caillat, Alexander Borshchevsky, Jet Propulsion Laboratory, California Institute of Technology, Pasadena CA.

New High ZT thermoelectric materials, namely zinc antimonide and skutterudite-based materials, which are currently being investigated for use in advanced segmented thermoelectric power uncouples, were developed in the advanced thermoelectric materials program at JPL. The recent progress in improving the thermoelectric properties of these proven materials as well as other candidate materials will be reviewed. Several classes of compounds are being studied, which are expected to have low thermal conductivity, chemical variability, and beneficial electronic properties for thermoelectrics. Compounds to be discussed include chevrel and other metal cluster based materials, spinel and defect nickel arsenide-type chalcogenides, incommensurate and other layered chalcogenides. An overview of the electronic, thermal, chemical and magnetic properties of these compounds will be given with an emphasis on the prospects for achieving higher ZT.

4:30 PM Z3.4

THERMOELECTRIC PROPERTIES OF A GROUP OF TERNARY THALLIUM CHALCOGENIDES. Bernd Wölfing, Christian Kloc, Ernst Bucher, Lucent Technologies, Bell Laboratories, Dept of Materials Physics Research, Murray Hill, NJ.

A group of ternary thallium chalcogenides is studied regarding its thermoelectric properties. This group of materials is derived from the semimetallic binary compound Tl_3Te_3 . The materials that belong to this group are Tl_9BiTe_6 , Tl_9SbTe_6 , Tl_4PbTe_3 and Tl_4SnTe_3 . Some of the corresponding Se-compounds exist as well. The thermopowers of these compounds vary over a range of $70 \mu\text{V/K}$ up to $700 \mu\text{V/K}$ at room temperature. The electrical resistivities are in the range of several $\text{m}\Omega\text{cm}$ to Ωcm at 300K. The thermal conductivity is about 1W/(mK) . So far the highest ZT achieved is 0.17 for pure Tl_9BiTe_6 . We expect to report further progress at the conference.

4:45 PM Z3.5

THERMOELECTRIC PROPERTIES OF A NEW FAMILY OF CUBIC COMPOUNDS $A_n\text{Pb}_m\text{Bi}_n\text{Q}_{2n+m}$ ($A = \text{K, Ag}$; $Q = \text{Se, Te}$). Stephan DeNardi, Sandrine Sportouch, Mercouri G. Kanatzidis, Department of Chemistry, Michigan State University, East Lansing, MI; Melissa Lane, John Ireland, Paul Brazis, Carl Kannewurf, Department of Electrical and Computer Engineering, Northwestern University, Evanston, IL; Tim Hogan, Department of Electrical and Computer Engineering, Michigan State University, East Lansing, MI; Ctirad Uher, Department of Physics, University of Michigan, Ann Arbor, MI.

We have designed and prepared several members of a large family of cubic compounds $A_n\text{Pb}_m\text{Bi}_n\text{Q}_{2n+m}$ ($A = \text{K, Ag}$; $Q = \text{Se, Te}$) which are related to the NaCl structure type, where A, Pb and Bi are disordered on the Na site and Q on the Cl site. These compounds are narrow gap semiconductors with adjustable band gaps in the range of ~ 0.80 to ~ 0.24 eV. The specific members APbBiQ_3 , APb_2BiQ_4 , APb_3BiQ_5 , APb_4BiQ_6 , and $\text{APb}_{10}\text{BiQ}_{12}$ have been investigated. Due to the extensive disorder (from the mass fluctuation present) in the lattice of these materials they all exhibit very low thermal conductivity ranging from 1.0 to 2 W/m-K . Physicochemical and charge transport data on these compounds as well as their Sb/Bi and Se/Te solid solutions will also be reported. Efforts to dope these materials will be described. Work supported by ONR.

SESSION Z4: QUANTUM WIRES & DOTS

Chair: Cronin B. Vining
Tuesday Morning, April 25, 2000
Golden Gate A1 (Marriott)

8:30 AM *Z4.1

HIGH THERMOELECTRIC FIGURES OF MERIT IN PbTe/PbSnSeTe QUANTUM DOT SUPERLATTICES. T.C. Harman, Patrick Taylor, D.L. Spears and M.P. Walsh, Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, MA.

High-quality PbTe/PbSnSeTe quantum dot superlattice (QDSL) structures have been grown by molecular beam epitaxy and investigated for high thermoelectric figures of merit ZT . Background information on the band structure and properties of PbSeTe alloyed with SnTe (in which the 300-K energy gap can approach zero) will be presented along with measurements on thick (about 60 to approximately 100 μm) QDSL films. Hall-coefficient, electrical-resistivity, Seebeck-coefficient, and x-ray data will be shown. The measurement of the thermal conductivity on thick QDSL structures utilizing the Peltier heat method will be discussed.

9:00 AM Z4.2

PREPARATION AND CHARACTERIZATION OF PbSe NANO-CRYSTAL (QUANTUM DOT) SUPERLATTICES. Wolfgang L. Gaschler, C.B. Murray, IBM-T.J. Watson Research Center, Yorktown Heights, NY; Kevin L. Stokes, Advanced Materials Research Institute, University of New Orleans, Lakefront, New Orleans, LA.

We present a high temperature (130 to 200°C) solution phase synthesis of monodisperse lead chalcogenide (PbSe , PbTe) nanocrystals (quantum dots). Nanocrystals with sizes tunable from 3 to 10 nm are isolated with controlled shape, structure and surface passivation. These nanocrystals show strong size-dependent absorption in the near IR due to quantum confinement. The monodisperse semiconductor nanocrystals self-organize during controlled evaporation to produce two and three dimensional superlattices (colloidal crystals, opals). We employ a combination of electron microscopy and x-ray scattering to develop a structural model of both the dispersed nanocrystals and the assembled superlattices. Sintering of the superlattices produces dense nanocrystalline films. We are investigating close-packed Quantum Dot solids for novel thermal and electronic transport properties that may be useful in thermoelectric applications.

9:15 AM *Z4.3

CARRIER POCKET ENGINEERING FOR THE DESIGN OF LOW DIMENSIONAL THERMOELECTRICS WITH HIGH ZT^{\dagger} . T. Koga^a, M.S. Dresselhaus^{b,c}. ^aDivision of Engineering and Applied Sciences, Harvard University, Cambridge, MA; ^bDepartment of Physics and ^cDepartment of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA.

The recently proposed concept of Carrier Pocket Engineering is explained in the context of the design of low dimensional thermoelectric materials with a high three dimensional thermoelectric figure of merit $Z_{3D}T$. The geometry of the superlattice, the crystal orientation along the growth direction and the carrier concentration are selected to optimize $Z_{3D}T$. Several examples of superlattices of comparable quantum well and barrier thicknesses will be considered, including $\text{GaAs/Ga}_{1-x}\text{Al}_x\text{As}$, Si/Ge , and others to demonstrate the relevant principles.

We would like to thank Prof. G. Chen, Prof. K. Wang, Dr. X. Sun, S.B. Cronin and Dr. G. Dresselhaus for valuable discussions and inputs.

We gratefully acknowledge support from ONR under MURI subcontract #205-G-7A114-01, and from the US Navy N00167-98-K-0024.

9:45 AM Z4.4

Abstract Withdrawn.

SESSION Z5: HALF-HEUSLER ALLOYS AND QUASICRYSTALS

Chair: Ctirad Uher
Tuesday Morning, April 25, 2000
Golden Gate A1 (Marriott)

10:30 AM Z5.1

EFFECTS OF THE ADDITION OF RHENIUM ON THE THERMOELECTRIC PROPERTIES OF THE ALUMINUM PALADIUM MANGANESE QUASICRYSTALLINE SYSTEM. A.L. Pope, T.M. Tritt, Clemson Univ, Dept of Physics and Astronomy, Clemson, SC; R. Gagnon, S. Legault, J. Strom-Olsen, Dept of Physics, McGill Univ, Montreal, CANADA.

Partially due to their lack of periodic structure, quasicrystals have inherently low thermal conductivity on the order of 1-2 W/mK . AlPdMn quasicrystals exhibit promising values of electrical conductivity ($500\text{-}800 \Omega\text{cm}^{-1}$) and thermopower ($80 \mu\text{V/K}$) with

respect to thermoelectrics. In an effort to further increase the thermopower and hopefully further minimize the thermal conductivity via phonon scattering, quaternary quasicrystals were grown with compositions AlMnPdRe . X-ray data confirms that the addition of the additional element does not alter the quasiperiodicity of the sample. Several batches of $\text{Al}_{1-x}\text{Pd}_2\text{Mn}_8-x\text{Re}_x$ were grown, adding up to 5% Re for Mn. Thermal, electrical and magnetic transport measurements have been performed.

10:45 AM Z5.2

THERMAL CONDUCTIVITY OF HIGHLY SUBSTITUTED TI-BASED HALF-HEUSLER COMPOUNDS. S. Bhattacharya, Dept of Physics and Astronomy, Clemson University, Clemson, SC; V. Ponnambalam, Dept of Physics, University of Virginia, Charlottesville, VA; A.L. Pope, Dept of Physics and Astronomy, Clemson University, Clemson, SC; Y. Xia, S.J. Poon, Dept of Physics, University of Virginia, Charlottesville, VA; T.M. Tritt, Dept of Physics and Astronomy, Clemson University, Clemson, SC.

Half-Heusler alloys with the general formula $\text{TiNiSn}_{1-x}\text{Sb}_x$ are currently being investigated as promising thermoelectric (TE) materials. These materials exhibit high thermopower (40-250 $\mu\text{V/K}$) and low electrical resistivities (0.1-8 $\text{m}\Omega\text{-cm}$) which yields a power factor ($\alpha^2\sigma T$) of 0.2-1.4 W/mK at room temperature. The challenge in these materials is to reduce the relatively high thermal conductivity ($\approx 10 \text{ W/mK}$). The focus of this research is to determine whether the thermal conductivity of TiNiSn can be reduced through Sb-doping on the Sn site. Highly doped half heusler alloys have shown marked reduction in thermal conductivity to values on the order of 3.5 - 4.5 W/mK . Systematic determination of thermal conductivity in a variety of these highly doped materials as well as Sb doped TiNiSn will be presented and discussed.

11:00 AM *Z5.3

TRANSPORT AND THERMOELECTRIC PROPERTIES OF HALF-HEUSLER PHASES BASED ON TRANSITION METALS. S.J. Poon¹, T.M. Tritt², S. Bhattacharya², V. Ponnambalam¹, Y. Xia¹, A.L. Pope² and R.T. Littleton². ¹University of Virginia, Dept. of Physics, Charlottesville, VA, ²Clemson University, Dept. of Physics & Astronomy, Clemson, SC.

Half-Heusler compounds constitute a new class of semimetals and semiconductors for studying electronic structure properties and thermoelectric properties. Upon alloying, several (Ti,Zr,Hf)-based alloys are found to exhibit power factors as high as $\approx 4 \times 10^{-3} \text{ W/m-K}^2$ at ambient temperature. Meanwhile, in some highly substituted alloys, the thermal conductivities are found to be reduced to $\approx 3 \text{ W/m-K}$ or lower. In view of the favorable thermoelectric parameters measured, attempts are being made to optimize the dimensionless figure of merit ZT in these alloy systems. Measurements performed at high temperatures will be presented. We will also present results on impurity conduction and semiconductor-semimetal crossover in alloys based on TiCoSb . Research supported by NSF at UVa, DARPA/ARO and ONR at Clemson U.

11:30 AM Z5.4

HIGH TEMPERATURE THERMAL CONDUCTIVITY MEASUREMENTS OF THE QUASI-CRYSTAL $\text{Al}_{70.8}\text{Pd}_{20.9}\text{Mn}_{8.3}$ USING THE 3 ω METHOD. Philip Davis and P. Barnes, Auburn University, Physics Dept., Auburn, AL; C. Vining, ZT Services, Auburn, AL; A.L. Pope, B. Schneidmiller, S. Kuriakose and Terry M. Tritt, Clemson University, Physics Dept., Clemson, SC.

The thermal conductivity of a quasicrystal, $\text{Al}_{70.8}\text{Pd}_{20.9}\text{Mn}_{8.3}$, was determined by the 3 ω (three-omega) method from 200K to 600K. The 3 ω method generally is less sensitive to radiative heat losses, which allows for an accurate determination of the thermal conductivity of materials at high temperatures. Initial measurements using a steady state technique from 10 K to 300 K indicate that the lattice thermal conductivity appears to be temperature independent at high temperature. This would imply that the phonon mean free path is limited by the complex structure of these materials. The results from the 3 ω technique were compared to a conventional steady-state thermal conductivity method on the same sample over the overlapping temperature range 200K to 300K. The 3 ω measurement was then extended to 600 K. The low thermal conductivity of quasicrystals (typically 1-2 W/m-K) suggest they may be of interest for thermoelectric applications above room temperature.

