A1-Texture Formation in Extruded Rods of (Bi,Sb)$_2$(Te,Se)$_3$ Thermoelectric Alloys

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The anisotropy in both the electrical and mechanical properties of (Bi,Sb)$_2$(Te,Se)$_3$ thermoelectric alloys, and in turn in their overall performance, requires a close control of the alloy texture. In this work we have investigated extruded rods of n- and p- type thermoelectric alloys with square (1 in.2) and circular (1 in. diameter) cross-sections. Figures of merit of up to 3.2 x 10-3 K-1 for p-type alloys and 2.8 x 10-3 K-1 for n-type alloys have been obtained for all extruded sizes. Texture investigations were made by X-ray diffraction, electrical characterization and mechanical testing in both the longitudinal and radial directions. Comparison of the experimental data with numerical simulations shows that there is a close correlation between the sample texture and the value of the equivalent plastic deformation experienced by the material during the hot extrusion process.

A1-Chemical Interactions and Thermoelectric Properties on the Bi$_2$Te$_3$-Bi$_2$Se$_3$ Section in the Interval Below 33.3 Mole % Bi$_2$Se$_3$

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By methods of differential-thermal analysis and X-ray-phase analysis it is proved that the Bi$_2$Te$_3$-Bi$_2$Se$_3$ section is a system with a continuous series of solid solutions, with the formation of Bi$_2$Te$_2$Se compound below the solidus line. The formation of this compound has been confirmed both in experiment and by thermodynamic analysis. It has been found that after zone melting the temperature values of the liquidus and solidus lines correlate with those obtained for equilibrium systems and mentioned in the literature. The boundary has been identified for the existence of Bi$_2$Te$_{3-x}$Se$_x$ solid solutions, which lies at 14 mole % Bi$_2$Se$_3$ (Bi$_2$Te$_{2.58}$Se$_{0.42}$). According to the results of thermodynamic analysis, the halogen interaction with stoichiometric cooling and generative material results in the formation of excess tellurium. Thermodynamic analysis shows chemical interactions (reactions) resulting in the formation of Bi$_2$Te$_2$Se. It has been found that in the two-phase zone, the Seebeck coefficient values dramatically change in a jumping manner, with the points of extremum located on the boundaries of the two-phase zone. In the zone of Bi$_2$Te$_2$Se compound occurrence (33.3 mole% Bi$_2$Se$_3$) the values of the Seebeck coefficient and power factor are minimal.

A1-Thermoelectric Properties of Bi0.9Sb0.1 Fabricated by Different Processing

Gui-Ying Xu, Ting-Jie Chen, Si-Tong Niu, Chang-Chun Ge
Alloy Bi$_{0.9}$Sb$_{0.1}$ with different microstructure were fabricated by different processing, such as hot pressing, plasma activated sintering and ultra high pressure sintering method, etc. The relations of the thermoelectric properties (including electronic conductivity, Seebeck coefficient and thermoconductivity) and the microstructure were investigated in detail. A new idea or research direction on improving the thermoelectric properties of thermoelectric materials was proposed and described.

Acknowledgments
This work is supported by the Natural Science Foundation of China, Grant No. 50042014 and 60176004.

A1-Transport Properties of PbI$_2$-doped PbTe

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This communication deals with the results of the electronic transport properties measurement obtained in cold compacted and sintered PbI$_2$-doped PbTe samples. These properties, i.e. the Seebeck coefficient, the electrical resistivity, the power factor, the electrons mobility and the Hall coefficient are important parameters in the design of thermoelectric materials.

Cast and single-crystal materials, based on PbI$_2$-doped PbTe, are known to be good n-type thermoelectric materials for the 450-800 K temperature range. It has also been established that the thermoefficiency of the material can be improved by generating an appropriate graded concentration of the dopant along the sample.

A powder metallurgy approach can be very useful for preparing such graded materials. Considering the sensitivity of the thermoelectric properties to various process variables, it is necessary to compare the results to those obtained for cast or single-crystal samples with similar concentrations. Such an approach is mandatory in order to determine the potential of graded sintered samples as compared to that of homogeneous cast samples.

The first steps for optimization of such powder metallurgy process have been presented before. This communication describes the electronic transport properties as were measured, with particular emphasis on a comparison with those of cast and single-crystal materials with similar dopant concentrations, as reported in the literature. The Seebeck coefficient and the electrical resistivity were measured in the temperature range of 300-800 K, the Hall coefficient and the electron mobility were measured in the temperature range of 80-300 K.

A1-20 Design, Synthesis and Characterization of Graded n-type PbTe

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The processing steps involved in the manufacture of Functionally Graded Materials (FGM) based on PbI2-doped PbTe, by means of a powder metallurgy approach, are currently being investigated in order to improve the thermoefficiency up to 800 K.

The graded samples were prepared by simultaneous cold compaction of PbTe powder layers containing different amounts of dopant, followed by a sintering treatment. The study included optimization of the various process variables, comparison of the transport properties of the individual homogeneous layers to published data regarding cast materials and synthesis of graded samples, containing equi-wide layers with different dopant concentrations.

This communication describes the latest progress in this research. The design, synthesis and characterization procedures for achieving graded samples with an optimal Power-Factor envelope will be reported.

A method for estimating the temperature distribution along the samples, which was essential for achieving the required dopant concentrations profile along the samples, will be also presented.

**A1-21 Solvothermal Preparation and Thermoelectric Properties of Quasi-Binary SnTe-Bi2Te3 Compounds**

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In this work, a series of polycrystalline samples of ternary compounds in the \((\text{SnTe})_x-(\text{Bi}_2\text{Te}_3)_y\) system were prepared by a solvothermal process based on the reaction between BiCl₃, SnCl₂, Te, KOH and KBH₄ in N,N-dimethylformamide (DMF) at 180 °C for 24 h, and followed by a sintering procedure of compacted pellets. The microstructures of samples were characterized by using XRD, TEM and SEM. The transport properties were also determined by the measurement of electric conductivity and Seebeck coefficient.

**Acknowledgments**

This work is supported by the National Natural Science Foundation of China under grant No. 50072010 and 59825102.

**A1-22 The Transport Properties of Pseudo-binary Alloys (PbTe)1-x-(SnTe)x By Pressureless Sintering**

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Pseudo-binary alloys \((\text{PbTe})_{1-x}\cdot(\text{SnTe})_x\) with different mole ratio \(x\) have been prepared by pressureless sintering. Contrary to an expectation, the densification of alloys \((\text{PbTe})_{1-x}\cdot(\text{SnTe})_x\) wasn’t obtained when sintered at higher temperature, and is opposite to the pore size growth, which can all be explained by different mechanisms referring to pore growth and densification. The temperature, corresponding to maximum Seebeck coefficients which decrease, shifts to higher temperature side, with mole ratio \(x\) increasing from 0 to 0.6. Besides, both seebeck coefficients and electrical resistivities, for the alloys sintered at 550 °C, are small than those for the alloys with the same mole ratio but sintered at 725 °C. The carriers in the alloys \((\text{PbTe})_{1-x}\cdot(\text{SnTe})_x\) with \(x = 0.2\) show p-type character irrelevant to the sintering procedures and transit from extrinsic to intrinsic state when temperature is elevated to 300 °C. On the other hand, however, the electric conductivity increases to its maximum value when \(x\) is increased to 0.6, and then decreases with \(x\) increasing. The power factor is maximized to as much as \(1.2 \times 10^{-4}\)\(^{\text{WK}^{-1}\text{m}^{-1}}\) at higher temperature region when the alloy with mole ratio \(x = 0.4\) is sintered at 550 °C.

**A1-23 Directional Solidified N-type Bi\(_2\)Te\(_3\)\(_{(3-x)}\)Se\(_x\) Using a VGF Method**

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Small sized thermoelectric module can be used for the elimination heat from which is generated by the electronic packages, for example, CPU cooler or laser diode. Thermoelectric materials with high ZT value are required for small sized thermoelectric module and it can be obtained by growing single crystal or directional solidification. Among the crystal growth process, the zone melting method has been widely used. However, using this method, micro homogeneity in composition can only be achieved from slow growth rates. Recently, Vertical Gradient Freezing Method has been developed to growing high quality crystals of opto electronic material. In this study, we explore the synthesis of directional solidified N-type Bi\(_2\)Te\(_{(3-x)}\)Se\(_x\) material having a high ZT by a Vertical Gradient Freezing Method.

*Acknowledgments*

*This work is supported by the Ministry of Science and Technology, Korea.*

**A1-24 Effects of PbTe doping on Thermoelectric Properties of \((\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}\)**

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We have investigated effects of PbTe doping on thermoelectric properties of \((\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}\). The samples \((\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8+x}\text{wt}\%\text{PbTe}(x=0, 0.05, 0.1, 0.3, 0.5)\) were fabricated by mechanical alloying and spark plasma sintering(SPS) method. The Seebeck coefficient, the electric conductivity and the thermal conductivity were
measured in the temperature range 50-250 degree C. The Seebeck coefficient decreased with increasing PbTe content. The electrical conductivity increased with increasing PbTe content. Power factor ($\sigma$) and average dimensionless figure of merit (ZT) were calculated.

**A1-25 Manufacturing and Characterization of Nano-sized PbTe Powders**

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Nano-sized PbTe powders were manufactured by the high-energy ball milling of a PbTe bulk, obtained by the water quenching of a melt. The dry milling using an Ar gas and the wet milling using an ethanol were applied during the ball milling. The prepared powders were characterized by the X-ray powder diffraction pattern analysis to obtain crystallographic parameters such as the crystallite size and the misfit strain. A pseudo-Voigt function was used for the determination of the integral breadth and the full width at half maximum (FWHM) of peaks broadened by the effect of crystallite size and misfit strain. The Scherrer method, the Williamson-Hall plot, the single line analysis and the full pattern Rietveld method were employed to calculate the size of crystallite and misfit strain with the consideration of instrumental broadening using standard sample. As results, we can observe the tendency that the crystallite size decreases and the misfit strain increases with increasing milling time. The crystallite size of powders was determined at the range of 15 ~ 100 nm in 50 ~ 150 hours milling time. The crystallite size and the misfit strain were different from crystallographic directions in this material, according to the Williamson-Hall plot and the single peak analysis.