11:45 AM Z5.5

STRUCTURAL STABILITY OF Ni CONTAINING HALF-HEUSLER COMPOUNDS. S.D. Mahanti and P. Larson, Department of Physics and Astronomy, Michigan State University, East Lansing, MI.

The nature of the ordering of the different elements within the unit cell of half Heusler compounds NiMP ($M = \text{Sc, Ti, Zr, Hf}$; $P = \text{Sn,}$

Sb) has been studied previously¹, but there exists some confusion about which ordering produces the lowest energy configuration for these materials and the reason for this ordering. The crystal structure determines the electronic structure of a material, while the electronic structure in turn determines which crystal structure will have the lowest energy. Using *ab initio* all-electron LAPW calculations within density functional theory², we have studied the electronic structures and total energies of six Ni-containing half-Heusler compounds. We find that the position of the Ni atom, either within one of the pockets formed by the NaCl substructure of *MP* or forming a part of the NaCl substructure, can change the electronic structure from a semiconductor to a zero-gap semiconductor to a metal.¹ The configurations which lead to the zero-gap semiconductor and metal phases have a lattice constant significantly larger than the experimental value and have a higher energy of approximately 2 eV/unit cell than the configuration leading to the semiconducting phase. Two processes which contribute to the stability of the lowest energy configuration of the half-Heusler compounds are (i) the stability of the NaCl substructure formed by *MP* (not containing Ni) and (ii) the Ni bonding in octahedrally coordinated pockets within the NaCl substructure of *MP*.

¹(a) S. Ogut and K. Rabe, Phys. Rev. B, 1995, 10443-10453, (b) S. Ishida, T. Masaki, S. Fujii, S. Asano, Physica, 1997, 237-238, 363-364. ²(a) P. Hohenberg and W. Kohn, Phys. Rev., 1964, 136, B864, (b) W. Kohn and L. Sham, Phys. Rev., 1965, 140, A1133. Supported by DARPA Grant No. DAAG55-97-1-0184.

SESSION Z6: TE THEORY

Chair: Thomas L. Reinecke
Tuesday Afternoon, April 25, 2000
Golden Gate A1 (Marriott)

1:30 PM Z6.1

THEORETICAL CALCULATIONS OF THE THERMAL CONDUCTIVITY IN FRAMEWORK (CLATHRATE) SEMI-CONDUCTORS. Jianjun Dong¹, Otto F. Sankey¹, Ganesh K.

Ramachandran², Paul F. McMillan² and Jan Gryko³. ¹Dept. of Physics and Astronomy, Arizona State University, Tempe, AZ, ²Dept. of Chem., Arizona State University, Tempe, AZ, ³Dept of Earth and Physical Sciences, Jacksonville State University, AL.

We have performed extensive *ab-initio* electronic structure calculations of guest metal atoms in semiconductor clathrates. Output of these calculations is the vibration mode patterns and frequencies of the framework and guest atoms. These calculations clearly show rattling modes of the guest atoms in such systems as $\text{Rb}_2\text{Sr}_6\text{Ga}_{14}\text{Ge}_{32}$, and these rattling modes are believed to interact with acoustic phonons and reduce the thermal conductivity. We will use the results of density functional calculations to model the thermal conductivity in open framework semiconductors. We seek to better understand the effect of the rattler on the thermal conductivity by comparing the thermal conductivity of rattling mode clathrate systems with that of guest free clathrates. We also compare the intrinsic thermal conductivity of guest free Si and Ge clathrates with that of their denser diamond phases. The calculations are performed using the interaction potentials obtained by density functional calculations in a molecular dynamics model of the Kubo linear-response heat-current correlation function.

1:45 PM Z6.2

ELECTRONIC STRUCTURE OF CsBi_4Te_6 . P. Larson and S.D. Mahanti, Department of Physics and Astronomy, D-Y Chung and M.G. Kanatzidis, Department of Chemistry, Michigan State University, East Lansing, MI.

Experimental and theoretical studies of thermoelectric materials with complex lattice and electronic structures are of great current interest. A new compound, CsBi_4Te_6 , has been recently discovered¹ which, if doped properly, yields a high thermoelectric figure of merit below room temperature. In order to understand the electronic structure of this compound, we have carried out *ab initio* LAPW calculations within DFT including the effect of spin-orbit interaction. CsBi_4Te_6 turns out to be an indirect gap semiconductor (band gap 0.38 eV) with the valence band maximum at Γ and the conduction band minimum along the Γ Z direction. The lowest conduction band (LCB) is dominated by states associated with the Bi-Bi bonds,² whereas the highest valence band (HVB) is predominantly Te character. The LCB has multiple minima while the HVB appears to be quasi-two dimensional. These features may be responsible for the observed thermoelectric properties of CsBi_4Te_6 . Comparisons will be made with the electronic structure of Bi_2Te_3 , the material from which the complex CsBi_4Te_6 is derived, as well as another complex material also derived from Bi_2Te_3 , BaBiTe_3 ³.

¹M.G. Kanatzidis, D-Y Chung, L. Iordanidis, K-S Choi, P. Brazis, M. Rocci, T. Hogan, C.R. Kannewurf, Mat. Res. Soc. Symp. Proc., 1999,

545, 233-246.

²D.-Y. Chung, T. Hogan, P. Brazis, M. Rocci-Lane, C. Kannewurf, M. Bastea, C. Uher, M.G. Kanatzidis, submitted to Science.

³P. Larson, S.D. Mahanti, M.G. Kanatzidis, Submitted to Phys. Rev. B.

Supported by DARPA Grant No. DAAG55-97-1-0184.

2:00 PM *Z6.3

WHERE SHOULD WE LOOK FOR HIGH ZT MATERIALS: SUGGESTIONS FROM THEORY. David J. Singh, Marco Fornari, I.I. Mazin and J.L. Feldman, Center for Computational Materials Science, Naval Research Laboratory, Washington, DC.

The key challenges in discovering new high ZT thermoelectrics are understanding how the nearly contradictory requirements of high electrical conductivity, high thermopower and low thermal conductivity can be achieved in a single material and based on this identifying suitable material systems. First principles calculations provide a materials specific microscopic window into the relevant properties and their origins. In this talk, we present specific examples of materials that are or are not good thermoelectrics along with the microscopic reasons. Suggestions are given for achieving higher values of ZT at room temperature in bulk materials.

2:30 PM Z6.4

THERMOELECTRIC PROPERTIES OF JUNCTIONS BETWEEN METAL AND MODELS OF STRONGLY CORRELATED SEMICONDUCTOR. Massimo Rontani and L.J. Sham, Dept of Physics, University of California San Diego, La Jolla, CA.

In recent years the search for new thermoelectric devices has attracted growing interest and research effort[1]. The quality of such devices is expressed by the dimensionless figure of merit ZT : even small improvements of its current upper limit (≈ 1) can turn into important technological applications. In this work we propose a junction between a metal and a narrow-gap strongly correlated semiconductor as a potential candidate for a high- ZT device, especially at temperatures below 300 K, where the need of novel thermoelectric materials is greater. In particular we have considered rare earth or transition metal semiconductor compounds, where conduction and valence bands are frequently strongly renormalized by correlation effects. We take as a model the Falicov-Kimball Hamiltonian, which we solve in the mean-field approach. Possible solutions are: (i) Electronic Ferroelectric[2], where, because of the Coulomb interaction between f -holes and d -electrons, the insulator ground state is a condensate of excitons. (ii) Narrow band semiconductor, characterized by d - f band hybridization. To obtain the electronic transport coefficients and eventually ZT we solve a two-band model in a finite-difference form. Temperature effects and the possibility of an "impurity" layer at the interface of the junction are also taken into account. We compute ZT vs temperature and impurity level energies. For a fixed average working temperature of the junction, an optimum energy of a rare earth impurity level exists which yields large ZT . Large ZT values are also favored at low temperatures. A possible implementation of a device is proposed. This work is supported by the NSF contract DMR9721444 and by INFN PRA99-SSQI. *Present Address: INFN-Dipartimento di Fisica, Università degli Studi di Modena e Reggio Emilia, Modena, Italy.

[1] See G.D. Mahan, in Solid State Physics 51, Academic Press, 1998, p. 81.

[2] T. Portengen, Th. Oestreich and L.J. Sham, Phys. Rev. Lett. 76, 3384 (1996).

2:45 PM Z6.5

ENHANCEMENT OF POWER FACTOR IN A THERMOELECTRIC COMPOSITE WITH A PERIODIC MICROSTRUCTURE. David J. Bergman and Leonid G. Fel, School of Physics and Astronomy; Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv, ISRAEL.

Recently, it was shown that the thermoelectric power factor of a high quality thermoelectric material can be enhanced by mixing it together with a "benign metal" (i.e., a metal with large electrical and thermal conductivities but a small Seebeck coefficient, and hence with poor thermoelectric properties) in the form of a two-constituent composite medium [1]. This was demonstrated in some very simple microstructures. One of those was a parallel slabs sandwich, which is a very anisotropic medium. The other was an isotropic "coated spheres assemblage". This is a very artificial kind of microstructure, where the system is made up entirely of coated spherical grains, which come in an infinite hierarchy of different sizes in order to fill up the entire volume, each grain with a spherical core of the benign metal constituent and a concentric spherical shell of the high quality thermoelectric constituent, and with the same core-to-shell volume ratio. In order to study the possibility of power factor enhancement in more realistic isotropic microstructures, we consider a number of periodic microstructures that have a cubic point symmetry under

rotations. In order to do this we first apply a decoupling transformation which transforms the coupled fields thermoelectric transport problem to uncoupled conductivity-like problems in two different composites with the same microstructure. Those two conductivity-like problems are then treated using some well known numerical methods developed earlier for periodic composites [2]. In particular, we study a microstructure where a simple cubic array of identical spheres of the benign metal is embedded in the high quality thermoelectric host. We also study a microstructure where those spheres come in two different sizes, the smaller ones fitting into the holes which are left in a simple cubic array of the larger spheres. [1]D.J. Bergman and L.G. Fel, J. Appl. Phys. 85, 8205 (1999). [2]D.J. Bergman and K.J. Dunn, Phys. Rev. B 45, 13262 (1992).

SESSION Z7: NEW MATERIALS II

Chair: Terry M. Tritt

Tuesday Afternoon, April 25, 2000

Golden Gate A1 (Marriott)

3:15 PM *Z7.1

CONNECTIONS BETWEEN CRYSTALLOGRAPHIC DATA AND NEW THERMOELECTRIC COMPOUNDS. Brian Sales, Bryan Chakoumakos, David Mandrus, Oak Ridge National Laboratory, Oak Ridge, TN; Veerle Keppens, National Center for Physical Acoustics, University of Mississippi, Oxford, MS.

New bulk thermoelectric compounds are normally discovered with the aid of simple qualitative structure-property relationships. Most good thermoelectric materials are narrow gap semiconductors composed of heavy elements with similar electronegativities. The crystal structures are usually of high symmetry (cubic, hexagonal, possibly tetragonal), and often contain a large number of atoms per unit cell. In the present work a new structure-property relationship is discussed which links atomic displacement parameters (ADPs) and the lattice thermal conductivity of clathrate-like compounds. For many clathrate-like compounds, in which one of the atom-types is weakly bound and rattles within its atomic cage, room temperature ADP information can be used to estimate the room temperature lattice thermal conductivity, the vibration frequency of the rattler, and the temperature dependence of the heat capacity. ADPs are reported as part of the crystal structure description, and hence ADPs represent some of the first information that is known about a new compound. For most ternary and quaternary compounds, all that is known is its crystal structure. ADP information thus provides a useful screening tool for the large and growing crystallographic data bases. Examples of the use and limitations of this analysis are presented for several promising classes of thermoelectric materials.

This work was supported by the Division of Materials Sciences, US Department of Energy and IIKW Belgium.

3:45 PM Z7.2

SEMICONDUCTORS CONTAINING MOLECULAR ANIONS: SINGLE CRYSTALS AND THE TETRATELLUROSTANNATE ANION $[\text{SnTe}_4]^{4-}$. Kevin J. Proctor, Francis J. DiSalvo, Dept of Chemistry and Chemical Biology, Cornell Univ, Ithaca, NY.

We hope to find materials with $ZT > 1$ at room temperature by designing semiconductors with large, complex, and highly symmetric (cubic or hexagonal) unit cells. These features should minimize the thermal conductivity and maximize the number of extrema in the bandstructure at the Fermi energy, N_v . Tetrahedral molecular anions were incorporated into binary tellurides to function as phonon scatterers, or rattlers, while maintaining the high symmetry of the binary telluride. Preliminary results on these new materials will be discussed with a focus on materials containing the tetratellurostannate anion, $[\text{SnTe}_4]^{4-}$, and the growth of single crystals by the vertical Bridgman technique.

4:00 PM Z7.3

THERMAL TRANSPORT PROPERTIES OF PENTATELLURIDE MATERIALS. B.M. Zawilski, Dept of Physics and Astronomy; R.T. Littleton IV, Dept of Materials Science and Engineering; D.R. Ketchum, Dept of Chemistry; J.W. Kolis, Dept of Materials Science and Engineering and Dept of Chemistry; Terry M. Tritt, Dept of Physics and Astronomy and Materials Science and Engineering Dept, Clemson Univ, Clemson, SC.

Measurements of the thermopower and resistivity of transition metal pentatellurides suggest that these materials are favorable for thermoelectric applications especially below room temperature. The electronic properties have been enhanced via substitutional doping to yield power factor values ($\alpha^2 \sigma T$) as high as 1.25W/mK at 150K. Thermal conductivity measurements are necessary to determine the effective figure of merit, ZT , for these materials. A Parallel Thermal Conductance technique has been developed to determine thermal

conductivity of single crystal pentatellurides. Experimental approaches and results of the measurement of thermal conductivity of a number of standards as well as preliminary results on these single crystal materials will be presented and discussed. Heat capacity measurements on pressed pellets of crystalline materials as a function of temperature will also be discussed.

4:15 PM Z7.4

COMPOSITIONAL AND STRUCTURAL MODIFICATIONS IN TERNARY AND QUATERNARY BISMUTH CHALCOGENIDES AND THEIR THERMOELECTRIC PROPERTIES.

Duck-Young Chung, Antje Mrotzek, Mercouri G. Kanatzidis, Michigan State University, Department of Chemistry and Center for Fundamental Materials Research, East Lansing, MI; Melissa Rocci-Lane, John Ireland, Paul Brazis, Carl R. Kannewurf, Northwestern University, Department of Electrical and Computer Engineering, Evanston, IL.

CsBi₄Te₆ doped with SbI₃ has shown very promising thermoelectric properties with ZT_{max} of 0.82 at 224 K. CsBi₄Te₆ has a layered structure composed of NaCl-type [Bi₄Te₆]⁻ slabs connected by unusual Bi-Bi bonds. These layers are separated by the rattling Cs⁺ ions. Solid solutions of CsBi_{4-x}Te_{6-x}Se_x (0 < x < 1.2) revealed a very interesting structural modification with wider cross-section of [Bi₄Te₆]⁻ slabs, while solid solutions of CsBi_{4-y}Sb_yTe₆ (0 < y < 0.8) still keep the original framework. AM₂Bi₃Te₇ (A = Cs, Rb; M = Bi, Sn) has a similar structural motif to that of CsBi₄Te₆ but the NaCl-type slabs are infinite. Solid solutions of AM₂Bi₃Te₇ were also synthesized and the results of further explorations into the A/M/Bi/Te system will be reported. Another structural evolution has been observed in the Pb/Bi/Se system. Pb₅Bi₆Se₁₄, Pb₈Bi₈Se₁₃, and Pb₅Pb₁₂Se₂₃ are homologues with different combination of alternating Bi₂Se₃- and PbSe-type layers. Looking into the property changes over the compositional and structural modifications in these three chemical systems should guide the search for optimized multinary bismuth chalcogenides.

4:30 PM Z7.5

DOPING STUDIES OF CsBi₄Te₆ THERMOELECTRIC MATERIALS. M.A. Lane, P.W. Brazis, J.R. Ireland, C.R. Kannewurf, Dept. of Electrical and Computer Engineering, Northwestern University, Evanston, IL; T. Kyratsi, D.-Y. Chung, M.G. Kanatzidis, Dept. of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, MI.

It has been previously demonstrated that CsBi₄Te₆ has basic properties that are favorable for thermoelectric applications. The initial doping program resulted in a ZT value of 0.8 in the vicinity of 200K for the p-type dopant, SbI₃. This result is superior to the ZT values for both undoped CsBi₄Te₆ and p-type Bi₂Te₃ and suggests that this material might be useful for applications well below room temperature. A similar study on the n-type material is in progress. This paper reports recent refinements that have been achieved in the optimization of both dopant type and concentration by a study of the transport parameters that determine the power factor and figure of merit.

This work is supported by ONR grant N00014-98-1-0443 and by DARPA through ARO (DAAG55-97-1-0184).

4:45 PM Z7.6

EXPLORING COMPLEX CHALCOGENIDES FOR APPLICATIONS IN THERMOELECTRIC DEVICES. Ying C. Wang and Francis J. DiSalvo, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY.

The best thermoelectric materials to date are bismuth telluride-based semiconductor materials with a figure-of-merit ZT about 1 at room temperature. In order to improve the performance efficiency of thermoelectric devices, better materials with higher figures of merit are needed. After theoretical studies and database searches, we summarized a series of empirical guides for exploring semiconductor thermoelectric materials. We have synthesized, modified and characterized various complex multinary chalcogenides. The role of high crystal symmetry in improving ZT has been investigated. We think that the technical challenges are the synthesis of compounds of high crystal symmetry and the carrier concentration control in complex chalcogenides.

SESSION Z8: POSTER SESSION

Chairs: Mercouri G. Kanatzidis, Subhendra D. Mahanti, Joseph Poon, Thierry Caillat and G. Chen
Tuesday Evening, April 25, 2000
8:00 PM
Salon 1-7 (Marriott)

Z8.1

SYNTHESIS, MICROSTRUCTURE AND THERMOELECTRIC

PROPERTIES OF FINE Bi-Te-Sb ALLOYS. Yijin Lu, Ce-Wen Nan, Jiming An and Xinmin Min, Advanced Materials Research Institute, Wuhan University of Technology, Wuhan, Hubei, CHINA.

Bismuth telluride-based alloys are one of the best thermoelectric materials in the state-of-the-art technology. They are commonly fabricated from their pure elements via a metallurgical melt processing. In the present work, an alternative approach, i.e., a chemical solution method, is employed to synthesize bismuth telluride-based alloys. The chemical process involves coprecipitation and homogeneous precipitation of Bi-Te-Sb in an aqueous solution, followed by a reduction in hydrogen atmosphere. The influences of the processing routes on microstructure and thermoelectric properties of the Bi-Te-Sb alloys are investigated, and a formation mechanism is suggested. This method provides a simple two-step process for the preparation of fine Bi-Te-Sb thermoelectric alloys.

Z8.2

SEMICONDUCTORS WITH COMPLEX ANIONS AS POTENTIAL THERMOELECTRIC MATERIALS. Thomas P. Braun and Francis J. DiSalvo, Cornell University, Dept of Chemistry and Chemical Biology, Ithaca, NY.

Currently available commercial thermoelectric (TE) materials are highly optimized. A significant improvement of their performance due to only minor modifications is rather unlikely. In order to find a new generation of TE materials it is necessary to envision new classes of compounds and materials that display novel features. We see a high potential in a new class of semiconductors that contain complex, tetrahedral anions like e.g. the thiophosphate ion (PS₄³⁻). These complex anions serve multiple purposes to increase ZT: It has been shown that ZT is directly proportional to the number of band extrema near the Fermi level. This degeneracy is only limited by the crystallographic symmetry and can reach a value of 48 for cubic systems. Because of their pseudo-spherical shape tetrahedral anions can form highly symmetrical, 'close packed' structures. Furthermore these complex anions possess internal vibrational degrees of freedom and are only weakly coupled to the host structure. As a result their thermal conductivity is expected to be low. As the known compounds of this class (e.g. Pb₃(PS₄)₂) exhibit large band gaps and very high electrical resistivities, we attempt to synthesize hybrid materials that contain both a covalent anionic network and isolated complex anions. In these compounds the electrical conductivity can be governed by the properties of network while the interspersed complex anions can act as anionic rattlers. Structures of this kind are known for the class of sillenites (Bi₁₂SiO₂₀) which contain SiO₄ tetrahedra incorporated into a Bi-O network. We are currently trying to synthesize related compounds with other chalcogenides. At the same time we are exploring possible reactions to incorporate e.g. the PS₄³⁻ ion into network structures. The synthesis of the layered compound Pb₃(PS₄)Br₃ proves that this can be done, while the properties of these new compounds remain to be determined.

Z8.3

LATTICE DYNAMICS STUDY OF ANISOTROPIC HEAT CONDUCTION IN SUPERLATTICES. Bao Yang, Gang Chen, Univ. of Cal. at LAX, Dept. of Mechanical and Aerospace Engineering, Los Angeles, CA.

Past studies on the thermal conductivity of superlattices suggest that the phonon group velocity reduction is the cause of the observed drop in the cross-plane thermal conductivity in semiconductor superlattices. In this work, we investigate the effects of the phonon group velocity on the thermal conductivity in both the in-plane and cross-plane directions of superlattices. The acoustic phonon spectra in all directions are computed using a face-centered cubic model of lattice dynamics for Si/Ge and GaAs/AlAs superlattices. We find that the in-plane thermal conductivity drop, caused by the reduced group velocity, is much less than the reported experimental results. This implies that other mechanisms, such as diffuse interface phonon scattering and dislocation phonon scattering, rather than the reduced group velocity, should make the major contribution to the in-plane thermal conductivity reduction.

Z8.4

STRUCTURE AND THERMOELECTRIC PROPERTIES OF NEW QUATERNARY TIN AND LEAD BISMUTH SELENIDES, K_{1+x}M_{4-2x}Bi_{7+x}Se₁₅ (M = Sn, Pb) AND K_{1-2x}Sn_{5-x}Bi_{11+2x}Se₂₂. Antje Mrotzek¹, Kyoung-Shin Choi¹, Duck-Young Chung¹, Melissa Lane², John Ireland², Paul W. Brazis², Tim Hogan³, Carl R. Kannewurf² and Mercouri G. Kanatzidis¹. ¹Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, MI, ²Department of Electrical Engineering and Computer Science, Northwestern University, Evanston, IL, ³Department of Electrical Engineering, Michigan State University, East Lansing, MI.

Recently, there has been great interest in finding new materials with superior thermoelectric applications and developing new concepts for designing new thermoelectric compounds. Our research is focussed on the study of multinary heavy element chalcogenide compounds. The synthetic investigations currently target quaternary systems containing alkali metals and covalent metal selenide and telluride frameworks. These materials tend to achieve low thermal conductivity by disorder of the metal atoms which creates mass fluctuation scattering of the lattice phonons. Here we describe the compounds $K_{1+x}M_{4-2x}Bi_{7+x}Se_{15}$ with $M=Sn, Pb$ and $K_{1-2x}Sn_{8-x}Bi_{11+x}Se_{22}$. The crystal structures of the two isostructural phases $K_{1.25}Pb_{3.5}Bi_{7.25}Se_{15}$ and $K_{1.41}Sn_{2.96}Bi_{7.63}Se_{15}$ and of $K_{0.66}Sn_{4.82}Bi_{11.18}Se_{22}$, that crystallizes in a new structure type, are closely related. Bi_2Te_3 -type and NaCl-type building units are connected to form a three-dimensional anionic framework with K^+ filled tunnels. The thermoelectric properties of these compounds were explored. These materials have low thermal conductivity (1.5 W/m Σ K) due to an extensive disorder of the metal atoms and possible rattling potassium atoms.

Z8.5
SYNTHESIS AND CHARACTERIZATION OF A THREE-DIMENSIONAL NETWORK OF 6-NM DIAMETER BISMUTH TELLURIDE WIRES. T.E. Huber, T. Lucas, Howard University, Department of Chemistry, Washington, DC.

It has been suggested that microengineering traditional thermoelectric materials into nanocomposites may lead to a significant improvement in their thermoelectric performance because of the reduction in thermal conductivity. We have synthesized random networks of Bismuth Telluride by high pressure injection of the melt in Porous Vycor Glass and studied the microstructure and crystalline structure of the composite. Our experiments to leach the silica from the composite will be reviewed. Results of measurements of the thermal conductivity of the resulting network will be discussed.

Z8.6
CHARACTERIZATION OF NEW MATERIALS IN A FOUR-SAMPLE THERMOELECTRIC MEASUREMENT SYSTEM. Nishant Ghelani¹, Sim Loo¹, Duck-Young Chung², Sandrine Sportouch², Stephan de Nardi², Mercuri G. Kanatzidis², Tim Hogan¹. ¹Department of Electrical and Computer Engineering, Michigan State University, East Lansing, MI, ²Chemistry Department, Michigan State University, East Lansing, MI.