**A1-26 Microstructure of Profiled Crystals (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ Grown by Directed Crystallization Method**

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Profiled (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$-polycrystals in the form of flat plates were grown by directed crystallization method. Microstructure peculiarities of crystals were studied. Influence of overstoichiometric tellurium concentration on microstructure changes was examined. It was shown that heat treatments at 573-873 K temperature range led to some alterations in the state of tellurium enriched phase. These alterations were explained by the character of Bi – Sb – Te phase diagram near (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ compositions.

**A1-27 Growing of Circular Cross-section Crystals by Directed Crystallization Method**

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Bi$_2$(Te$_{0.95}$Se$_{0.15}$)$_3$ based crystals of n-type and (Bi$_{1.25}$Sb$_{0.75}$)$_2$Te$_3$ based crystals of p-type with cross-section (1_3) 0.02 mm in diameter and 40 mm in length are grown by directed crystallization method. Thermoelectric properties of crystals are examined. Practical use of crystals with such geometry for production of thermoelectric devices is shown.

**A1-28 Influence of Alloy Scattering on the Electron Mobility in n-type (Bi$_{1-x}$Sb$_x$)$_2$(Te$_{1-y}$Se$_y$)$_3$ Thermoelectric Materials**

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We have studied the effect of Se and Sb on the electron mobility in n-type (Bi$_{1-x}$Sb$_x$)$_2$(Te$_{1-y}$Se$_y$)$_3$ alloys produced by mechanical alloying and extrusion, over the composition range corresponding to 0 $\leq$ x $\leq$ 0.125 and 0 $\leq$ y $\leq$ 0.07. The introduction of Se and Sb in pure Bi$_2$Te$_3$ is of interest because both of these elements reduce the lattice contribution to the thermal conductivity, thus allowing a marked increased in the thermoelectric performance of the (pseudo-binary) alloy. The transport properties were measured in the range from 77 to 300 K, where we observed a systematic decrease in the mobility with increasing Se and Sb content. This decrease has been analyzed and compared to what would be expected from alloy scattering effects alone. We conclude that Se has a more significant impact on electron mobility than Sb because the difference in electronegativity between Te and Se is much larger than that between Bi and Sb. Further understanding of the alloying scattering mechanism is important for the development of new thermoelectric materials and also to increase the thermoelectric performance of conventional alloys.

**A1-29 Solvothermal Preparation and Transport Properties of Quasi-Binary PbTe-Bi$_2$Te$_3$ Compounds**

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In this work, quasi-binary compound PbTe-Bi$_2$Te$_3$ was prepared by a solvothermal method followed by a post heat-treatment, based on the reaction between BiCl$_3$, Pb(NO$_3$)$_2$, Te, KOH and KBH$_4$ in N,N-dimethylformamide (DMF) at 180 °C for 24 h. The microstructures of samples were characterized by using XRD, TEM and SEM. The transport properties were also determined by the measurement of electric conductivity and Seebeck coefficient. A possible formation mechanism in the solvothermal process is proposed.

**Acknowledgment**
This work is supported by the National Natural Science Foundation of China under grant No. 50072010 and 59825102.

**A2- Skutterudites: Promising Power Conversion Thermoelectric Materials**

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Skutterudites have emerged as one of the most promising new thermoelectrics for power conversion applications in the intermediate range of temperatures up to near 1000K. Making use of void filling, doping and alloying one can form both n- and p-type conducting structures with the figure of merit exceeding the value of unity. Large power factors, together with large atomic displacement parameters that bode well for a possible significant reduction of the lattice thermal conductivity upon void filling, are an important aspect of the skutterudite structure. I review the progress made in the manipulation of the skutterudite structure to achieve high thermoelectric performance and I will highlight the latest attempts to fabricate highly efficient n-type forms of the material.

**A2- Recent Advances in Filled Skutterudite Systems**

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Filled skutterudites with various compositions have been studied extensively since they were reported being promising thermoelectric materials. A lot of the studies so far have focused on both synthesizing new filled skutterudites, and on revealing the influence of the filler atoms and their filling fractions on the thermoelectric transport properties. It was found that the maximum filling fraction for a given skutterudite system is greatly influenced by the ionic radius and the valence of the filler atoms in the skutterudite crystal structure. As for the multi-filling approach, the thermodynamic stability of the filled skutterudite structure depends strongly on the difference of the chemical and physical behavior between the co-filling atoms. The present paper will review the synthesis of filled skutterudites with special emphasis on the relation between their thermodynamic stability and the properties of the filler atoms. The influences of filling fraction, filler atoms and multi-filling on the thermoelectric transport will be also discussed.

**A2- The Synthesis of Metastable Skutterudites and Crystalline Superlattices**

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We have used controlled crystallization of elementally modulated reactants to prepare a series of kinetically stable, crystalline skutterudites 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 at large exotherm on annealing at temperatures below 200°C for all systems studied. 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.

**A2- Chromium Doping of Cobalt Triantimonide**

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We have fabricated and studied the structural, magnetic, and electrical transport properties of Cr-doped binary skutterudites of the form Co$_{1-x}$Cr$_x$Sb$_3$. The solubility limit for Cr in the crystal lattice of CoSb$_3$ is less than $x = 0.01$ for induction melted and annealed samples. It is shown that the lattice parameter increases linearly with increasing Cr content $x$. With substitution of Cr for Co, the electrical resistivity decreases drastically. Cr is trivalent, and essentially not altering the carrier concentration of the host CoSb$_3$. The role of grain size in affecting the carrier scattering mechanism is discussed. These results will be compared to those of Fe- and Ni-doped CoSb$_3$.

**A2- A Novel Skutterudite Phase in the Ni-Sb-Sn System: Phase Equilibria and Thermoelectric Properties**


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A novel ternary phase, Sn$_y$Ni$_4$Sb$_{12-x}$Sn$_x$, has been characterised exhibiting a wide range of homogeneity (at 250°C, 2.4 ≤ x ≤ 5.6; 0 ≤ y ≤ 0.31; at 350°C, 2.7 ≤ x ≤ 5.0; 0 ≤ y ≤ 0.27). Sn$_y$Ni$_4$Sb$_{12-x}$Sn$_x$ crystallises in a skutterudite based structure in which Sn atoms are found to occupy two crystallographic inequivalent sites: (a) Sn and Sb atoms randomly share the 24g site and (b) a small fraction of Sn atoms occupies the 2a (0,0,0) position, with an anomalously large isotropic atomic displacement parameter. Eu$_{0.8}$Ni$_4$Sb$_{5.8}$Sn$_{6.2}$, Yb$_{0.6}$Ni$_4$Sb$_{6.7}$Sn$_{5.3}$ and Ni$_4$As$_{0.1}$Ge$_{2.9}$ are isotypic skutterudite. Depending on the particular composition, metallic as well as semiconducting states appear. The crossover from semiconducting to metallic behaviour is discussed in terms of a temperature dependent carrier concentration employing a simple model density of states with the Fermi energy slightly below a narrow energy gap. This model accounts for the peculiar temperature dependent electrical resistivity. Skutterudites are characterised by a number of localised lattice vibrations, which were elucidated by Raman measurements and used to quantitatively describe the specific heat data. Eu containing compound exhibits long range magnetic order ascribed to the 4f7 electronic configuration of Eu, i.e., divalent Eu. The thermoelectric properties of rare earth filled tin skutterudites are rather attractive: Eu$_{0.56}$Co$_4$Sb$_{11}$Sn exhibits a thermopower value of -160µV/K at room temperature.

Acknowledgment
This research was sponsored by the Austrian FWF under grant P12899 and P13778 as well as by a grant for an international joint research project NEDO (Japan). The authors are grateful to the OEAD for support within the framework of the Austrian-French bilateral exchange program Amadee, project V.9. We thank E. Leroy for the SX100 electron microprobe measurements.

A2-Filled and Unfilled CoSb$_3$ Doped with Ni

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Optimization of binary skutterudite-based thermoelectric materials can take place via both filling the characteristic voids of the structure and by doping the covalent framework of the structure. We present a study in which both routes are explored concomitantly. The thermoelectric transport properties for the skutterudite system Ba$_y$Ni$_x$Co$_{4-x}$Sb$_{12}$ with 0 ≤ x ≤ 0.2 and 0 ≤ y ≤ 0.44 are examined over a wide temperature range. Divalent Ba readily fills the cages of the skutterudite structure and is effective in reducing the thermal conductivity of the material. The presence of a small amount of Ni has the same effect on compounds both with and without the Ba filler atoms: it increases the electron concentration, reduces the thermal conductivity, and enhances the
thermoelectric power factor. The overall result of incorporating small concentrations of Ni into the structure is to increase the thermoelectric figure of merit ZT. In the case of $\text{Ba}_{0.3}\text{Ni}_x\text{Co}_4\text{Sb}_{12}$, ZT is increased by 50% at 800 K to a value of 1.2 for $x = 0.05$. We will discuss the role of Ni on the scattering mechanisms and how this may influence the thermoelectric performance. Details of the microstructure will also be presented and discussed.

**A2- New Series of Skutterudite: $\text{Ce}_{1-z}\text{Yb}_z\text{Fe}_4\text{Sb}_{12}$**

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The skutterudite family, with general formula $\text{MX}_3$ (where $\text{M}=\text{Co, Rh, Ir}$ and $\text{X}=\text{P, As, Sb}$) shows promising thermoelectric properties with high thermopower and high electrical conductivity, but rather high thermal conductivity. Higher figure of merit is achieved by the insertion of rare earth elements in the large voids of the structure, whose rattling reduces lattice thermal conductivity, to form filled skutterudite compounds with general formula $\text{RE}_y\text{M}_4\text{X}_{12}$ (where $\text{R}=\text{rare earth, M=Fe, Ru, Os}$ and $\text{X}=\text{P, As, Sb}$). The electrical transport properties are improved by substituting $\text{Co}$ or $\text{Ni}$ for $\text{Fe}$ in the filled skutterudite. However, in $\text{RE}_y\text{Fe}_4-x\text{M}_x\text{X}_{12}$ with $\text{M}=\text{Co}$ or $\text{Ni}$, the rare earth insertion and the $\text{Fe/M}$ ratio are linked, consequently it is very difficult to achieve good thermal and electrical properties with an optimum carriers concentration at the same time. We will report the synthesis of new series of skutterudite compounds $\text{Ce}_{1-z}\text{Yb}_z\text{Fe}_4\text{Sb}_{12}$ and new experimental results on this system (XRD, EPMA, magnetic susceptibility, Ce and Yb LIII absorption edges, and transport properties). Double doping technique with a single valency element ($\text{Ce}^{3+}$) and a mixed valency element ($\text{Yb}^{n+}$, $2=n=3$) happens to be a promising way of preparing new thermoelectric materials by varying the electrical properties independently of the rare earth incorporation, which favours low thermal conductivity.