A new transport measurement system has been developed for thermoelectric characterization of materials. This system has been used to characterize several new materials in the $CsBi_4Te_6$, $A_2Bi_8Se_{13}$ ($A = K, Rb, Cs$), $HoNiSb$, $Ba/Ge/B$ ($B = In, Sn$), and $AgPbBiQ_3$ ($Q = S, Se, Te$) systems. Some of these materials were fabricated by the alkali-polychalcogenide flux technique, developed at Michigan State University, while others were synthesized by direct combination of the elements. Thermoelectric figures of merit, ZT, are reported for these new materials as a function of temperature from 4.2 K to 400 K. Measurements of electrical conductivity, thermoelectric power, and thermal conductivity were simultaneously obtained for each sample in a four-sample computer controlled measurement system. Ac and dc electrical conductivity and thermal conductivity were obtained using standard four-probe configurations. A high density of data points were obtained by the slow pulsed technique for thermoelectric power and thermal conductivity measurements. Typical run times to fully characterize four samples from 80 K to 320 K in 5 K steps are approximately 50 hours. This paper provides a detailed description of the four-sample transport measurement system and data interpretation for the above material systems.

Z8.7
THERMOELECTRIC MATERIALS MEASUREMENT SYSTEM FOR DOPING AND ALLOYING TRENDS. Sim Loo¹, Duck-Young Chung², Mercuri G. Kanatzidis², Tim Hogan¹. ¹Department of Electrical and Computer Engineering, Michigan State University, East Lansing, MI, ²Chemistry Department, Michigan State University, East Lansing, MI.

The polychalcogenide flux technique has been used to produce a number of new materials, some of which have shown promising thermoelectric properties. The next stage in the development of these materials is an investigation of doping and alloying trends for the purposes of ZT optimization. As an aid in this investigation, the polychalcogenide flux technique has recently been modified to produce samples at much higher rates. To benefit from this upgrade, the thermoelectric characterization techniques must be able to match this rate, which could be as high as 100 samples per week. This paper presents a computer controlled 36-sample system for thermoelectric power and two-probe electrical conductivity measurements as a function of temperature (77 - 475 K). Trends in the power factor ($S^2\sigma$) as a function of doping and alloying are reported for the $K_2Bi_8Se_{13}$

and $CsBi_4Te_6$ material systems. More thorough studies on the most promising materials identified by this method are obtained through a second measurement system also presented at this conference.

Z8.8
CRYSTAL GROWTH OF TERNARY AND QUATERNARY ALKALI METAL BISMUTH CHALCOGENIDES USING BRIDGMAN TECHNIQUE. Theodora Kyratsi, Duck-Young Chung, Kyoung-Shin Choi, Antje Mrotzek and Mercuri G. Kanatzidis, Michigan State University, Dept. of Chemistry and Center of Fundamental Materials Research, East Lansing, MI.

Our exploratory research in new thermoelectric materials has identified the ternary and quaternary bismuth chalcogenides β - $K_2Bi_8Se_{13}$, $K_{2.5}Bi_{8.5}Se_{14}$, $CsBi_4Te_6$, and $KM_4Bi_7Se_{15}$ ($M = Pb, Sn$), to have promising properties for thermoelectric applications. All these materials have needle-like morphology so they are highly anisotropic. In order to achieve long and well-oriented needles for which, consequently, the best thermoelectric performance is expected, we developed a modified Bridgman technique for their bulk crystal growth. The results of the crystal growth experiments as well as electrical conductivity, Seebeck coefficient and thermal conductivity measurements for the compounds obtained from this technique will be presented.

Z8.9
A NEW EXPERIMENTAL TECHNIQUE FOR SEEBECK MEASUREMENTS. E. Hatzikraniotis, Th. Kyratsi*, K. Chrissafis, Physics Dept. - Section of Solid State Physics, Aristotle University of Thessaloniki, GREECE. *Dept. of Chemistry, Michigan State University, East Lansing, MI.

In this work we report a new experimental technique for thermopower measurements. The experimental technique consists on a modification of the usual procedure of an applied thermal gradient, as well as on a novel approach of data recording and analysis. The principle of operation is based on the alternating temperature difference. The sample to be measured is mounted between two small cartridge heaters that can be controlled independently and set the edges of the sample to different temperatures. Two thermocouples are mounted on the sample's edges and used to monitor both the temperature (T1 and T2 respectively) and the sample's thermo-EMFs (E1, E2). Instead of fixing the temperature of the two edges, on/off controllers were used to produce a small amplitude periodic thermal gradient of alternating sign along the sample. Two experimental processes were investigated: The usual approach, i.e. recording all the four thermal voltages, namely thermocouple EMFs and sample's thermo-EMFs during the applied thermal gradient and evaluate the Seebeck coefficient from the slope of ≈ 1 or ≈ 2 vs. the temperature difference. A new approach is also investigated, where just the sample's thermo-EMFs are recorded, and the Seebeck coefficient can be calculated from the dependence E2 vs. E1. In this work, we compare the two methods with respect to different heating-cooling profiles. Data taken on standards will be reported. The experimental probe, designed for thermopower measurements on small ($L > 2mm$) or larger samples, is easily modified to allow also conductivity and Hall effect measurements at a wide temperature range from 80 to 600K. Design details and measurement specifics will also be discussed.

Z8.10
THERMOELECTRIC PROPERTIES OF DOPED IRON DISILICIDE. Jun-ichi Tani, Hiroyasu Kido, Osaka Municipal Technical Research Institute, Dept of Inorganic Chemistry, Osaka, JAPAN.

β -iron disilicide has been studied as a candidate material for thermoelectric conversion applications, because of its superior features such as large Seebeck coefficient, low electrical resistivity, and chemical stability. There have been many attempts to dope some additives into iron disilicide to alter its semiconducting properties. In the present study, the thermoelectric properties of Re, Ir, Pt doped iron disilicide ($Fe_{1-x}M_xSi_2$; $M=Re, Ir, Pt$) have been measured in the temperature range 300 and 1200K. The systematic variation of the thermoelectric properties with regard to doping will be discussed.

Z8.11
TRANSPORT PROPERTIES OF THE DOPED THERMOELECTRIC MATERIALS $K_2Bi_{8-x}Sb_xSe_{13}$ AND $K_{2.5}Bi_{8.5}Se_{14}$. P.W. Brazis, M.A. Lane, J.R. Ireland, C.R. Kannewurf, Northwestern University, Dept of Electrical and Computer Engineering, Evanston, IL; D.-Y. Chung, T. Kyratsi and M.G. Kanatzidis, Department of Chemistry, Michigan State University, East Lansing, MI.

The synthesis, physicochemical, spectroscopic, and structural characterization of the compounds β - $K_2Bi_8Se_{13}$ and $K_{2.5}Bi_{8.5}Se_{14}$ have been previously reported and point to promising materials for thermoelectric applications**. Compared with α - $K_2Bi_8Se_{13}$, which

has a room temperature electrical conductivity of 2 S/cm and a Seebeck coefficient ranging from -210 to -260 $\mu\text{V}/\text{K}$. $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ and $\text{K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$ show excellent electrical conductivity values at room temperature while maintaining high Seebeck coefficients. In this work, the optimization of the compound $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ is continued by the introduction of varying concentrations of several different dopants. The value of x in $\text{K}_2\text{Bi}_{8-x}\text{Sb}_x\text{Se}_{13}$ was varied in order to find the composition with minimum thermal conductivity. Where possible, transport measurements were carried out on both single crystal and polycrystalline ingot material. From these data the trends in the key parameters were identified for optimizing the power factor and figure of merit. A similar program is in progress for $\text{K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$ and preliminary results will be presented.

*This work supported in part by ONR Grant N00014-98-1-0443 and by DARPA through ARO (DAAG55-97-1-0184).

**D.-Y. Chung et al., *Chem. Mater.* 9, 3060 (1997).

Z8.12

THERMOELECTRIC CHARACTERISTICS OF THE HOT-PRESSED $(\text{Bi,Sb})_2\text{Te}_3/(\text{Pb,Sn})\text{Te}$ FGM FOR POWER GENERATION. Dae-Joong Yeon, Tae-Sung Oh, Hong Ik Univ, Dept of Metallurgical Engineering and Materials Science, Seoul, KOREA; Dow-Bin Hyun, Korea Institute of Science and Technology, Center for Materials Processing, Seoul, KOREA.

The p-type $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3/(\text{Pb}_{0.7}\text{Sn}_{0.3})\text{Te}$ functionally gradient materials (FGM) with various segment ratio were fabricated by hot pressing the mechanically alloyed $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$ and 0.5 at% Na_2Te -doped $(\text{Pb}_{0.7}\text{Sn}_{0.3})\text{Te}$ powders. The thermoelectric properties and output power of the hot-pressed $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3/(\text{Pb}_{0.7}\text{Sn}_{0.3})\text{Te}$ FGM were compared with those of the $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$ and 0.5 at% Na_2Te -doped $(\text{Pb}_{0.7}\text{Sn}_{0.3})\text{Te}$ alloys. At temperatures above 200°C, the $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3/(\text{Pb}_{0.7}\text{Sn}_{0.3})\text{Te}$ FGM exhibited a superior figure-of-merit to those of the $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$ and the 0.5 at% Na_2Te -doped $(\text{Pb}_{0.7}\text{Sn}_{0.3})\text{Te}$ alloys, implying that the thermoelectric energy conversion efficiency can be improved by FGM. With increasing the temperature difference (ΔT) larger than 300°C, The output power of the FGM became higher than the value of the $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$ alloy. Maximum output power of 72.6W was obtained for the $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3/(\text{Pb}_{0.7}\text{Sn}_{0.3})\text{Te}$ FGM with ΔT of 320°C.

Z8.13

STRUCTURAL AND THERMOELECTRIC PROPERTIES OF EPITAXIAL RHENIUM SILICIDE THIN FILMS. Christoph Kleint, Armin Heinrich, Joachim Schumann, Horst Griessmann, Institute of Solid State and Materials Research Dresden, GERMANY.

Because of its small lattice misfit to silicon, $\text{ReSi}_{1.75}$ is a promising candidate for silicide / silicon multilayers for room temperature thermoelectric applications. We have prepared $\text{ReSi}_{1.75}$ single films on Si and SOS with thicknesses in the 10 nm-range using both conventional silicide formation procedures like Solid Phase Epitaxy (SPE) and Reactive Deposition Epitaxy (RDE) and codeposition processes (Facing Target Sputtering, FTS) to find growth conditions for low surface and interface roughness. To avoid rotation twinning, which is found for deposition on Si (100) and Si (111) due to symmetry reasons, we have studied $\text{ReSi}_{1.75}$ epitaxy on Si (110). Whereas thin $\text{ReSi}_{1.75}$ films prepared by RDE and SPE exhibit a low crystalline quality (large roughness and holes), X-ray reflectometry reveals smooth interfaces with well defined thickness oscillations for FTS-grown films. $\text{ReSi}_{1.75}$ films on Si (110) do not show rotation twinning, however a complicated epitaxial relationship is found, which does not correspond to the low misfit relationship expected from geometrical considerations. Thermopower and resistivity have been investigated for films on SOS in the temperature range between 70 and 1000 K, thermal conductivity data at room temperature were obtained by the 3Ω -method. We also present first results of experiments concerning the deposition of silicon on top of $\text{ReSi}_{1.75}$ films which were undertaken to check the possibility of silicide / silicon multilayer preparation.

Z8.14

CELLULAR AUTOMATA SIMULATIONS FOR GUIDING THERMOELECTRIC MATERIALS DEVELOPMENT AND DEVICE DESIGN. Peter P.F. Radkowski III, Timothy D. Sands, Graduate Group in Applied Science and Technology, University of California, Berkeley, CA.

The thermoelectric performance of nanoscale, quantum-confined systems may be enhanced by selectively manipulating electron and phonon scattering. To aid in the design of such material configurations, a coupled cellular automata simulation is being developed. A charge carrier automaton and a lattice vibration automaton represent scattering effects on a mesoscopic scale. The automata are coupled by quantum mechanical scattering matrices. In this manner, the simulation intimately links the time and space

evolution of charge carrier and phonon populations. This non-equilibrium transport simulation is highly suitable for characterizing heterogeneous, anisotropic and nanoscale material configurations. The investigation addresses random defects and substitutions, irregular boundary conditions and interfaces, and contact resistances. The simulation includes a mixed-mode representation of the phonon population. This linear combination of phonon modes may prove to be a critical tool in assessing the relative performances of superlattices and quantum wires fabricated from polar and non-polar materials. The charge and heat current data predicted by the simulation are compatible with experimentally measured data. It is anticipated that this coupled cellular automata technique will be extended to address the heat, charge and optical processes of microelectronics including semiconductor lasers and photovoltaic devices.

Z8.15

DEVELOPMENT OF FILMS GROWTH TECHNOLOGY OF THE HIGHEST MANGANESE SILICATE AND INVESTIGATION OF THEIR THERMOELECTRIC PROPERTIES. Adham Paiziev, Tuklkun Kamilov, Inst. of Electronics, Dept. of Positron Diagnostics, Tashkent, UZBEKISTAN.