**A2- Electronic and Thermoelectric Properties of $\text{YbyFe}_4-x\text{NixSb}_{12}$ Filled Skutterudites**

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Filled skutterudite compounds containing Yb ions with unstable 4f-electrons are of special interest as one of the most promising new thermoelectric materials. We have synthesized p-type Yb-filled skutterudite compounds ($\text{Yb}_y\text{Fe}_{4-x}\text{Ni}_x\text{Sb}_{12}$) by spark plasma sintering technique and investigated their electronic and thermoelectric properties. The electronic structure of p-type $\text{Yb}_y\text{Fe}_{4-x}\text{Ni}_x\text{Sb}_{12}$ compounds has been studied by x-ray photoelectron spec-troscopy. In these materials, valence-band and core-level
photoelectron spectra clearly indicate the intermediate valence (mixed valence) states of Yb between divalent and trivalent. The lattice thermal conductivity decreases from 0.1 W/cmK for CoSb$_3$ to 0.01 W/cmK for Yb$_{y}$Fe$_{4-x}$Ni$_x$Sb$_{12}$. The Seebeck coefficient increases with increasing carrier concentration in contrast to a behavior of ordinary semiconductors. This is due mainly to the large increase of carrier effective mass. We discuss the valence fluctuation (mixed valence) of Yb ions and the strong hybridization of Yb 4f states with the valence band states, and their relation to the electronic and thermoelectric properties for p-type Yb$_{y}$Fe$_{4-x}$Ni$_x$Sb$_{12}$ filled skutterudite compounds.

**A2- La Doping Effect in Thermoelectric Properties of Skutterudite Compound CeRu$_4$P$_{12}$**


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Filled Skutterudite compounds La$_{1-x}$Ce$_{x}$Ru$_4$P$_{12}$ (x=1, 0.9, 0.8, 0.7) have been prepared at high temperature and high pressure. The thermoelectric properties have been investigated. Seebeck coefficient of La$_{1-x}$Ce$_{x}$Ru$_4$P$_{12}$ were measured in the range of temperatures 100-700K, resistivity were measured from 2K to 300K and thermal conductivity were measured at room temperature. Resistivity shows that all these compounds have semiconducting behavior. Seebeck coefficient measurement of CeRu$_4$P$_{12}$ exhibits p-type conduction above 140K, but at lower temperatures changes to n-type. CeRu$_4$P$_{12}$ has significantly large seebeck coefficient (Maximum value=436 V/K) at 180K. Maximum peak of seebeck coefficient shifted to lower temperature with La doping. The resistivity and thermal conductivity decreased with increase of La percentage. Doping effect of La has been found to increase power factor through the wide range of temperatures. The maximum value of the power factor can be controlled with the La dopant. High power factor values in the order of 10-3W/mK2 have been found at La$_{0.1}$Ce$_{0.9}$Ru$_4$P$_{12}$, which could be the potential candidate of thermoelectric material below and above room temperature.

**A2- Synthesis and Thermoelectric Properties of Co$_{(1-x)}$Ni$_x$P$_3$ and CoP$_x$As$_{(3-x)}$ Skutterudites**

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**A2-21 Preparation and Thermoelectric Properties of Y$_{2}$Fe$_x$Co$_{4-x}$Sb$_{12}$**

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Y-filled skutterudite, $Y_xFe_xCo_{4-x}Sb_{12}$, has been synthesized by melting method and solid reaction method, and the thermoelectric properties have been studied. The lattice thermal conductivity of $Y_xFe_xCo_{4-x}Sb_{12}$ decreases significantly with increasing $Y$ filling fraction in the Sb-icosahedron voids. The lattice thermal conductivity of $Y_xFe_xCo_{4-x}Sb_{12}$ exhibits a glass-like temperature dependence that shows no remarkable peak at low temperature and is much lower than the well-known Ln-filled and Ba-filled compound. The electric transport of the Y-filled compound has been also investigated with comparing to the skutterudite compounds with other filler atoms and the effect of filler atoms on the thermoelectric properties of filled skutterudites is discussed.

A2-22 Lattice Parameters in Filled Skutterudite Antimonide - Effect of Filling

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In skutterudite and filled skutterudite materials atomic positions are specified by a set of lattice parameters i.e., the lattice constant $a$ and the internal ($u$, $v$) parameter. The latter determines the positions of the pnictogen atom in (filled) skutterudite materials. These lattice parameters can be determined theoretically by the minimization of the total energy from the first principal band structure calculation, for example, the full potential linearized augmented plan wave (FLAPW) method with the density function theory. In typical skutterudite antimonide it has been found that these theoretical lattice parameters are in good agreement with experimental values, and the calculated band gap is rather sensitive to the position of Sb atom. The situation in filled skutterudite is expected be similar. Theoretical lattice parameters are calculated for $LaCo_{4}Sb_{12}$. The calculated lattice constant increase by about 1 %. The calculated values in the increase rate of the lattice constant for the increase of filling factor in La atom agrees well with the experiment. This theoretical determination of lattice parameter is used to discuss electronic structures, their features and the relation to thermoelectric properties in various filled skutterudite antimonides.

A2-23 Effect of BN and C60 Particle Dispersion on the Thermoelectric Performance of $Ba_xCo_{4}Sb_{12}$

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Ba\textsubscript{y}Co\textsubscript{4}Sb\textsubscript{12}-BN and Ba\textsubscript{y}Co\textsubscript{4}Sb\textsubscript{12}–C\textsubscript{60} composites were prepared by solid state reaction and sintering process. The TEM and SEM observation showed that the C\textsubscript{60} nano-particles disperse uniformly in the Ba\textsubscript{y}Co\textsubscript{4}Sb\textsubscript{12} crystal grains while the BN particles disperse in the boundaries of the matrix. The constituent phases of the samples were determined by XRD. Thermal conductivity, thermopower, and electrical resistivity in the temperature range between 300K and 900K were measured. The effects of the particle contents and distribution on the thermoelectric properties of Ba-filled skutterudites are discussed.

**A2-24 Thermoelectric Properties of M\textsubscript{y}Co\textsubscript{4-y}Sb\textsubscript{12} (where M = Sm,Gd, Dy, and Er, y = 0.04-0.32)**

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Semiconductors with the skutterudite structure AB\textsubscript{3} (where A is a transition metal element such as Co, Rh, Ir and Pn and a pnictogen elements such as P, A and Sb) possess attractive potential for high ZT values. Here M\textsubscript{y}Co\textsubscript{4-y}Sb\textsubscript{12} (where M = Sm,Gd, Dy, and Er, y = 0.04-0.32) were fabricated by different processing. The effects of the rare metal elements and the microstructure on the thermoelectric properties were investigated.

**Acknowledgments**

*This work is supported by the Natural Science Foundation of China, Grant No. 50042014 and 60176004.*

**A3- Stability of Clathrates**

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There has been a recent resurgence of interest on the study of the structures and properties of clathrates with frameworks consist of Group IV or Group III-V elements. It was demonstrated experimentally that with suitable dopings these clathrate materials can exhibit semi-conducting, metallic and superconducting properties. Furthermore, it has been suggested that the unique and anomalously low thermal conductivity can be exploited for high efficiency thermoelectric applications. In this presentation, the structural principles regarding the stability of these novel materials will be examined using a real space description based on the morphology of the local structure. Theoretical and experimental results on the characterization of the electronic and thermal properties of selected systems will be discussed.

**A3- Thermoelectric Clathrates**
Clathrates have been attracting growing interest due to their industrial and technological applications. These materials are being studied for their thermoelectric and superconducting properties by several authors. The more stable state of tetrahedral network (sp3) of silicon or germanium is cubic and in the presence of guests like Ba, Sr, etc. the tetrahedral network of Si or Ge prefers next stable cage like structure know as clathrates, because the volume of the cubic structure is not sufficient to accommodate the guest. The rattling motion of guest atoms at the center of the cage is supposed to lower the lattice thermal conductivity. In the present work, we prepared Ba$_{8}$Ga$_{16}$Si$_{30}$ and Ba$_{8}$Al$_{16}$Si$_{30}$ clathrates by arc melting and characterized their electrical and thermal properties in the temperature range of 300K to 873 K. The highly polished surface of the as prepared sample is analyzed by scanning electron microscopy (SEM) and electron beam microanalysis (EPMA) for their surface morphology and composition respectively. SEM observation shows no secondary phase as observed in Sr-Ga-Si clathrates by arc melting. The observed low thermal conductivity in the temperature range studied is explained with rattling motion of guest atoms at the center of cage. In addition Rietveld refinement is also carried out to know the position of Ga, Al and Si.

Acknowledgments

One of the authors (D. N.) is grateful to Science and Technology Agency (STA) of Japan for awarding the research fellowship.

A3- Synthesis and Structural Characterization of New Mixed Clathrate Ba$_{8}$Ge$_{1-x}$Sn$_{x}$

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Mass-difference-scattering of the phonons is one of the most effective and well-understood concept for reducing the thermal conductivity in thermoelectric materials. Alloys based on Si-Ge mixtures are a typical prototype where point defects scatter mainly the high frequency phonons. Owing to the peculiarity of their crystalline structure, the clathrates of Si, Ge and Sn have been shown to be very effective in scattering the low frequency phonons. Therefore, one can expect that scattering the phonons in the whole frequency range can be achieved by making a solid solution based on the clathrate structure. In addition to the expected reduction in the thermal conductivity, the electrical properties can be tuned by varying the composition. In the present work, we present some
preliminary results of the synthesis and the structural characterization of new mixed clathrates in the system \( \text{Ba}_8\text{Ge}_{1-x}\text{Sn}_x \).

**A3-21 Thermoelectric Properties of \( \text{Ba}_8\text{Ga}_x\text{Ge}_{46-x} \) Clathrate Compounds**

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The group-IV based clathrate compounds are currently being studied as one of the most promising candidates for thermoelectric applications because they combine glasslike thermal conductivity and good electronic transport properties. The control of these unique properties to improve the thermoelectric properties is challenging. To accomplish this purpose, it is of primary importance to develop physical models to explain the interaction between the guest atoms and the framework, and their relationship to the electronic structure and transport properties. Therefore, we have synthesized \( \text{Ba}_8\text{Ga}_x\text{Ge}_{46-x} \) clathrate compounds with varying compositions by arc melting and spark plasma sintering techniques and investigated their structural, electronic and thermoelectric properties. X-ray diffraction analysis, electron probe microanalysis, and thermal analysis were conducted to check the crystal structure, composition, and homogeneity of samples. Hall, Seebeck, and thermal conductivity measurements were performed in a wide temperature range. The effect of Ga composition on electronic and thermoelectric properties is discussed. The electronic structure and bonding states are also discussed from the results of x-ray photoelectron spectroscopy measurements.