The particular interest to the highest manganese silicate (HMS) is associated with its possible use in devices sensitive to light in the IR-range. Our HMS films of 3-5 (m in thickness were grown under temperature of 1000-10400C for 12- 15 min with the following slow cooling with temperature gradient of ~ 30 -35 grad/min. The thermal electromotive force coefficient was approximately + 700 (V/grad with fast-action of ~ 10 -7C. Thus obtained p-type silicate films had the following parameters: surface resistivity $\text{RS} = 80$ -100 Om/cm, Hall mobility ($H = 7$ -30 cm^2/Vs , charge carrier concentration ($= 1019$ -1020 cm^{-3} (at 300 K). The structure of the obtained films was studied by a high energy electron diffraction technique in an EMR-102 electron diffraction camera, at the accelerating voltage 75 and 100 kV. It was established that at the initial growth stage films consisted of the mixture of polycrystalline cubic monosilicade MnSi ($a = 4.56\text{\AA}$), and highest tetragonal manganese silicate MnSi 1.71-1.75 ($a = 5.50$, $c = 15.90\text{\AA}$) and in some instances needle-like tetragonal silicate crystals with the same unit cell parameters. The results of electron diffraction and optical analysis indicate that the unique properties of the grown films are due to HMS layers alone. The considerable improvements of the properties are achieved by increasing the thickness and the homogeneity of HMS layers. It allows us to create the devices for registration non-selective flows of different intensive and also their form and duration of impulse thermal radiation.

Z8.16

ELECTRIC AND THERMOELECTRIC PROPERTIES OF QUANTUM WIRES BASED ON BISMUTH SEMIMETAL AND ITS ALLOYS. Albina Nikolaeva, Pavel Bodiul, Dmitrii Gitsu, Gheorgii Para, Institute of Applied Physics, Academy of Science, Kishinev, MOLDOVA.

Due to anomalous small characteristic energies, large wavelength de Broglie and free path lengths of carriers on energy and impulse, bismuth manifests significant sensitivity to doping, pressure, magnetic and electric fields and sizes of samples. We have developed a technology for preparation of bismuth semimetal and its alloys in the form of thin monocrystal wires and nanoconstrictions, cased in a glass cover with a wide set of diameters. This allowed to carry out a complex investigation of the electric and thermoelectric properties in the temperature range 4.2-300 K, at the magnetic fields up to 14 T, depending on the diameter, doping impurity and strain. The resistance anomalous behavior (increasing while the temperature decreases (300-77K) when the diameter diminishes, together with the thermopower sign change and the maximum formation in the positive region in the same temperature range gave a possibility to conclude that the surface scattering of the carriers is dominating. Annealing, laser recrystallization, chemical etching allowed to change the character of the surface scattering of the charge carriers significantly, as well as to found optimal conditions for increasing thermoelectric figure of merit in the temperature range 300-77 K. These wires used as thermoelectric transducers are characterized also by high mechanical strength, the glass cover safely protects them from the surroundings influence.

Z8.17

Abstract Withdrawn.

Z8.18

LIMITS OF SCALING IN THERMOELECTRIC MICROCOOLERS. Leo P. Bulat, Levon D. Akopyan, St. Petersburg State Academy of Refrigeration, Dept of Electrical Engineering, St. Petersburg, RUSSIA.

It is well known that practically all elements and systems of electronics should have optimum temperature conditions. Thence appear a problem of develop and design of electronic elements with a

local (spot) cooling and a problem of the temperature stabilization. A using of the thermoelectric method of refrigeration is the best practical method of cooling chips and other electronic components from a cost and efficiency viewpoint. From the other hand, the trend of microminiaturization of electronic components also requires microminiaturization of thermoelectric coolers for electronics. The modern thermoelectric coolers may have the thickness about 20 μm with the temperature difference between cold and hot sides of 50C. Under those conditions of very large temperature gradients all transport equations of traditional theory of thermoelectricity in semiconductors become incorrect. Therefore, we need to found a limit of scaling: the limited values of temperature gradients, power density output and thickness of semiconductor cooling films, that result in change of traditional theory of thermoelectricity. In the present paper a theory of scaling in microminiature thermoelectric coolers is proposed. New nonlinear effects result in changing of all equations for heat and electric transport as for kinetic coefficients. The limits of scaling have been founded. Nonlinear analytical formulas for all kinetic coefficients and for thermoelectric figure of merit under such conditions also have been received. The theory shows that in typical cases the nonlinear effects lead to increase of the thermoelectric figure of merit of the material. Also the coefficient of performance (COP) of the microminiature thermoelectric cooler begin increase under the heat fluxes of 300-500 W/cm^2 . Such result is in consent with known experimental data.

Z8.19 FIGURE OF MERIT ENHANCEMENT IN DOPED SEMI-CONDUCTORS NEAR PERCOLATION THRESHOLD.

Elena I. Rogacheva, Kharkov State Polytechnic University, Dept of Theoretical and Experimental Physics, Kharkov, UKRAINE.

According to the ideas, we have developed and proved experimentally, in any solid solution there is a critical concentration of impurity (less than ~ 1 at.%) corresponding to the percolation threshold at which percolation channels are formed and a qualitative change in the state of solid solution takes place. In the range of small impurity concentrations the main contribution into the free energy is made by entropy term TS whose role increases as temperature grows. It raises probability of the processes connected with the growth of configuration entropy stimulating delocalization of atoms relative to the basic structural positions, formation of new types of defects, etc. When approaching the percolation threshold, the maximum degree of disorder is reached and fast growth of fluctuations is observed like in case of second type phase transitions. By realizing disordered structures of such type, one can obtain qualitatively new properties that are absent in the host material. It is proposed to use this universal physical phenomenon when developing efficient thermoelectric materials by applying solid solution compositions close to the percolation threshold. It is shown that in the specified region decrease in phonon thermal conductivity more than offsets the one in charge carrier mobility and the Seebeck coefficient increases. The factors affecting ZT magnitude (charge carrier concentration, size and electrochemical factors, band structure) in the critical region are considered. The prospects of using impurity atoms of variable valence are grounded. The proposed method can be applied to semiconductor materials of any type in order to improve their thermoelectric properties by doping. Examples of creating efficient materials based on the IV-VI compounds for power generation applications by using this method are given. Similar critical phenomena can be observed in the system of the second phase particles when their number exceeds a certain threshold value.

Z8.20

²³Na AND ²⁹Si NMR AND XPS STUDIES OF SODIUM/SILICON CLATHRATES. Jiliang He, Christopher I. Ratcliffe, Valery I. Smelyanski, John S. Tse, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, CANADA.

Following the work of Nolas et al.[1] on $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$, the clathrates $\text{Na}_8\text{Si}_{46}$ and $\text{Na}_x\text{Si}_{136}$ ($1 < x < 24$) have been recognized as potential thermoelectrics, as these materials fit the phonon-glass/electron-crystal model. Prior to this, the main focus of interest in the sodium/silicon clathrates was their conductivity, and the metal-insulator behavior of the $\text{Na}_x\text{Si}_{136}$ phase which is reported to occur as the level of Na is reduced below about $x=8$. The variable composition of these materials is attractive as it provides a potential means of tuning properties. Here we present the ²³Na and ²⁹Si NMR spectroscopy of the fully Na-loaded phases and of intermediate Na-loaded Str.II. The new results considerably improve and extend on the previous NMR work [2-5] and allow a fully consistent interpretation of the sometimes puzzling NMR behavior. It is now possible to relate the details of the ²³Na and ²⁹Si NMR spectra for the highest Na-loaded materials to the crystal symmetry, and unequivocally identify resonances due to Na in small and large cages of both structures and of all Si crystallographic types but one. The relative intensities of the Na lines are in full agreement with this new

assignment. Both nuclei show large Knight shifts which arise from hyperfine interactions with the conduction electrons, and there is an unexpected temperature dependence of the ²⁹Si shift in $\text{Na}_8\text{Si}_{46}$. As Na is removed from Str.II the spectra of both ²³Na and ²⁹Si broaden and the ²⁹Si spectra change quite dramatically, due to changing interactions between the host and guest. XPS studies indicate that the apparent stability of the sodium/silicon clathrates is due to a protective layer of silica. We also hope to present new results on the K_8Ge_{46} clathrate.

- [1] G.S. Nolas, J.L. Cohn, G.A. Slack, S.B. Schujman, Appl. Phys. Letts, (1998), 73, 178.
 [2] J. Gryko, P.F. McMillan, O.F. Sankey, Phys. Rev. B, (1996), 54, 3037.
 [3] J. Gryko, P.F. McMillan, R.F. Marzke, A.P. Dodokin, A.A. Demkov, O.F. Sankey, Phys. Rev. B, (1998), 57, 4172.
 [4] E. Reny, M. Menetrier, C. Cros, M. Pouc (1998) 1, 129.
 [5] F. Shimizu, Y. Maniwa, K. Kume, H. Kawaji, S. Yamanaka, M. Ishikawa, Phys. Rev. B, (1996), 54, 13242, and Synthetic Metals, (1997), 86, 2141.

Z8.21

HIGH-Z CERIUM-HEXABORATE THIN FILMS FOR LOW-TEMPERATURE APPLICATIONS. Armen Gulian, USRA/NRL, Washington, DC; Armen Kuzanyan, Sergey Harutyunyan, Ashot Gyulamiryan, Violetta Vartanyan, Georgi Badalyantz, Institute for Physics Research, National Academy of Sciences, ARMENIA; Nicholas Giordano, Todd Jacobs, Physics Department, Purdue Univ., IN; Kent Wood, Gilbert Fritz, Syed Qadri, NRL, Washington, DC; Deborah Van Vechten, ONR, Arlington, VA.

We have deposited and investigated thin films of lanthanum hexaborate with 1% of lanthanum replaced by cerium. Due to the Kondo-mechanism this material in a bulk single-crystalline form has the highest known Zeebeck coefficient at sub-K temperatures and is a good candidate for several thermoelectric applications at very low temperatures. We show the dependence of the kinetic properties of thin films (such as the conductivity and Seebeck coefficient as a function of the temperature) on their thickness, substrate material and deposition conditions. Theoretical limits for possible applications of these films in devices are considered with a focus on detectors and refrigerators.

Z8.22

COMPARISON OF BULK PHYSICAL PROPERTIES OF BINARY SKUTTERUDITE COMPOUNDS. Michael Kaeser, Terry Tritt, Clemson University, Dept. of Physics and Astronomy, Clemson, SC; Joshua R. Williams, David C. Johnson, University of Oregon, Dept. of Chemistry and Materials Science Institute, Eugene, OR; George Nolas, Marlow Industries, Research and Development Division, Dallas, TX.

The interest in compounds with the skutterudite structure for possible use as higher efficiency thermoelectric materials has spawned a great deal of research and synthetic work in this area. Included in this effort is the synthesis of new metastable binary skutterudite compounds via the elemental multilayer precursor method. Until now, these metastable compounds have been synthesized in thin-film form only. Physical data including thermopower, electrical conductivity and thermal conductivity from bulk samples of four previously reported binary skutterudite compounds FeSb_3 , CoSb_3 , NiSb_3 , and IrSb_3 will be presented, compared and discussed. This will be the first report of bulk transport property measurements on two metastable compounds, FeSb_3 and NiSb_3 .

Z8.23

SPECTROSCOPIC INVESTIGATION OF PHONONS IN SOME (Si,Ge,Ga)-CLATHRATE BASED STRUCTURES. Ganesh K. Ramachandran¹, Paul F. McMillan^{1,2}, Jianjun Dong³, Jan Gryko⁴, Zhenxian Liu⁵, Russel J. Hemley⁵ and Otto F. Sankey³. ¹Department of Chemistry and Biochemistry, ²Center for Solid State Science, ³Department of Physics and Astronomy, Arizona State University, Tempe, AZ, ⁴Department of Earth and Physical Sciences, Jacksonville State University, Alabama, AL, ⁵Geophysical Laboratory, Center for High Pressure Research and NSLS, Washington, DC.