**A4- Detailed Optimization of the Properties of \( \text{Fe}_{1-x}\text{Co}_x\text{Si}_{2+z} \) for Energy Conversion and Thermal Sensors**

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N-type Co doped FeSi\(_2\) is known to be a stable material for high temperature energy conversion purposes. A powdermetallurgical preparation route for doped iron disilicide based on mixing by ball milling and subsequent hot pressing has been established at DLR during recent years. A study on the properties of a set of \( \text{Fe}_{1-x}\text{Co}_x\text{Si}_{2+z} \) sample compositions (\( x = 0-0.08; z = 0-0.1 \)) prepared by hot uniaxial pressing (HUP) will be presented. A pronounced maximum of the Seebeck coefficient is observed at low Co concentration disappearing with increasing \( x \). Detailed investigation allows to identify the concentration of Co and Si according to optimum thermoelectric properties for power generation and sensor applications with regard to a given temperature region. The practical aim is to identify best compositions based on the specific preparation route including all its technological steps and complete description of the purity of the starting material. The
influence of ball milling as well as the aging of the material at elevated temperatures will
be discussed. The latter is substantially influenced by the presence of iron/cobalt
monosilicides and thus the control of the Fe:Si ratio is a critical issue.

Finally, an ambiguous influence of carbon doping will be reported.

Acknowledgments
One of the authors is supported by a Marie Curie Fellowship of the EU, No. HPMF-CT-
2000-00639.

A4- Thermoelectric Properties of FeSi$_2$-TiB$_2$ Composites

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Two series of FeSi$_2$-TiB$_2$ composites with composition near the percolation
threshold were prepared applying two different routes: 1). Co-doped FeSi$_2$ powder (5
at% Co) with various amounts of TiB$_2$ powder added was homogenized by planetary ball
milling. 2). Wet mixing of the powders. Both these precursors were hot pressed after
drying. SEM observations show that for the first route FeSi$_2$ grains are smaller than those
of TiB$_2$, while in the second latter this was vice versa. The percolation threshold for both
routes was found at a volume ratio of 0.255 and 0.145, respectively. The thermal and
electrical conductivity and the Seebeck coefficient were measured in dependence on
temperature. The results show that the thermal and electrical transport behavior is
different in these two series of composites. The figure of merit for the first route is
always lower than that of the sample with no TiB$_2$ added, while for the second route it is
similar to pure Co-doped FeSi$_2$. The results indicate that the thermoelectric properties of
FeSi$_2$-TiB$_2$ composites can be adjusted by differences in the preparation process and that
the thermoelectric properties of Co-doped FeSi$_2$ could be improved by preparing
composites with TiB$_2$ in which the TiB$_2$ grains are much finer than the FeSi$_2$ grains.

Acknowledgments
This work is supported by the Alexander von Humboldt Foundation of Germany.

A4- The effect of Ge doping on p-type Higher Manganese Silicides (HMS)

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Higher Manganese Silicides (HMS) is a promising p-type material for
thermoelectric generation at high temperature around 800K. It is well known that HMS
has peculiar layered structures and contains plate-type of monosilicides (MnSi) in
precipitate with thickness of few microns in the as-grown boules by Czochralski or
Bridgman method. It is supposed that they bring the anisotropic thermoelectric properties.

To substitute the constitutional elements by the ones in the same group of valence is a conventional technique to improve the thermoelectrical performance, especially to reduce the lattice thermal conductivity. Here we shall discuss the effects of Ge doping on MnSi1.74 grown by Bridgman method. It was found that Ge behaves as a p-type dopant. Furthermore, the temperature dependence from room temperature to 800K of electrical conductivity, Seebeck coefficient, and thermal conductivity for parallel and perpendicular to c-axis as well as thermoelectric figure of merit will be shown.

A4- Annealing Effect on Thermoelectric Performance for Hot-press Sintered Chromium Silicides (CrSi₂)

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The effect of annealing process on thermoelectric properties has been researched for hot-press sintered chromium silicide (CrSi₂) in order to enhance the thermoelectric performance. Annealing time under a proper annealing temperature was found to affect the transport properties such as carrier concentration, Hall mobility and scattering mechanism, so that the thermoelectric properties such as Seebeck Coefficient and electrical conductivity were dependent on the annealing time. The experiments have been carried out for 0.9atm% Ag-doped chromium silicides produced by the hot-press sintering process varying annealing time of 12, 24h, 36h and 48h at 1273K in annealing temperature. The scattering mechanism was changed with increasing annealing time to shift from the mixed mode of ionized impurity scattering with phonon scattering to phonon scattering for the temperature range from 300K to 650K. For samples of more than 36h in annealing time the phonon scattering mode was dominant for overall temperature range similar to that for a single crystal sample of undoped chromium silicide. It was clarified that the annealing time highly affected thermoelectric performance and temperature dependence of thermoelectric properties and the optimum annealing process surely existed for 0.9atm% Ag-doped, hot-press sintered CrSi₂ system. For example, the power factor was obtained 2.5x10⁻³ W/m²K at 800K in maximum for the sample of 24h in annealing time, while it was 1.5x10⁻³ W/m²K at 650K in maximum for the as-hot-press-sintered sample.

A4-21 Electronic Structures of Semiconducting Alkaline-Earth Metal Silicides

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Electronic structures and densities of states of the following alkaline-earth metal silicides have been calculated using the first-principle pseudopotential method; Mg₂Si, BaSi₂, Ca₂Si, Sr₂Si. Energetics of these in their equilibrium structures in comparison
with other hypothetical structures (i.e., CaSi$_2$- or SrSi$_2$-type BaSi$_2$, Ca$_2$Si type Mg$_2$Si, Mg$_2$Si-type Ca$_2$Si, and Mg$_2$Si-type Sr$_2$Si) are also considered to clarify the structural change of alkaline-earth metal silicides with the promotion to the heavier elements. Their semiconducting behaviors could be predicted though the energy bang gaps calculated were about 40% of the actual measured values. Effect of doping and the nonstoichiometry on the generation of the localized energy level between the energy gap is also discussed.

**A4-22 The Effect of Crystal Grain Size on Thermoelectric Properties of Sintered FeSi$_2$**

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The sintered materials of FeSi$_2$ doped with Mn or Co, which showed p- or n-type conduction, were prepared by the cold-press and sintered technique. The effect of crystal grain size on the thermoelectric properties was investigated for both the materials. Mean sizes of the original powder d, as-sintered grain Cs and annealed grain Ca decreased exponentially with increasing ball-milling duration. The Cs of the Mn-doped material was larger than that of the Co-doped one and the Ca was as well. Seebeck coefficient and electrical resistivity of the Mn-doped material increases with an increasing Ca. On the other hand, _ of the Co-doped one was constant independently of Ca and _ decreased with an increasing Ca. Hall mobility of both the materials exhibited independence of Ca. For the Mn-doped material, Hall carrier concentration nH decreased with an increasing Ca, whereas that for the Co-doped one increased. This result indicates that the Ca dependence of _ and _ is equal to the nH dependence. The grain boundary is probable to have a function of forming holes. For Mn doping, a decreasing tendency of nH with an increasing Ca is due to a decrease in grain boundary. For Co doping, a decrease in grain boundary reduces holes that can compensate electrons, resulting in an increasing tendency of nH with an increasing Ca.

**A4-23 Electrical and Microstructural Analyses on the Co-doped FeSi$_2$ Prepared by Vacuum Hot Pressing**

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Co-doped n-type FeSi$_2$ powders have been prepared by mechanical alloying and sintered by vacuum hot pressing (VHP). As-VHPed compacts were composed of untransformed mixture of Fe$_5$Si and FeSi phases. Vacuum annealing at 830°C led to the thermoelectric semiconducting Fe$_2$Si phase transformation, but some residual metallic and phases were unavoidable. Electronic transport parameters and thermoelectric properties were remarkably changed by annealing due to the transformation from metallic and phases to semiconducting phases. Microstructural analysis was also carried out by using SEM and TEM.
Acknowledgments
This work was supported by grant No. 2001-1-30100-001-2 from the basic research program of the Korea Science & Engineering Foundation.

**A4-24 Direct Formation of \(-\mathrm{FeSi}_2\) on Substrate in Evacuated Sealed Ampoule**

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A simple preparation method of \(-\mathrm{FeSi}_2\) on substrates was proposed by the isothermal process in a evacuated sealed ampoule. The mechanism of this reaction process was investigated using Si powder or Fe-Si mixed powder and sputtered Fe films on Si substrates or sapphire substrates. Compacted powder was encapsulated in an ampoule separated from substrates with Fe films. From the reaction on substrates using Si powder, it was found that vaporized Si from Si powder reacted with solid Fe and \(-\mathrm{FeSi}\) was formed. The \(-\mathrm{FeSi}\), thus formed, initiates the reaction with solid Si to form \(-\mathrm{FeSi}_2\). Furthermore, it was found that vaporized Fe, existing together with vaporized Si from Fe-Si mixed powder, promoted the formation of \(-\mathrm{FeSi}_2\) single phase on substrates. This results reveal the effect of vaporized Fe on activating silicidation on substrates and the possibility of maintaining the Fe/Si composition ratio nearly stoichiometric on silicidation. The isothermal process in a evacuated sealed ampoule containing sputtered Fe films on Si substrates and Fe-Si mixed powder is thus found to be appropriate for the synthesis of \(-\mathrm{FeSi}_2\) single phase on substrates.

Acknowledgments
This work was partially supported by the Japanese Ministry of Education, Culture, Sports, Science and Technology Grant for the Promotion of the Advancement of Research (High-Tech Research Center) and by the Waseda University Grant for Special Research Project, Grant No. 2001A-109.

**A4-25 Thermoelectric Properties and Electronic Structure of Mn-Si Ceramics**

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We have prepared Mn-Si ceramics using the spark plasma sintering (SPS) and the vacuum melting methods. Temperature dependencies of thermoelectric properties such as Seebeck coefficient, electrical conductivity and thermal conductivity are measured for the temperature range from 300 K to 900 K. The magnitude and the temperature dependence of Seebeck coefficients are similar to the previous best result. However so far the magnitude of the electric conductivity is small, which is improved by the doping. Most of the samples are brittle. It is found that this weakness of the mechanical strength is improved very much by the doping effects of some impurity atom. The electronic structure is calculated by means of the full-potential linearized augmented plane wave
A4-26 Phase Transformation and Thermoelectric Properties of N-type FeSi2 Processed by Mechanical Alloying

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N-type Fe<sub>0.98</sub>Co<sub>0.02</sub>Si<sub>2</sub> powders have been produced by mechanical alloying process and consolidated by vacuum hot pressing. As-milled powders were of metastable state and fully transformed to α-FeSi<sub>2</sub> phase by subsequent isothermal annealing. However, as-consolidated iron silicides consisted of untransformed mixture of α-Fe<sub>2</sub>Si<sub>5</sub> and α-FeSi phases. Isothermal annealing has been carried out to induce the transformation to a thermoelectric semiconducting α-FeSi<sub>2</sub> phase. The transformation behavior of α-FeSi<sub>2</sub> was investigated by utilizing DTA, a modified TGA, SEM, and XRD analyses. Isothermal annealing at 830ºC in vacuum led to the thermoelectric semiconducting α-FeSi<sub>2</sub> phase transformation, but some residual metallic α- and α-primes were unavoidable. Microstructures of iron silicides were investigated using SEM and TEM. Thermoelectric properties of α-FeSi<sub>2</sub> materials before and after isothermal annealing were evaluated in this study.

Acknowledgments
This work was supported by grant No. 2001-1-30100-001-2 from the basic research program of the Korea Science & Engineering Foundation.

A5- N-doped Superlattice Structures with both Positive and Negative Seebeck Coefficients

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In order to change the sign of the Seebeck coefficient for a semiconductor, it is necessary to change the type of the dopant impurities. In an N-doped semiconductor, when dopant energy level is near the conduction band, Seebeck coefficient is positive. We will present detailed theoretical calculation of electron transport perpendicular to superlattice layers. It is shown that in the miniband conduction regime, it is possible to tailor the miniband width and the doping so that the overall average energy of moving carriers is lower than the Fermi energy and thus negative Seebeck coefficient can be achieved. Calculations for InGaAs-based superlattice material will be presented. This method can be generalized to other material systems and p-type doping. This will allow fabrication of both n- and p- thermoelectric elements using the same type of doping.
A5- High Temperature Thermoelectric Properties of Bi implanted Silicon Thin Film


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A thin film thermoelectrics with artificially controled nano-structure has been widely studied from a view point of micro cooling and sensing applications. Among the many processing techniques, ion implantation is one of the solutions to realize precise control of dose amount of the impurities and its structure in thin film. We have presented at the last conference that the high carrier density near 1020 cm$^{-3}$ was successfully achieved by implantation of Bi atom as a metastable state. The thermoelectric properties were controllable by post-annealing temperature for the high-dose samples. It has been pointed out that the Bi atoms could form Bi nano-clusters in the silicon crystal during the annealing process and thus the conduction could be governed by hopping conduction rather than the band conduction of silicon crystal.

In this study, the conduction mechanism of the Bi-implanted silicon thin film at elevated temperature was investigated. Bi ion was implanted into device layer of silicon-on-insulator substrate at some different conditions. Dose amount and post-annealing temperature was taken as parameters ranging from 3 x 1014 to 3 x 1016 cm$^{-2}$ and from 373K to 1000K. The in-plane electrical conductivity and Seebeck coefficient were evaluated in temperature range from 350K to 1000K. The annealing effects were observed from 373K to 1000K, and the electrical conductivity, the Seebeck coefficient, and the power factor increased monotonously with increasing the annealing temperature. The electrical conductivity showed $T^{-1/4}$ dependence which suggested that the conduction was dominated by variable range hopping mechanism.

A5- Figure-of-Merit of Fine-Grained Polycrystalline Silicon Thin Films

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The thermoelectric properties of phosphorous and boron doped fine-grained polycrystalline silicon thin films have been measured. The thermal conductivity of the films is reduced by one order of magnitude compared to the undoped single crystalline material whatever the doping level and the doping atoms. The electrical conductivity is reduced by the fine-grained structure of the layer but in a less extend than the thermal conductivity and the thermopower is almost unchanged. As a consequence, the figure-of-merit of these thin films is larger than that of the bulk materials doped at similar carrier concentrations. These measurements suggest that grain size reduction can be effective in
enhancing ZT, whereas previous measurements on sintered materials were countering it. A link is made between the deposition parameters, the microstructure, and the transport properties.

Acknowledgments

This work was supported by the Jet Propulsion Laboratory (contract 1217092) and DoD/ONR MURI (N00014-97-1-0516).

A5-21 Thermoelectric Characteristics of Si/Ge Superlattice Thin Film at Low Temperature

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Recently, an anomalously large thermoelectric power was observed in Si / Ge superlattice thin films by NDA group, where the temperature was over 400 K. We have been studied thermoelectric characteristics of thin films at temperatures from room temperature (RT) to low temperature less than 100 K. A similar thin film of Si / Ge superlattice prepared by NDA group also shows high thermoelectric power of approximately 50 µV / K at RT. This thermoelectric power goes down to be negative at lower temperature, and it consequently reaches around -200 µV / K at 100 K. Characteristics under magnetic field at these temperatures is also measured and no magnetic field effect is observed. Effects of heating process and Au dopant into Ge layers are also to be discussed.

A5-22 The Study for Thermal Annealing Effects on the Thermoelectric Properties of the Amorphous Si-Ge-Au Thin Films

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We have already reported about anomalously large thermoelectric properties of the Si-Ge-Au amorphous thin films. The thermoelectric properties change through thermal annealing, because these thin films are in quasi-stable state. And more, electrical resistivity and thermoelectric power have different annealing dependence. In order to distinguish the thermal annealing effects on the electrical resistivity and on the thermoelectric power, the amorphous Si-Ge-Au thin films were annealed sequencally with temperature range between room temperature and 1000 K. Electrical resistivity was stabilized at a whole temperature range by the 1st cycle thermal anneal. On the other hands, thermoelectric power was not stabilized even after several anneal cycles. Therfore we can deduce that electrical resistivity and thermoelectric power of the amorphous Si-Ge-Au thin films could be affected by different factors of amorphous structure. Electrical
resistivity could be affected by the amorphous structure that is easy to stabilized, in opposition that thermoelectric power could be affected by the another amorphous structure that is not to be stabilized by thermal anneal up to 1000K.

**A5-23 Thermoelectric Properties of Si$_{1-x}$Ge$_x$ Fabricated by Different Processing**

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Si$_{1-x}$Ge$_x$ is one of the best thermoelectric materials used for high temperature generator. Here the work was focused on the effect of microstructure on the thermoelectric properties. Si$_{1-x}$Ge$_x$ with different microstructure was fabricated by different processing and the thermoelectric properties were investigated.

**Acknowledgments**

*This work is supported by the Natural Science Foundation of China, Grant No. 50042014 and 60176004.*

**A6- Thermoelectrical Properties of the Compounds ScM$_{10}$Sb and YM$_{10}$Sb (M$_{10}$: Ni, Pd, Pt)**

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During the past years different studies on Half-Heusler compounds by many authors showed good thermoelectric properties. In a material scanning program the compounds ScM$_{10}$Sb and YM$_{10}$Sb (M$_{10}$: Ni, Pd, Pt) were investigated. The synthesis was done by arc melting of the elements. One half of the material was examined as it was, the other half after a heat treatment under different conditions. The cubic lattice parameter was determined by x-ray powder diffraction to 6.280 Å for YNiSb, 6.544 Å for YPdSb, 6.532 Å for YPtSb, 6.062 Å for ScNiSb, 6.312 Å for ScPdSb and 6.312 Å for ScPtSb. The thermoelectrical measurements showed a figure of Merit ZT of 0.0039 (300 K) for YNiSb, 0.0124 (360 K) for YPdSb, 0.024 for ScNiSb, 0.054 for ScPdSb and 0.009 for ScPtSb. Doped YPtSb and doped ScPdSb showed the best features for thermoelectrical application. Upon extrapolation of the dimensionless figure of merit up to 400 K, it reached values of 0.141 and 0.100 respectively.

**A6- Effects of Metallic Elements on Thermoelectric Properties of Silicon Borides**

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Silicon borides have excellent potential as high-temperature thermoelectric materials because of their high melting point and relatively large Seebeck coefficient. In the present work, effects of metallic elements on thermoelectric properties of the silicon borides were examined. The silicon borides containing some metallic elements were prepared by a plasma melting method. Silicon, boron and metallic elements powder were melted in a high-frequency induction plasma flame, and the silicon borides including metallic elements were formed. The crystal structures of the samples were characterized by X-ray diffraction (XRD), and the morphologies were observed by scanning electron microscope (SEM). Electrical properties such as Seebeck coefficient, electrical conductivity and Hall effect of the samples were measured. The Seebeck coefficient of the boride reached about 300 V K\(^{-1}\), the electrical conductivity was above 30000 S m\(^{-1}\). Since carrier mobility of the sample was less than about 1 cm\(^2\)V\(^{-1}\)s\(^{-1}\) and increased with an increase of temperature, the conduction mechanism of silicon borides seems to be a polaron hopping. The effect of metallic elements was increasing Seebeck coefficient, and the carrier mobility of silicon borides decreased by adding metallic elements.

A6- Preparation and Thermoelectric Properties of ZnO-TiB\(_2\) Composites

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Using effective medium theoretical analysis, Bergman and Levy have recently predicted that the power factor of a two-phase composite (consisting of a thermoelectric phase and a highly conducting phase) can be much higher than that of the single thermoelectric (TE) phase, if the sign of the Seebeck coefficient for both phases is the same and the high conducting phase is coated with the TE phase. In this work, we try to validate this prediction by experiment. We choose ZnO as a TE phase and TiB\(_2\) as a highly conducting phase. ZnO-coated TiB\(_2\) powders are prepared via sol-gel processing, using zinc acetate, ammonia and TiB\(_2\) powder as starting materials. SEM observations indicate that the TiB\(_2\) particles are coated with very fine ZnO particles. ZnO-coated TiB\(_2\) composite samples were pressure-less sintered in argon. The thermal and electrical conductivity and the Seebeck coefficient of the composites were measured in dependence on temperature. The thermoelectric properties of the composites are compared with pure thermoelectric ZnO.