Very low values of the thermal conductivity characteristic of a phonon glass have been experimentally demonstrated in a class of crystalline materials formed by open-framework structures of the group IV elements Ge and Sn, usually in combination with group III elements such as Ga (1,2). These materials are semiconductors or semimetals, with useful values of the Seebeck coefficient, and are excellent candidates for high figure-of-merit phonon-glass-electron-crystal (PGEC) (3) thermopower materials. It is believed that (a) avoided crossings away from the Brillouin zone center between the essentially dispersionless heat carrying acoustic phonons (due to the vibrations of the IV-III framework) and low lying (0-75 cm^{-1}) guest rattling modes, coupled with (b) intrinsic anharmonicity of the rattler mode potential(4) are largely responsible for the thermal behaviour of these

materials. However, no direct experimental evidence for the existence of the low lying rattler modes or their nature have been reported to date. Infrared reflectance/absorption and Raman scattering are ideal for tracking the framework and guest rattling modes in these structures. We have collected preliminary IR reflectivity data of type II $\text{Na}_x\text{Si}_{136}$ clathrates as well on several $\text{A}_8(\text{Ga}_x\text{Ge}_{46-x})$ type II structures with known low thermal conductivity. The IR data are taken using the NLS IR beamline U2A in transmission and reflectance mode, in far-, mid- and near-IR regions. The data give information on the electronic bandgap and carrier concentration for semimetallic and narrow gap semiconducting samples. Complementary Raman investigations are under way. The data show evidence for the zone centre optical phonons associated with rattler vibrations, and their harmonic vs anharmonic nature that can be correlated with the low thermal conductivity. The optical bandgap measurements of the $\text{Na}_x\text{Si}_{136}$ series reveal unexpected features as a function of Na content, compared with the bulk conductivity and Hall coefficient measurements. Raman spectra of (Ga,Ge)-containing clathrates show extremely broad bands indicative of substantial framework cation disorder, that must be taken into account in evaluating and understanding the low thermal conductivity values.

(1) G.S. Nolas et al., Appl. Phys. Letts. 73, (2), 178 (1998).

(2) J.L. Cohn et al., Phys. Rev. Letts. 82, 779 (1999).

(3) G.A. Slack, Mater. Res. Soc. Symp. Proc. 478, 47 (1997).

(4) J. Dong et al., Proceedings of Intl. Conf. Thermoelectrics (1999), in press.

SESSION Z9: THERMIONICS

Chair: Gerald D. Mahan

Wednesday Morning, April 26, 2000

Golden Gate A1 (Marriott)

8:30 AM Z9.1

THERMAL CONDUCTIVITY OF Bi/Sb SUPERLATTICES.

David W. Song, Theodorian Borca-Tasciuc and Gang Chen, Mechanical and Aerospace Engineering Department, University of California at Los Angeles, Los Angeles, CA; Sunglae Cho, Yunki Kim and John B. Ketterson, Department of Physics & Astronomy, Northwestern University, Evanston, IL.

$\text{Bi}_{1-x}\text{Sb}_x$ alloys are known to be good n-type thermoelements for temperatures around 80 K because of their exceptionally high mobility to lattice thermal conductivity ratio. Recently, atomic-scale ordered Bi/Sb superlattice alloys have been prepared using MBE. Their electronic structure can be independently tuned via either the composition ratio or the superlattice period. These unique properties, which are distinct from those in random alloys, are believed to be a consequence of new atomic configurations. In order to evaluate thermoelectric performance of these systems, we have performed temperature-dependent cross-plane thermal conductivity measurement using a differential $3-\omega$ method. In this talk we will present the effects of the superlattice period, atomic scale and larger, on the thermal conductivity and also compare with those of the corresponding random alloys.

Work supported by ONR MURI (N00014-97-1-0516). Work at Northwestern supported by DARPA (DAAG55-97-1-0130).

8:45 AM Z9.2

GROWTH AND CHARACTERIZATION OF EPITAXIAL $\alpha\text{-Sn/PbTe}(111)/\alpha\text{-Sn}$ AND $\text{Bi/PbTe}(111)/\text{Bi}$ HETERO-STRUCTURES FOR THERMIONIC REFRIGERATION. J.G. Kim, H.H. Weitering, The University of Tennessee, Knoxville, TN; F.A. Modine, D.M. Zehner, Oak Ridge National Laboratory, Oak Ridge, TN.

Metal/semiconductor multilayer structures are promising candidates for small-scale refrigeration and power-generation applications. In order to maximize the efficiency of such devices near room temperature, the semiconductor barrier material needs to have a small band gap, low thermal conductivity, and exhibit good epitaxy with respect to the metal layer. Two metal/semiconductor hetero-junctions and multilayers, namely, $\alpha\text{-Sn/PbTe}(111)/\alpha\text{-Sn}$ and $\text{Bi/PbTe}(111)/\text{Bi}$, have been investigated in this study. Both structures were grown in a molecular beam epitaxy system equipped with Low Energy Electron Diffraction and Auger Electron Spectroscopy. Epitaxial multilayers were grown successfully in both cases. Ex-situ Atomic Force Microscopy results show that the morphology of the $\text{PbTe}(111)$ layer is especially smooth for the Bi/PbTe/Bi system; the $\alpha\text{-Sn/PbTe}/\alpha\text{-Sn}$ system has a greater rms roughness. Furthermore, for the first time, a long-range $\text{PbTe}(111)(\sqrt{3}\times\sqrt{3})R30^\circ$ surface reconstruction has been observed which indicates that the semiconductor film on the metal substrate is of good epitaxial quality. Schottky barrier measurements on these metal/semiconductor hetero-junctions as well as the test results of a cooling device made of these structures will be reported. Research sponsored by the Office of Naval Research and by the

Division of Materials Science, U.S. Dept. of Energy under contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

9:00 AM *Z9.3

THERMOELECTRIC AND THERMIONIC EMISSION COOLING IN SUPERLATTICES. Ali Shakouri, Suquan Li, Jack Baskin School of Engineering, University of California, Santa Cruz, CA.

A unified theory is developed to calculate heat and current transport perpendicular to the layers in a superlattice structure. Different regimes of thermoelectric and thermionic emission cooling are identified. Maximum cooling power and efficiency are calculated and prospects for integrated cooling of electronic and optoelectronic devices are described.

9:30 AM Z9.4

UPPER LIMITATION TO THE PERFORMANCE OF SINGLE-BARRIER THERMIONIC EMISSION COOLING. M.D. Ulrich, P.A. Barnes, Department of Physics, Auburn University, AL; Cronin B. Vining, ZT Services, Auburn, AL.

We have re-examined solid-state thermionic emission cooling from first principles and report two key results. First, electrical and heat currents over a semiconductor - semiconductor thermionic barrier are determined by the chemical potential measured from the conduction band edge, not the energy band offset between the two materials as is sometimes assumed. Second, we show the upper limit to the performance of thermionic emission cooling is equivalent to the performance of an optimized thermoelectric device made from the same material. An overview of this theory will be presented and instrumentation being developed to experimentally verify the theory will be discussed.

9:45 AM Z9.5

MINIMUM THERMAL CONDUCTIVITY OF SUPERLATTICES. M.V. Simkin, G.D. Mahan, Department of Physics and Astronomy, University of Tennessee, Knoxville and Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

The phonon thermal conductivity of a multilayer is calculated for transport perpendicular to the layers. There is a cross over between particle transport for thick layers to wave transport for thin layers. The calculations show that the conductivity has a minimum value for a layer thickness somewhat smaller than the mean free path of the phonons.

SESSION Z10: SKUTTERUDITES II

Chair: David C. Johnson

Wednesday Morning, April 26, 2000

Golden Gate A1 (Marriott)

10:30 AM Z10.1

PARTIALLY-FILLED SKUTTERUDITES: OPTIMIZING THE THERMOELECTRIC PROPERTIES. G.S. Nolas, R&D Division, Marlow Industries, Dallas, TX; M. Kaeser, T.M. Tritt, Department of Physics, Clemson University, Clemson, SC; H. Sellinshcheg, J.R. Williams, D.C. Johnson, Department of Chemistry, University of Oregon, Eugene, OR.

The skutterudite family of compounds continues to be of interest for thermoelectric applications. This is due to the low thermal conductivity obtained when filling the voids with small diameter, large mass interstitials such as trivalent rare-earth ions[1]. There is now a substantial experimental and theoretical effort in attempting to increase the power factor in these compounds while maintaining the low thermal conductivity. One such approach involves partially-filling the voids in attempting to optimize the power factor while maintaining low thermal conductivity.[1] In this report experimental research on skutterudites with the voids partially filled with heavy mass rare-earth ions is reported.

[1] G.S. Nolas, D.T. Morelli and T.M. Tritt, Ann. Rev. Mater. Sci., vol. 29, pp. 89-116 (1999), and references therein.

10:45 AM Z10.2

BULK SYNTHESIS OF COMPLETELY AND PARTIALLY Sn FILLED CoSb_3 USING THE MULTILAYER REPEAT METHOD. Heike Sellinshcheg, David C. Johnson, University of Oregon, Dept. of Chemistry and Materials Science Institute, Eugene, OR; Michael Kaeser, Terry M. Tritt, Clemson University, Department of Physics, Clemson, SC; George S. Nolas, R&D Division, Marlow Industries, Dallas, TX.

Considerable work in the field of thermoelectric materials continues to be aimed at optimizing the thermoelectric properties of skutterudite compounds. Filled skutterudite compounds possess very low thermal

conductivities due to the scattering of a wide range of phonon modes caused by a loosely bound "filler" cation incorporated in the void of the structure. The incorporation of a filler cation is the source for several difficulties in the skutterudite synthesis because such a weakly bound atom causes structural instability. Many skutterudite compounds decompose at the temperatures needed to overcome solid state diffusion barriers. The multilayer repeat synthesis [1] has shown to be a powerful method to circumvent these difficulties and several skutterudites which are metastable with respect to decomposition into binary compounds have been synthesized successfully. Recently, this method has been upscaled and now bulk samples can be generated via this synthetic route. Here we report on the synthesis of partially and completely Sn-filled CoSb_3 structures. Structural and chemical analysis as well as Seebeck coefficient, resistivity and thermal conductivity measurements of the ternary compounds synthesized in bulk will be presented.

[1] M.D. Hornbostel, E.J. Hyer et al., *Inorganic Chemistry* 36, p. 4270-4274 (1997).

11:00 AM *Z10.3

TRANSITION METAL SUBSTITUTION AND ITS EFFECT ON THE THERMAL CONDUCTIVITY OF SKUTTERUDITES. Ctirad Uher, Jihui Yang, University of Michigan, Department of Physics, Ann Arbor, MI; Gregory P. Meisner, Materials and Processes Laboratory, GM R&D and Planning, Warren, MI.

Filled skutterudites are among the materials that have the best prospect to be developed into a useful thermoelectric. The essential feature of the structure-its two voids per unit cell-provides for filling with rare-earth atoms that rattle and increase phonon scattering. As a consequence, lattice thermal conductivity of filled skutterudites is much suppressed in comparison to the unfilled, binary skutterudites. It has been shown recently that the presence of a neighboring transition metal necessary to compensate the structure electronically, has also a significant effect on degrading the thermal conductivity. In fact, this effect is far greater than what one would expect based on the differences in the atomic masses and ionic radii. To clarify the influence of the transition metal compensation on the thermal conductivity, we have prepared a series of CoSb_3 samples doped with Fe and Ni and measured their thermal conductivity in the temperature range 2-300K. We observe a dramatic reduction in the lattice thermal conductivity with the increasing iron content that amounts to an order of magnitude suppression of the thermal conductivity at its peak value and more than a factor of two lower value at room temperatures. Scattering mechanisms that may be responsible for such a large effect will be discussed.

11:30 AM Z10.4

TRANSMISSION ELECTRON MICROSCOPE CHARACTERIZATION OF DEFECTS IN THE PARTIALLY FILLED SKUTTERUDITE STRUCTURE. J.S. Harper, R. Gronsky, Univ of California at Berkeley, Dept of Materials Science and Mineral Engineering, Berkeley, CA.

The partially-filled skutterudite structure has been proposed as a potentially good thermoelectric material with phonon scattering attributed to the rattling of the filling ions. This investigation seeks a detailed understanding of the relationship between the atomic structure of these partially-filled skutterudites, including their defect structures, and their thermoelectric performance. Initial microstructural characterization has been performed using transmission electron microscopy on a sample of 1.6% Ce, 22.8% Co, 1.6% Ni, 4.9% Ge, and 69.1% Sb, which has been found to have the skutterudite structure by x-ray diffraction. Electron diffraction patterns exhibit superlattice reflections characteristic of long range ordering in the system. Attention is currently given to the defect structures in this partially-filled structure, with eventual extension to other similar systems, using phase contrast imaging and spatially-resolved compositional analysis.

11:45 AM Z10.5

A MOESSBAUER AND X-RAY ABSORPTION SPECTRAL STUDY OF FILLED AND UNFILLED SKUTTERUDITES. Gary J. Long, Dimitri Hautot, Department of Chemistry, University of Missouri-Rolla, Rolla, MO; F. Grandjean, Institut de Physique, Université de Liège, BELGIUM; G.P. Meisner and J. Yang, GM Research and Development Center, Warren, MI.