Acknowledgments
This work is supported by the Alexander von Humboldt Foundation of Germany.

A6- Enhanced Thermoelectric Performance Due to Ultrafine Heterostructures Embedded in Sintered Al-doped ZnO

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Incorporation of ultrafine heterostructures, inclusions and cavities, are investigated on thermoelectric performance of Al-doped ZnO sintered body, which has so far been the best n-type oxide candidate material at high temperature \( (ZT = 0.3 \text{ at } 1000 \degree C) \). Since the power factor of the oxide as high as \( 15-20 \times 10^{-4} \text{ W/mK}^2 \) is well comparable to those of conventional high-temperature materials such as Si-Ge, reduction of high thermal conductivity of the oxide is the most promising for achieving higher ZT. Effects of ultrafine heterostructures embedded in sintered bodies of \( \text{Zn}_{0.98}\text{Al}_{0.02}\text{O} \) will be reported. Into the starting powder mixture, 10wt% of \( \text{ZrO}_2 \) fine powders or polymethylmethacrylate (PMMA) fine beads were added; both are expected to form heterogeneous ultrafinestructures as phonon scattering centers, while the latter is intended to form cavities (voids) rather than oxide particulate inclusions. Zirconia was selected according to the literature as an inert and stable oxide counterpart of the ZnO matrix. The polymer beads are expected to be burned out during sintering process of the oxide and thus form isolated cavities within dense sintered bodies. Although the reduction of the thermal conductivity is the weakest for the smallest polymer beads of 0.1-0.2 \( \mu \text{m} \) in diameter, this sample shows remarkable enhancement of the thermopower at around 500 \( \degree C \), keeping the electrical conductivity virtually intact compared to the completely dense sample without the polymer beads. This sample thereby reaches the maximum power factor of \( 40 \times 10^{-4} \text{ W/mK}^2 \), almost doubling the ZT value. Effects of the size of the polymer beads will be also discussed.

**A6- Thermoelectric Properties of Spin-coated Polyaniline Films**

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Conductive polyaniline films were cast and stretched to investigate on thermoelectric properties. The thermoelectric properties of the stretched polyaniline films in the direction parallel to the stretching direction was much higher than that of the unstretched counterpart, and increased with increase of the drawing ratio. The experimental results of X-ray diffraction patterns and Vis-near IR spectra have revealed that the increment is due to extended coil-like conformation and ordering of polyaniline molecules.\(^1\)

Here we report thermoelectric properties of spin-coated conductive polyaniline films. The polyaniline films showed a tendency of increase in thermoelectric properties with decreasing in thickness of the film. Vis-near IR spectra and X-ray diffraction patterns of the films have indicated that such increment of thermoelectric properties does not originate from ordering of the molecules but are only due to extended coil-like conformation of polyaniline molecules in the film.


**A6- Some features of the conduction band structure, transport and optical properties of n-type \( \text{Mg}_2\text{Si-Mg}_2\text{Sn} \) alloys**
Mg$_2$Si$_x$Sn$_{1-x}$ alloys are the perspective material for thermoelectric generators at moderate temperature. However, the absence of reliable data on their band structure parameters does not permit to estimate a possible limit thermoelectric efficiency of these materials.

According to the phase diagram, characterized by a peritectic reaction, there are two wide regions of solid solutions in pseudo-binary system Mg$_2$Si$_x$Sn$_{1-x}$ near components Mg$_2$Si and Mg$_2$Sn. They are separated by a two-phase range (0.4 <x< 0.6).

Here we shall report the results of the complex study of electrical conductivity, Hall coefficient (80–800 K), thermopower (300–800 K) and optical spectra in plasma reflection interval (2-40 μm) for n-type samples of different composition. The properties of each composition with different x were investigated in carrier concentration range varying from $5\times10^{17}$ to $5\times10^{20}$ cm$^{-3}$.

Combined analysis of kinetic and optical properties resulted in determination of conduction band basic parameters. Considerable difference of these parameters for x <0.4 and x>0.6 areas was obtained.

**A6-21 Thermal Conductivity Control of ZnO Thermoelectric Ceramics using Hot-pressing Method**

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For the purpose of decreasing thermal conductivity of n-type ZnO thermoelectric oxide materials, nanostructural Al doped ZnO ceramics was prepared by hot-pressed sintering technique at 950°C. The averaged grain size of the prepared ZnO ceramics was under 1μm. Low thermal conductive Al doped ZnO ceramics was observed by decreasing grain size. Thermal conductivity of the hot-pressed 1mol%Al doped ZnO ceramics was about 20W/mK at 25°C, which is half value of the normal sintered products. This result may be related to increase number of grain boundary as a factor of increasing thermal resistance in polycrystalline products. Furthermore, the electrical conductivity, and the power factor of the hot-pressed Al doped ZnO ceramics was higher than that of normal sintered dense materials.

**Acknowledgments**

This work has been supported by METI, Japan, as part of the Synergy Ceramics Project. Part of the work has been supported by NEDO. The authors are members of the Joint Research Consortium of Synergy Ceramics.

**A6-22 Thermoelectric Properties of Mixed layered Compounds TiS$_{2-x}$Se$_x$ (0 <x <2)**
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Seebeck coefficients (S) were measured in TiS$_{2-x}$Se$_x$ for 0 ≤ x ≤ 2 in the temperature range 77-280K. For TiS$_2$ (x=0), S was negative and its absolute value increased linearly with temperature, attaining to 170 µV/K or somewhat larger, depending on individual samples, at 280K. With increasing x, the absolute value of temperature coefficient (TC) of S decreased in the temperature region T 150K. At x 0.5, TC was reduced to zero and changed its sign for larger x. This behavior is explained by the fact that valance band of this system consists of S 3p and/or Se 4p bands and shifts upward with increasing x. For TiSe$_2$ (x=2), S became positive for T 270K due to the increasing effect of valance band with increasing temperature. The charge density wave (CDW) transition at 200K in TiSe$_2$ opens the CDW gap and pushes down the lower CDW band edge with decreasing temperature. Below 150K, S is controlled by the upper CDW band consisting of Ti 3d band. Thermoelectric behavior of this system can be totally explained by above band picture. The present experiments suggest a possibility of raising S in TiS$_2$ by a substitution for Ti to modulate the 3d band.

**A6-23 Preparation of p and n-type SiC-based Thermoelectric Materials by Spark Plasma Sintering**

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We report on the preparation by Spark Plasma Sintering (SPS) and the thermoelectric properties of p and n-type SiC. The α-SiC powder was used as starting material, then the elements of N and Al were doped for n and p-type conduction, where Si$_3$N$_4$ and Al$_4$C$_3$ were selected as the source materials of dopants, respectively. The crystal structure of the sintered materials is cubic (α-SiC) for undoped and Si$_3$N$_4$-doped SiC, while hexagonal (α-SiC (6H) type) for Al$_4$C$_3$-doped SiC. The relative density in all the sintering materials is more than 80% of the theoretical one. Electrical resistivity decreases and Seebeck coefficient increases with temperature, therefore we found that power factor depends both on temperature and impurity concentration and takes a maximum with impurity concentration of 7wt% at 700°C.

**A6-24 Thermopower study of NiO-based system**

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Thermoelectric power of NiO-based ceramics have been investigated as a function of temperature and dopants (Li, Ti, Ag) amount. The thermopower is positive for all the samples in the temperature range from 300K to 1000K, showing that these samples behave as p-type semiconductors. The Li, Ag and Ti dopants have a remarkable effect on thermopower of the NiO-based oxides, respectively. The density and effective mass of carrier are calculated on the basis of the experimental data. A structure model was set up for Li and Ti co-doped NiO sample according to the dopant concentration dependence of the thermopower. The results are analyzed and discussed to provide guidelines for optimization of the thermopower of NiO-based materials.

Acknowledgments
The work is supported by National Natural Science Foundation of China, Grant No. 59825102 and 50072010.

A6-25 Thermoelectric Properties of YBCO High Tc Superconductors

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Polycrystalline samples of YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) superconductors were synthesized from oxides by solid state reaction. Measurements of electrical conductivity ($\sigma$), thermoelectric power ($S$) and thermal conductivity ($\kappa$) of YBCO compounds were carried out in the temperature range 77K and 300K and the behavior of the thermoelectric merit figure (ZT) were analyzed.

The effect of Ag doping and the oxygen content of YBCO samples on the electrical and thermal properties were studied and their influence on the thermoelectric merit figure (ZT) was also studied. The possible use of YBCO compounds as active or passive legs of Peltier junctions has been investigated.

Acknowledgments
This work was supported by Universidad Nacional de Colombia.

A6-26 Synthesis and Sintering of ZrNiSn Thermoelectric Compounds

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The ZrNiSn-based half-Heusler compounds belong to a class of narrow-gap semiconductors, which are currently being investigated for their potential application as thermoelectric materials. Obtaining single-phased and dense ZrNiSn-based compounds is the key to improve their thermoelectric performances. In contrast to the commonly used
arc melting method, samples in the present paper were prepared by the solid-state reaction from element powders at 1173K under a flowing argon atmosphere for 4-7 days. The constituent phases and the element compositions were determined and showing that samples were of single phase and stoichiometric. ZrNiSn powder was then consolidated by using the spark plasma sintering technique. The effect of sintering temperature and holding time on the density was discussed. It is found that, dense ZrNiSn compounds with fine grain size and homogeneous microstructure were achieved under the condition of 1123K-40MPa-25min.

**A6-27 Thermoelectric Properties of Nb$_3$(Sb, Te)$_7$ Compounds**

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Niobium antimony telluride, Nb$_3$(Sb, Te)$_7$, was synthesized and tested for thermoelectric properties in the Thermoelectrics group at the Jet Propulsion Laboratory. The forty atoms per unit cell of Nb$_3$Sb$_2$Te$_5$ and its varied mixture of atoms yield a complicated structure, suggesting that Nb$_3$Sb$_2$Te$_5$ and related compounds may exhibit low thermal conductivity and hence a higher ZT value. Nb$_3$(Sb, Te)$_7$ compounds were synthesized and subsequently analyzed for their Seebeck voltage, heat conduction, and electrical resistivity. Results showed that Nb$_3$Sb$_2$Te$_5$ exhibits reasonably low values of resistivity and thermal conductivity for use as a desirable semi-conductor, but its low Seebeck coefficient of 14 _V/K precludes usage as a thermoelectric material. The antimony to tellurium ratio was varied to observe the behavior of a series of Nb$_3$Sb$_x$Te$_{7-x}$, where 1_ x_ 6, and the resulting data indicated that this series reaches its highest resistivity at the Sb:Te doping ratio of 3:4, but only Nb$_3$Sb$_2$Te$_5$ has single-phase composition. Additionally, the Seebeck voltage and resistivity both tend to rise with increasing temperature for the entire Nb$_3$(Sb, Te)$_7$ family, indicating that these compounds are semi-metallic rather than semi-conducting.