The temperature dependencies of the Mössbauer spectral isomer shifts and the logarithm of the spectral absorption areas in $\text{Ce}_{0.98}\text{Fe}_4\text{Sb}_{12}$ and $\text{Ce}_{0.35}\text{FeCo}_3\text{Sb}_{12}$ yield effective Mössbauer temperatures of ca. 500 and 400 K, respectively, values which are substantially higher than the Debye temperatures of ca. 300 K observed for these compounds. These differences indicate that the high frequency vibrations of the iron sublattice are weakly coupled to the lower frequency vibrations of both the partially filled cerium sublattice and the antimony sublattice. The 295 K iron and cobalt K-edge and

cerium L_{III} -edge XANES and EXAFS spectra have been obtained for the $\text{Ce}_x\text{Fe}_{4-y}\text{Co}_y\text{Sb}_{12}$ skutterudite compounds. At both K-edges all of the compounds, both filled, with $x > 0$, and unfilled, with $x = 0$, show very similar XANES spectra with extensive structure which arises from multiple scattering by the antimony near neighbors. Both of the K-edges are increased in energy by ca. 2 eV above that observed in metallic iron or cobalt. The cerium L_{III} -edge XANES spectra all yield a single peak at ca. 5725 eV, a peak which is characteristic of trivalent cerium. Further, no significant shift in the energy of this peak is observed with changing cerium content. The iron and cobalt K-edge EXAFS oscillations are very similar in $\text{Ce}_{0.98}\text{Fe}_4\text{Sb}_{12}$, $\text{Ce}_{0.60}\text{Fe}_2\text{Co}_2\text{Sb}_{12}$, and $\text{Ce}_{0.22}\text{Fe}_{0.5}\text{Co}_{3.5}\text{Sb}_{12}$, and can be fit with 6 and 12 antimony near and next near neighbors at ca. 2.5 and 4.5 Å, respectively, distances which are in agreement with the expected skutterudite crystal structure. The cerium L_{III} -edge EXAFS oscillations do not change significantly with cerium content.

SESSION Z11: DEVICES, MEASUREMENTS, & APPLICATIONS

Chair: Jeff W. Sharp
Wednesday Afternoon, April 26, 2000
Golden Gate A1 (Marriott)

1:30 PM Z11.1

OPTIMIZATION AND PATTERNING OF BISMUTH NANOWIRES ARRAYS BY ELECTROCHEMICAL DEPOSITION.

J.H. Barkyoumb, J.L. Price, N.A. Guardala, N. Lindsey, D.L. Demske, J. Sharma, Carderock Division, Naval Surface Warfare Center, West Bethesda, MD, H.H. Kang and L. Salamanca-Riba, Dept. of Materials and Nuclear Engineering, Univ. of Maryland, College Park, MD.

Bismuth nanowires for thermoelectric applications have been made by electrochemical deposition from an aqueous Bi solution into nanoporous mica substrates. The nanoporous substrates are created by acid etching damage tracks that are produced in the mica using heavy-ion irradiation. In this work, further improvements in the fabrication process are made by investigating the electrochemical growth at the 1-d to 2-d transition region at the nanochannel-substrate surface interface as a function of deposition time and electrochemistry. The problem of electrochemical growth of contacts to the nanowires as compared to vacuum deposition of contacts will be discussed. The ion-beam irradiation technique naturally lends itself to patterning of the nanochannels on the template. This can be combined with selective electrochemical deposition to produce arrays of patterned nanowires or arrays of selectively doped nanowires.

1:45 PM Z11.2

EVALUATION OF A THERMOELECTRIC DEVICE UTILIZING POROUS MEDIUM. Hideyuki Yasuda, Itsuo Ohnaka, Youichi Inada, Kimitaka Nomura, Osaka University, Dept. Adaptive Machine Systems, Osaka, JAPAN.

A thermoelectric device consisting of the porous part and the bulk part was proposed. The generated power is discussed in terms of the two different efficiencies; one is efficiency of the thermoelectric energy conversion, and the other is efficiency of heat exchange between the device and heating / cooling fluids. Increase of heat exchange area by using porous medium will improve the efficiency of heat exchange between heating / cooling sources and the device, and consequently increase generated power per unit device area, although porous medium increases electric resistivity of the device and reduces the efficiency of the thermoelectric energy conversion. The presently proposed porous device exhibits its advantage in the case of low heat transfer coefficient between the device and the heating / cooling sources, i.e. exhaust gas is used for heating source. Estimation based on physical properties of FeSi_2 indicated that generated power of the partially porous device per unit area can be several times higher than that of the bulk one in case of gas heating / cooling system. A novel processing for porous medium has been developed for the porous thermoelectric materials. By applying the processing, the partially porous thermoelectric devices were produced. In experiments of power generation, it has been confirmed that generated power per unit area of the partially porous FeSi_2 device was more than 10 times higher than that of the bulk device (conventional type).

2:00 PM Z11.3

ELECTROCHEMICAL DEPOSITION OF $(\text{Bi,Sb})_2\text{Te}_3$ FOR THERMOELECTRIC MICRODEVICES. Jean-Pierre Fleurial, Jennifer A. Herman, G. Jeffrey Snyder, Amy M. Ryan and Ratnakumar V. Bugga, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA.

New experimental methods have been developed to electrochemically deposit p-type Sb-rich $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ and Pb-doped Bi_2Te_3 thick films. We have successfully grown films that are dense and have a

smooth surface morphology. These films were deposited potentiostatically at room temperature in an acidic aqueous electrolyte. Experimental deposition of Bi₂Te₃ alloys into various thick nanoporous templates made out of opal or anodized alumina has also been achieved. Miniaturized thermoelements for microdevices (25 μm tall, 50 μm diameter) were grown by plating through thick photoresist templates. The experimental techniques developed, as well as the electrical and thermal transport properties of some of the films and filled templates, will be presented.

2:15 PM Z11.4

TRANSIENT LOCAL COOLING USING THERMOELECTRICS. A. Ravi Kumar, R.G. Yang and G. Chen, Mechanical and Aerospace Engineering Department, University of California at Los Angeles, Los Angeles, CA; J.-P. Fleurial Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA.

Recent developments in the fabrication of thermoelectric microcoolers allow placing the cooler very near to the active region of thin film devices that need to be cooled. One potential application is integration of these microcoolers into the semiconductor lasers and detectors packaging, allowing a better thermal management of these devices. In thermoelectrics, it is known that the lowest temperature observed under steady dc current flow is not the limit. Further lower temperatures can be achieved by superimposing strong transient current pulse on the optimum steady state operation current. This additional instantaneous cooling can be used in pulsed operation of lasers that require the active region to be at the lowest temperature possible before it is operated. We report theoretical analysis of the transient thermal response of thermoelectric microcoolers and the integrated thin-film devices. This analysis provides a means to examine the effectivity and viability of thermal management of the thin-film devices using the transient mode operation of thermoelectric coolers.

*Work supported by DARPA HERETIC Program and DOD MURI.

2:30 PM Z11.5

P SiGe/Si SUPERLATTICE COOLER. Xiaofeng Fan, Gehong Zeng, Edward Croke^a, Gerry Robinson, Chris LaBounty, Ali Shakouri^b and John E. Bowers, Department of Electrical and Computer Engineering, University of California, Santa Barbara, CA. ^aHRL Laboratories, LLC, Malibu, CA, ^bBaskin School of Engineering, University of California, Santa Cruz, CA.

SiGe is considered to be a good thermoelectric material for high temperature applications. It has been used for thermo-nuclear power generation in satellites for deep space missions. In this paper, fabrication and characterization of single-element thin film superlattice SiGe/Si coolers of p-type are described for room temperature applications. Superlattice structures were used to enhance the device performance by reducing the thermal conductivity between the hot and the cold junctions, and by providing selective emission of hot carriers through thermionic emission process. These coolers can be monolithically integrated with other microelectronic devices and provide high cooling power densities to improve the performance. The sample was grown in a Perkin-Elmer Si molecular beam epitaxy (MBE) growth chamber on a 125mm diameter, (001)-oriented Si substrate, doped to 0.001 - 0.006 Wcm. The structure of the samples consisted of a 3 m thick Si_{0.7}Ge_{0.3}/Si superlattice grown symmetrically strained on a buffer layer designed so that the in-plane lattice constant approximated that of relaxed Si_{0.9}Ge_{0.1}. Alloyed Ti/Al metallization was used to achieve specific contact resistivity on the order of 10⁻⁷ W cm² to the p-type SiGe material. Cooling of 2.7K at room temperature and 4.2K at 70C over 3m superlattice thermal barriers was measured, corresponding to cooling power densities of hundreds of watts per square centimeter. The results show that SiGe/Si coolers can work well at room temperature and work better at high temperature due to larger thermal spread of carriers near the Fermi energy and lower thermal conductivity of the cooling and heating junctions. Applications in many microelectronic systems are promising. This work is supported by the DARPA HERETIC program and sponsored by the Department of the Army, Army Research Office.

2:45 PM Z11.6

PROGRESS IN THE DEVELOPMENT OF SEGMENTED THERMOELECTRIC UNICOUPLES AT THE JET PROPULSION LABORATORY. T. Caillat, J.-P. Fleurial, G.J. Snyder and A. Borshchevsky, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA.

A new version of a segmented thermoelectric unicycle incorporating advanced thermoelectric materials with superior thermoelectric figures of merit has been recently proposed and is currently under development at the Jet Propulsion Laboratory (JPL). This advanced segmented thermoelectric unicycle includes a combination of state-of-the-art thermoelectric materials based on Bi₂Te₃ and novel

p-type Zn₄Sb₃, p-type CeFe₄Sb₁₂-based alloys and n-type CoSb₃-based alloys developed at JPL. Although the segmented unicycle currently being developed is expected to operate between 300 and 975K, the segmentation can be adjusted to accommodate various hot-side temperatures depending on the specific application. This paper illustrates various segmentation alternatives and the predicted efficiency and characteristics of the corresponding unicycles. The latest developments of the bonding of the thermoelectric materials together and to the interconnects are described. Efforts are now focusing on the fabrication of a unicycle designed for thermal and electrical testing. A precise measurement of the experimental efficiency could be somewhat difficult in particular of the potential various heat losses involved at high temperatures. The experimental set-up designed for minimizing these difficulties is described and discussed.

SESSION Z12: DISCUSSION PERIOD: FUTURE DIRECTIONS IN THERMOELECTRIC RESEARCH

Chair: Terry M. Tritt
Wednesday Afternoon, April 26, 2000
Golden Gate A1 (Marriott)

3:15 PM SPECIAL AWARDS FOR SYMPOSIUM Z

3:30 PM DISCUSSION PERIOD

ARO, NSF, DARPA AND DOE representatives will be presenting and participating in a question and answer session.

SESSION Z13: CLATHRATES

Chair: Glen A. Slack
Thursday Morning, April 27, 2000
Golden Gate A1 (Marriott)

8:30 AM Z13.1

TRANSPORT PROPERTIES OF TYPE-I AND II SEMI-CONDUCTING CLATHRATES. G.S. Nolas, R&D Division, Marlow Industries, Dallas, TX; J.L. Cohn, Department of Physics, University of Miami, Coral Gables, FL; M. Kaeser, T.M. Tritt, Department of Physics, Clemson University, Clemson, SC.

Compounds with clathrate-hydrate type crystal lattice structures are currently of interest in thermoelectric materials research. This is due to the fact that semiconducting compounds can be synthesized with varying doping levels while possessing low, even glass-like, thermal conductivity. Up to now most of the work has focused on type-I Si and Ge clathrates. Sn-clathrates however are viewed as possessing the greatest potential for thermoelectric cooling applications due to the larger mass of Sn and the expected small band-gap, as compared to Si and Ge-clathrates. Basically, transport data on type-I Sn-clathrates has only recently been reported.[1] In this report ongoing experimental research on Si, Ge and Sn type-I and II clathrates is presented. [1] G.S. Nolas et al. Chem. Mat. 11, pp. 2470-2473 (1999); G.S. Nolas et al, Proceedings of the 18th International Conference on Thermoelectrics.

8:45 AM Z13.2

SYNTHESIS, STRUCTURE AND THERMOPOWER CHARACTERISTICS OF SOME (Si-Ge) BASED CLATHRATE STRUCTURES. Ganesh K. Ramachandran¹, Paul F. McMillan¹, Jianjun Dong², Jan Gryko³ and Otto F. Sankey². ¹Department of Chemistry and Biochemistry and ²Department of Physics and Astronomy, Arizona State University, Tempe, AZ, ³Department of Earth and Physical Sciences, Jacksonville State University, AL.