**A6-28 Thermoelectric Properties of Metal-Hexaborides**

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Boron and borides are expected to be promising candidates for high-temperature thermoelectric conversion materials. Most of the boron-rich semiconductors possess p-type conduction, and n-type ones are necessary for the application to thermoelectric devices. Although negative Seebeck coefficients were obtained in boron carbide and _-rhombohedral boron by metal doping, the absolute values of them were small or they changed to positive at high temperature. In the present study, we examined thermoelectric properties of metal-hexaborides, because their metal to boron ratio is larger than those of the doped boron carbides and _-rhombohedral boron, and some of them were reported to be semiconductor. We prepared some metal-hexaborides (MB$_6$; M=Ca, Yb, and Y), and their Seebeck coefficient and electrical conductivity were measured from room temperature to 1000 (K). Large negative Seebeck coefficients were observed in CaB$_6$ and
YbB₆, though YB₆ possessed small values. The maximum values for CaB₆ and YbB₆ were -280 (V/K) at 900 (K) and -120 (V/K) at 1000 (K), respectively. In addition, calculated power factors for CaB₆ and YbB₆ were more than 10⁻³ (W/mK²) at high temperatures. In the hexaborides, Ca and Yb atoms are thought to exist as divalent cations, while Y atoms are trivalent. Thus the metal-hexaborides with divalent cations are expected to be candidates for n-type thermoelectric materials at high temperature.

Acknowledgments
This work is supported in part by NEDO (New Energy and Industrial Technology Development Organization).

**A-29 Thermoelectric Properties of Layer-Structured (ZnO)ₖIn₂O₃ (k=5 and 9)**

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This work investigates the temperature dependence of the electrical conductivity(σ), Seebeck coefficient(S), and thermal conductivity(κ) for layer-structured (ZnO)₅In₂O₃ (k=5 and 9). Due to the strong electrical anisotropy of these compounds, highly textured crystal-axis-oriented ceramics are essential to achieve a high σ. Textured ceramic specimens of yttrium-substituted (ZnO)₅In₂O₃, which have the highest figure of merit (ZT≈0.33 at 1073 K) of n-type oxides, have been successfully fabricated using the reactive templated grain growth (RTGG) method. The relationship between microstructure and electrical transports are given, with emphasis on the RTGG process for controlling thermoelectric performance. Furthermore, we discuss the origin of the low σ values (~ 2 W/mK) of these compounds in comparison with Al-doped ZnO ceramics, which have a very high σ (~ 40 W/mK). Interface scattering between the InO₂- and (InZnk)O₆+ layers in this compound is believed to be the major source of the low observed κ.

**A-30 Temperature dependence of the figure-of-merit of Ag₀.20₈Sb₀.2₇₅Te₀.₅₁₇**

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We have evaluated figure-of-merit Z of the p-type Ag₀.20₈Sb₀.2₇₅Te₀.₅₁₇ boule in the temperature range from 300 to 700K. The boule was unidirectionally grown using a
Bridgman furnace and subsequently rapidly cooled by Ar to form a Widmannstätten structure of a high temperature phase AgSbTe$_2$, which could be desirable for power generation. Though the boule looked a homogeneous Widmannstätten structure, XRD patterns revealed that some precipitates of Ag$_2$Te and Sb$_2$Te$_3$ were contained in the boule and increased in volume in the growth direction. The maximum figure-of-merit Z$_{\text{max}}$ was different in the portions of the boule. The value of $2.0 \times 10^{-3}$ was at 620K for the former half portion of the boule and that of $1.7 \times 10^{-3}$ was at 585K for the latter half portion. The Ag$_{0.208}$Sb$_{0.275}$Te$_{0.517}$ boule with less precipitates showed higher Z at higher temperatures.

### A7- Physics of the thermoelectric oxide NaCo$_2$O$_4$: A guide to new thermoelectric oxides

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Since high thermoelectric performance in NaCo$_2$O$_4$ was found in 1997, various transition-metal oxides were extensively examined as a thermoelectric material. In this talk, I will briefly summarize the physics developed in NaCo$_2$O$_4$, and explain the mechanism of the superior thermoelectric properties of this compound. A key issue is that NaCo$_2$O$_4$ exhibits no structural, electronic, and magnetic transitions from 1 to 1000 K. This implies that a large amount of entropy at high temperatures is not released down to low temperatures, which is an origin for the heavy-fermion-like states.

Since NaCo$_2$O$_4$ is a p-type oxide, an n-type oxide with high thermoelectric performance is indispensable to all-oxide thermoelectric devices. In the latter half of my talk, I will review our strategy how to design an n-type transition-metal oxide, though our attempts are not yet successful.

### A7-Thermoelectric Properties in Single Crystal of Ca-Co-O system

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Single crystalline Co-based layered oxides have been reported as candidates of materials for thermoelectric power generation because of their high performance. In Ca-Co-O system, however, detail of the thermoelectric properties is not clear, because the single crystal without substitutions is not reported. Recently, synthesis of single crystalline Ca$_3$Co$_4$O$_9$ is succeeded in by flux method. Shape of the crystal is plate-like, and its dimensions are almost 5x10x0.01 mm$^3$. At 500 °C, Seebeck coefficient, $S$, and electrical resistivity, $\rho$, of the specimen are ca. 150 $\mu$V•K$^{-1}$ and ca. $1 \times 10^{-5}$ $\Omega$•m, respectively, and its thermo conductivity, $\kappa$, is nearly 3 W•m$^{-1}$•K$^{-1}$. Therefore, figure of merit, $ZT = S^2T/\kappa$, is more than 0.5. Relative lower $\kappa$ even its low electrical resistivity maybe comes from misfit structure between CoO$_2$ layer and Ca$_2$CoO$_3$ slab. Bi
substitution for Ca sites should decrease more, that is, ZT of (Ca,Bi)$_3$Co$_4$O$_9$ has to be more than 1.

Acknowledgments

This work is supported by Industrial Technology Research Grant Program in '02 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

A7- Combinatorial exploration of thermoelectric materials: substitution effect of Ca$_3$Co$_4$O$_9$ Composition Spread Libraries

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We investigated various substitution effects in Ca$_3$Co$_4$O$_9$ system using a combinatorial approach in order to explore optimal composition for thermoelectric properties at high speed. The samples were prepared using a composition-spread technique developed using pulsed laser deposition with a moving mask. The fabricated composition-spread thin film libraries, which have a continuous compositional variation along one direction of the substrate surface, were divided into the 10 pieces of rectangular shape by the fixed mask during the film fabrication, and the temperature dependence of a Seebeck coefficient and the electric conductivity were rapidly evaluated. The substitution elements are Mg, Sr, Ba, Ag, and Ba for Ca-site; Zn and Cu for Co-site, in the substitution range of 0.0 to 0.2. The temperature dependence of the electric conductivity shows significantly different by elemental substitution with small changes in Seebeck coefficient.

A7- Development of New-type Cobalt Oxide Thermoelectric Materials

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Single phase cobalt oxide thermoelectric materials, AxCoO2 with A=Na,Sr, Ca and Ba, [A’2CoO3]z[CoO2] with A’=Ca,Sr (the 349-phase), z=0.62 and [Ca2(Co1-yCuy)2O4]z[CoO2] with y=0.33 are synthesized successfully by the ion-exchange method or solid state reaction method. Seebeck coefficient, electric resistance and magnetization of these oxides are measured in the temperature range from 4K to 300K. These cobalt oxides show p-type conductivity and relatively high Seebeck coefficient, i.e., about 120 _V/K or above at 300K. The electric resistance of normally sintered samples are at the level of 10 m_ohm cm there. New nomenclature, the naming system, of modulated layered cobalt oxide thermoelectric materials, e.g., the latter two ones, is proposed according to the numbers of stacking cation layers, namely Co121 for [Ca2CoO3]0.62[CoO2] , (Co,Cu)-221 for [Ca2(Co1-yCuy)2O4]z[CoO2] and Bi-221 for
[Bi0.87SrO2]2[CoO2]1.82, respectively. The top letter is the cation(s) sitting in the rocksalt layer(s). The 1st, 2nd and 3rd digits indicate the numbers of the rocksalt-type metal-oxygen layer(s), alkali metal-oxygen layer(s) and conducting triangle cobalt oxygen layer(s) in a unit cell, respectively.

A7- The effects of the Misfit Structure on Thermoelectric Properties of Bi2-xPbxSr2Co2Oy single crystals

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The layered Co oxide Bi2-xPbxSr2Co2Oy that has a misfit structure shows high thermoelectric performance. It consists of the alternating stack of the hexagonal CoO2 layer and the rock salt Bi2-xPbxSr2O4 layer with the misfit along the b axis. It is, then, interesting how the misfit structure affects on the thermoelectric properties. Since it has two subcells with different symmetry, the symmetry of the electronic states would be altered to induce in-plane anisotropy in physical properties. Moreover the misfit structure would induce chemical pressure along the b-axis direction. We have investigated the in-plane anisotropy in the resistivity and thermopower, which is found to be anomalously large, possibly coming from the anisotropic chemical pressure. As for the x dependence, the thermopower is enhanced with increasing Pb contents up to x=0.4. Since Pb doping enhances the misfitness, this result shows that the thermoelectric properties would be improved by controlling the misfit structure.