Promising thermoelectric characteristics have been demonstrated in a series of gallium substituted type I (M_xT₄₆) clathrate structures based on Si, Ge and Sn (1,2). In these compounds, gallium substitutes some of the framework atom sites and electronic compensation via endohedral alkali (alkali earth) elements results in electrically-neutral semiconducting compounds whose low thermal conductivities are reminiscent of glasses. Our work is focused on clathrates involving group IV elements. Type I clathrates with Si (Na₈Si₄₆; K₇Si₄₆) have fully stoichiometric frameworks and are semimetallic; analogous clathrates with Ge (K₈Ge₄₄; Rb₇Ge₄₅) have vacancies on the framework sites and are semiconducting. We report characterization of the structure, stoichiometry and electrical and thermal conductivity of these clathrates. We have now also synthesized group IV clathrates with mixed framework atoms M_x(Si,Ge)_{46-d} and we will report their structural characterization and electronic properties. (1) G.S. Nolas et al., Appl. Phys. Letts. 73(2), 178 (1998). (2) J.L. Cohn et al., Phys. Rev. Letts. 82, 779 (1999).

9:00 AM *Z13.3

ULTRASOUND STUDIES OF CLATHRATE THERMOELECTRICS. Veerle Keppens, University of Mississippi, National Center for Physical Acoustics, University, MS; Christiane Laermans, K.U. Leuven, Dept. Physics, Leuven, BELGIUM; David Mandrus, Brian C. Sales, Bryan C. Chakoumakos, Oak Ridge National Laboratory, Solid State Division, Oak Ridge, TN.

Motivated by the search for improved thermoelectric materials, several compounds have attracted attention that combine the high electron mobilities found in crystals with a low thermal conductivity κ , approaching κ -values typical for glasses. The common structural feature of these "electron crystal phonon glass" (ECPG) materials is that they contain loosely bound atoms that reside in a large crystalline "cage"; these materials are thus "inclusion compounds or "crypto-clathrates". A particular class of clathrates is formed by the filled skutterudite antimonides [1]. More recently, the Ge-clathrate $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ was found to be an ECPG material, having a truly glasslike thermal conductivity while maintaining the crystalline electronic properties. Here we report Resonant Ultrasound Spectroscopy and low-temperature ultrasonic attenuation measurements for filled and unfilled skutterudites and for Ge-clathrates. These data reveal that an unusual elastic behavior complements the thermal properties of the filled skutterudite and indicate the presence of low-energy vibrational modes. The attenuation at low-temperatures in the single-crystalline Ge-clathrate is very glasslike and can be explained with the phenomenological Tunneling Model, used to describe the low-temperature properties of amorphous solids.

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

9:30 AM Z13.4

SODIUM/SILICON CLATHRATE $\text{Na}_8\text{Si}_{46}$ AS A POTENTIAL HIGH EFFICIENCY THERMOELECTRIC MATERIAL. Jiliang He, Christopher I. Ratcliffe, John S. Tse, Chris A. Tulk, Kentaro Uehara, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, CANADA; Mary Anne White, Dept. of Chemistry, Dalhousie University, Halifax, Nova Scotia, CANADA.

The efficiency of a thermoelectric material is directly proportional to the electrical conductivity and inversely proportional to the thermal conductivity with the proportionality constant known as the Seebeck coefficient [1]. Therefore, a good candidate for a thermoelectric material must possess the contradictory properties: it must be a good metal but behave as a thermal insulator. Recent research into the thermal conductivity of clathrate compounds has shown that a crystalline solid can exhibit anomalous glassy thermal behavior if there are strong couplings between the localized excitations and the lattice vibrations [2,3]. Based on this observation, it is likely that the silicon clathrates, with alkali metals such as Na or K as guest, are potentially thermoelectric materials [4,5]. In this presentation the measurement of the thermal, electrical and expansion properties of sodium/silicon clathrate $\text{Na}_8\text{Si}_{46}$ will be presented. Theoretical prediction of the Seebeck coefficients with the concentration of the Na-dopant will also be discussed [6].

[1] G.S. Nolas, J.L. Cohn, G.A. Slack, S.B. Schujman, *Appl. Phys. Letts.*, (1998), 73, 178.

[2] J.S. Tse, V. Shpakov, V. Murashov, V. Belosludov, *J. Chem. Phys.*, (1997), 107, 9271.

[3] J.S. Tse, C.I. Ratcliffe, Y.P. Handa, B.M. Powell, V.R. Sears, *J. Phys. Chem.*, (1997), 101, 4491.

[4] J.S. Kasper, P. Hagemuller, M. Pouchard, C. Cros, *Science*, (1965), 150, 1713.

[5] C. Cros, M. Pouchard, P. Hagemuller, *Bull. Soc. Chim. France*, (1971), 2, 379.

[6] V.I. Smelyansky, J.S. Tse, *Chem. Phys. Letts.*, (1997), 264, 459.

9:45 AM Z13.5

SYNTHESIS AND CHARACTERIZATION OF LARGE SINGLE CRYSTALS OF SILICON AND GERMANIUM CLATHRATE-II COMPOUNDS, AND A NEW TIN COMPOUND WITH CLATHRATE LAYERS. Svilen Bobev, Slavi C. Sevov, Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN.

We have synthesized large single crystals of clathrate-II compounds of silicon and germanium by employing mixed alkali-metal counter-cations. The combinations of alkali metals are rationally selected in order to fit the different cages of the clathrate structure. This leads to the following stoichiometric and fully occupied clathrates: $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$, $\text{Rb}_8\text{Na}_{16}\text{Si}_{136}$, $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$, and $\text{Rb}_8\text{Na}_{16}\text{Ge}_{136}$. The compounds were characterized by single-crystal X-ray diffraction. They are very stable at a variety of extreme conditions such as heat, acids, hydrothermal treatment, etc. We report conductivity measurements on single crystals and thermopower measurements on pellets. A new compound with a novel clathrate-like structure forms when small and large cations are combined with tin. The new

material, $\text{Na}_{18}\text{Cs}_6\text{Sn}_{46}$, is made of layers of clathrate-I and interlayer stuffing of Sn_4 -tetrahedra and alkali-metal cations. The formula can be rewritten as $\text{Na}_6\text{Cs}_6\text{Sn}_{34}+3(\text{Na}_4\text{Sn}_4)$. The compound is stable in air, and is being tested at other conditions. Measurements of its thermoelectric properties are currently conducted. Ideas on where and how to look for similar materials in the isoelectronic heteroatomic systems of Groups III and V will be discussed.

SESSION Z14: THIN FILMS TE

Chair: Alexander Borshcheysky
Thursday Morning, April 27, 2000
Golden Gate A1 (Marriott)

10:30 AM Z14.1

ELECTRODEPOSITION OF Bi_2Te_3 NANOWIRE COMPOSITES. A.L. Prieto, M.S. Sander, A.M. Stacy, University of California-Berkeley, Dept. of Chemistry, Berkeley, CA; R. Gronsky, T.D. Sands, University of California-Berkeley, Dept. of Materials Science and Mineral Engineering, Berkeley, CA.

Widespread applications of thermoelectric materials are limited because of low efficiency. Bulk Bi_2Te_3 has yielded compositions with a high thermoelectric figure-of-merit (ZT) through the use of doping. It is postulated that further enhancements in ZT may be attained by engineering the microstructure to enhance carrier mobility while suppressing the phonon component of the thermal conductivity. This may be achieved by fabricating Bi_2Te_3 in the form of one-dimensional (1-D) nanowires. We have deposited nanowires of Bi_2Te_3 under different electrodeposition conditions and of varying diameters. Characterization of the composite materials has been completed using X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Energy dispersive X-ray spectroscopy has been used to determine the stoichiometry of the wires. Preliminary data on the correlation between the diameter of the wires and their thermal and electrical conductivity will be presented.

10:45 AM Z14.2

THERMOPOWER OF Bi NANOWIRE ARRAY COMPOSITES. T.E. Huber, Chemistry Department, Howard University, Washington, DC.; M.J. Graf, Department of Physics, Boston College, Chestnut Hill, MA; C.A. Foss, Jr., Department of Chemistry, Georgetown University, Washington, DC.

The small effective mass and high mobility of Bi, make Bi nanowires a promising system for thermoelectric applications. Dense arrays of 20-200 nm diameter Bi nanowires were fabricated by high pressure injection of the melt. Transport properties and Seebeck coefficient are investigated for Bi nanowires with various wire diameters and Te or Sn doping concentrations, as a function of temperature ($1\text{ K} < T < 300\text{ K}$) and magnetic field ($B < 1\text{ T}$). These measurements are interpreted in terms of Dresselhauss's model of Bi quantum wires. The prospect for using Bi nanowire arrays for thermoelectric applications is discussed.

11:00 AM Z14.3

ELECTROSYNTHESIS OF DIMENSIONALLY REDUCED THERMOELECTRIC MATERIALS BY ELECTROCHEMICAL ATOMIC LAYER EPITAXY. Curtis Shannon, Igor Nicic, Hong Yin, Auburn Univ, Dept of Chemistry, Auburn, AL; Michael J. Bozack, Peter A. Barnes, Auburn Univ, Dept of Physics, Auburn, AL.

Research on thermoelectric materials has experienced a resurgence in the past five years driven by a number of concerns, including the environmental impact of freon-based cooling technologies, the conversion of waste heat to electrical power and the active cooling of modern electronic device components. In parallel with advances in materials synthesis, several strategies based on the fabrication of novel low dimensional device architectures have been proposed in an effort to improve overall thermoelectric efficiency. In this paper, we will discuss the development of electrochemical routes to dimensionally reduced thin film thermoelectric materials. Electrochemical atomic layer epitaxy (EC-ALE) is a near equilibrium, room temperature materials growth technique that can be used to produce high quality, epitaxially oriented polycrystalline deposits in a layer-by-layer fashion on a wide variety of conducting substrates. A large number of compound semiconductors have been grown using this technique. In addition, the fact that electrodeposition can be carried out at room temperature means that layered structures with extremely abrupt interfaces, including semiconductor/semiconductor and metal/semiconductor junctions, can be fabricated using this method. In EC-ALE, a surface-limited electrochemical reaction, such as underpotential deposition, is used to synthesize a binary compound by successive deposition of each element from its respective solution precursor. The use of EC-ALE to synthesize thin films of bismuth chalcogenide and bismuth antimonide phases with an aim of

producing layered structures of these materials for use in thermoelectric applications will be reported. More specifically, we will discuss the development of deposition cycles for each element of the target compounds, as well as the characterization of the ph.

11:15 AM Z14.4

EXPERIMENTAL INVESTIGATION OF THIN FILM InGaAsP COOLERS. Chris LaBounty, Patrick Abraham, John E. Bowers, University of California, Santa Barbara, Dept of Electrical and Computer Engineering, Santa Barbara, CA; Ali Shakouri, University of California, Santa Cruz, Jack Baskin School of Engineering, Santa Cruz, CA.

Most optoelectronic devices for long haul optical communications are based on the InP/InGaAsP family of materials. Thin film coolers based on the same material system can be monolithically integrated with optoelectronic devices such as lasers and photodetectors to control precisely the output characteristics such as wavelength and optical power. Superlattice structures of InGaAs/InP and InGaAs/InGaAsP are used to optimize the thermionic emission cooling beyond what is possible with only the Peltier effect. A careful experimental study of these coolers is undertaken. Mesa sizes, superlattice thickness, and ambient temperature are all varied to determine their effect on cooling performance. A three-dimensional, self-consistent thermal-electric simulation is used to understand the experimental observations and to predict what will occur for other untested parameters. The packaging of the coolers is also determined to have consequences in the overall device performance. Cooling on the order of 1 to 2 degrees over 1 μm thick barriers is reported. *This work was supported by the Office of Naval Research and the Army Research Office through DARPA/HERETIC program contract No. 442530-25845.

11:30 AM Z14.5

MICRO-FABRICATED TEST STRUCTURES FOR IN-PLANE THERMOELECTRIC PROPERTY CHARACTERIZATION OF THIN FILMS. T. Borca-Tasciuc¹, G. Chen¹, J.L. Liu² and K.L. Wang². ¹Mechanical and Aerospace Engineering Department, ²Department of Electrical Engineering University of California at Los Angeles, Los Angeles, CA.

In this work we present an experimental technique for the characterization of thermoelectric properties of thin films in the in-plane direction. The technique employs a micro-fabricated array of heaters/sensors deposited onto the film in order to monitor the temperature, the Seebeck voltage and the electrical voltage of the thermoelectric film. The thermal conductivity of the film is measured from the decay of the temperature profile detected by arrays of temperature sensors around a microscale heater. The temperature profile and the Seebeck voltage monitored by the voltage electrodes are used to determine the Seebeck coefficient of the thermoelectric films in the in-plane direction. The substrate influence on the thermal conductivity measurements is reduced by the removal of the substrate over a wide area underneath the heater and the monitoring electrodes. Electrical conductivity measurements are carried out without heating based on the 4-point-probe method. Test structures are fabricated and thermoelectric properties characterization is carried out for Si/Ge superlattices and silicon-on-insulator thin films. Work supported by DOD/ONR MURI (N00014-97-1-0516).