A7- Electronic Structure of Misfit-layered Calcium Cobaltite

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We have performed the first-principles calculations on (Ca2CoO3)xCoO2, within the generalized gradient approximation. The optimized structure, consisting of a triple rock-salt-type Ca2CoO3 subsystem and a CdI2-type CoO2 subsystem in which their respective octahedra are significantly distorted, gives good agreement with recent experiment. The calculated electronic structures show two-dimensionally dispersive eg bands across the Fermi energy, which yield a p-type conductivity in the rock-salt subsystem, while the Fermi energy lies in the crystal field gap of the d states in the CoO2 subsystem. The calculated density of states is consistent with features of the measured X-ray photoemission spectra. Total energies of the spin-polarized calculations show that an antiferromagnetic ordering of the Co atoms in the rock-salt subsystem is stable in the ground state. We discuss temperature dependence of resistivity below room temperature observed in experiment in terms of magnetic interactions in a modeled Heisenberg Hamiltonian.
A7- Preparation and Properties of Co-based Oxide Single Crystal Composites

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It has been reported that Co-based oxide single crystals with layered structures show good thermoelectric properties. The properties of their bulk materials, however, are suppressed to be low because of high electrical resistivity (\(\rho\)). This is due to an electrical two dimensionality. In order to decrease \(\rho\), Co-based oxide single crystal composites were prepared using a hot pressing technique. The composites consist of Ca\(_3\)Co\(_4\)O\(_9\) (Co-349) large single crystals and Co-349 powder. Seebeck coefficient (S) of the composites is comparable to that of a hot-pressed sample without the single crystals. On the other hand, \(\rho\) is reduced by half by the incorporation of the large single crystals. Improvement of the grain alignment and percolation into the single crystals of the current would decrease \(\rho\) of the composites. Power factor (= S \(\rho\)) of the composites increases with temperature and is over 1.0 mWm-1K-2 at 973 K in air.

Acknowledgments
This work is supported by Industrial Technology Research Grant Program in '01 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

A7- Thermoelectric Properties of Ca\(_3\)Co\(_4\)O\(_9\)-based Ceramics Textured by Templated Grain Growth Method


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The applications of recently reported layer-structured oxide thermoelectric materials are dependent of texture engineering technique to enable the extraction of the highly anisotropic properties in a bulk form. We fabricated highly textured Ca\(_3\)Co\(_4\)O\(_9\)-based ceramics by using plate-like particles as a template. Plate-like powder and fine powder with the composition of (Ca\(_2.7\)Na\(_{0.15}\)Bi\(_{0.15}\)Co\(_4\)O\(_9\)) were synthesized and wet-mixed at the ratio of 1:4. The slurry was tape-cast into a form with the platelets aligned parallel to the tape surface. The tapes were stacked, and sintered or hot-pressed at 1193 K. The resultant ceramics showed highly preferred orientation with the \{001\} plane parallel to the tape surface. The electrical conductivity in the direction of the ab-plane was improved to 1.8 x 104 S/m at 1073 K by the texture given. The maximum power factor reached 5.9 x 10-4 W/mK2 at the same temperature.

A7- Thermophysical Behavior and the Effect of the Crystal Structure on the Thermoelectric Properties of NaxCoO\(_2\)–

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Recently, there is a strong interest in finding new, superior thermoelectric materials. In this context the highly anisotropic cobalt oxide NaxCoO2 exhibits promising thermoelectric properties. Four different phases of the non-stoichiometric oxide are known [1]: \(-\)NaxCoO2 (0.9 \( \leq x \leq 1 \)), \(\prime\)-NaxCoO2 (\(x = 0.75\)), \(-\)NaxCoO2 (0.55 \( \leq x \leq 0.6\)) and \(-\)NaxCoO2 (0.55 \( \leq x \leq 0.74\)) depending on composition and reaction temperature. So far only \(-\)NaxCoO2 (0.55 \( \leq x \leq 0.74\)) was reported to possess large thermopower [2] and was studied in detail. Despite the corresponding stoichiometry of \(-\), \(\prime\) and \(\prime\)-NaxCoO2, respectively, no phase transition has been reported for \(-\)NaxCoO2. This aspect motivated our study of the thermophysical behavior of \(-\)NaxCoO2 by means of TG/DTA, DSC, XRD and SEM/EDX. Three different modifications, \(-\), \(\prime\) and \(\prime\)-NaxCoO2, are involved in its decomposition above 600 °C under Ar atmosphere finally yielding in CoO. In contrast no phase transition is detected in air up to 1100 °C. Samples with various contents of \(-\) and \(\prime\)-NaxCoO2 have been prepared by heat treatment of \(-\)NaxCoO2 under Ar. The influence of the phase ratio \(-\)NaxCoO2/CoO and \(\prime\)-NaxCoO2/\(-\)NaxCoO2, respectively, on the thermoelectric properties was studied. The thermoelectric properties of \(-\) and \(\prime\)-NaxCoO2 were investigated as well to study the effect of the crystal structure on the thermoelectric properties of NaxCoO2.


Acknowledgments
This work is supported by the Deutsche Forschungsgemeinschaft, No. KA 664/10-1

A7-20 Exploration of n-type oxides by high throughput screening
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It has been reported that Co-based oxide single crystals with layered structures show good thermoelectric properties. These oxides show p-type thermoelectric properties. In order to realize thermoelectric power generation, n-type oxides possessing thermoelectric properties as good as p-type oxides are indispensable. We are exploring new n-type oxides using a combinatorial technique, in which 500 specimens can be prepared and estimated their thermoelectric properties in a day. The water solutions of metal nitric acid were used as starting materials. One library with 100 specimens on a 100 x 100 mm alumina plate before heat treatment can be prepared for an hour. Estimation of thermopower and electrical resistance was performed using two and four terminal
methods, respectively by 140 specimens/h. In the binary system, La-Ni-O is found out to show n-type thermoelectric properties.

Acknowledgments

This work is supported by Industrial Technology Research Grant Program in '01 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

A7-21 Growth and Characterization of NaxCoO2- crystals

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Recently, it has been discovered that oxide materials with layered structure, such as NaxCoO2 and Ca3Co4O9, possess excellent thermoelectric properties. The NaxCoO2 (0.5≤x≤1) system, which consists of alternate CoO2 and Na layer, has four crystallographic phases with the different Na content. Each phase shows the different electrical transport properties because Na supplies electric carriers for the CoO2 layer. So, it is important to grow the crystal of each phase in order to measure the characteristics. In this study, we grew large single crystals of NaxCoO2- by a flux method. Using two kinds of the flux, the crystals with the different phase and the different Na content, Na0.6CoO2- (phase) and Na0.9CoO2- (phase), were obtained. The in-plane thermoelectric properties of the two types of the crystal growths were measured. The thermoelectric power values of the phase and the phase were increased with temperature and reached 96 _V/K and 87 _V/K at 450 K, respectively. The electrical resistivity of the phase exhibited metallic temperature dependency and 1.3 m_cm at 300 K.

A7-22 Crystal Structure and Thermoelectric Properties of the Composite Crystal [(Ca1-xSrx)2CoO3]pCoO2

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Layered composite crystal cobaltite [(Ca1-xSrx)2CoO3]pCoO2 with 0 = x = 0.25 are synthesized at 920 °C in flowing oxygen gas. The modulated crystal structure of the samples is determined in accordance with a four-dimensional formalism from powder neutron diffraction data. With increasing x, the modulation amplitude in Co-Co conducting paths becomes less marked. The non-doped sample (x = 0) exhibits the resistivity = 15 m_cm and the thermoelectric power S = 130 _V/K at 300 K. Both the and S values decrease with x but the decrease in values is steeper than that of the S values. The sample with x = 0.20 shows = 9 m_cm and S = 105 _V/K at 300 K. The
power factor $S_2/\gamma$ increases with $x$, from $1.1 \times 10^{-4}$ W/mK$^2$ ($x = 0$) to $1.4 \times 10^{-4}$ W/mK$^2$ ($x = 0.20$) at 300 K. This improvement in thermoelectric performance can be explained in terms of the reduction of displacive modulation of the Co-Co conduction paths in the CoO$_2$ sheets.

**A7-23 Thermoelectric Properties of Na$_x$Co$_2$O$_4$ Prepared by the Polymerized Complex Method**

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Na$_x$Co$_2$O$_4$ powders were synthesized by using a polymerized complex (PC) method and then the polycrystalline samples were prepared by a pressureless sintering and hot-pressing. The microstructure and thermoelectric properties were investigated, and their differences between the conventional solid-state reaction (SSR) method and PC method were evaluated. The crystal grain size of the sample prepared by the PC method was remarkably smaller than that of the sample prepared by the SSR method. The degree of c-axis orientation of the samples prepared by both methods was nearly equivalent from the F-values calculated by the Lotgering’s method. The in-plane electrical resistivity increased and the out-of-plane thermal conductivity decreased compared with the sample prepared by the SSR method because of the enhancement of carrier and phonon scattering caused by the reduction in the crystal grain size. Especially, for the hot-pressed sample, $\gamma$ markedly decreased because of its small grain size. As a result, the figure of merit was improved over the whole temperature range and showed the maximum value of $6.5 \times 10^{-4}$ (K$^{-1}$) at 773K.

**A7-24 Thermoelectric Properties of Ag-doped Ca$_3$Co$_4$O$_9$ Ceramic**

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Ca$_3$Co$_4$O$_9$-based ceramics with layered crystal structure were prepared by a sol-gel method followed by different sintering procedures. The electrical conductivity and Seebeck coefficient were measured from 200 to 700. The electrical conductivity of the ceramic samples depends on different sintering procedures dramatically. Seebeck coefficient is positive and rises with the increase of Ag-doped amount.

**Acknowledgments**

The work is supported by National Natural Science Foundation of China, Grant No. 59825102 and 50072010.

**A7-25 Site-selective Doping of Transition Metal Cations into NaCo$_2$O$_4$**
NaCo2O4 shows outstandingly prospective thermoelectric properties among the oxide candidate materials in thermoelectrics. The layered crystal structure of the oxide is believed to be responsible for its highly promising thermoelectric performance. Although partial cation substitution has widely been studied, attempts appear to be limited within the similar groups of the elements; alkaline or alkaline earth cations for the Na site, and transition metal cations for the Co site. A Ni-based layered oxide LiNiO2 has essentially the same crystal structure as that of NaCo2O4, and has been studied as an active cathode material for lithium secondary batteries. It was reported that Ni cations in LiNiO2 can migrate to the Li site during charge-discharge operation, because the ionic radii of Li and Ni cations are very close (0.90 and 0.83 Å, respectively). We have investigated site-selective doping of Ni in order to experimentally explore the roles of the Na and Co sites of NaCo2O4. The selective doping is carried out changing preparation procedures of the oxide. Cation "substitution" is intended by incorporating Ni(NO3)2 into a Co-deficient starting mixture of Na2CO3 and Co3O4 prior to the first heat treatment. Cation "exchange" is, on the other hand, carried out by heating a mixture of Ni(NO3)2 and a single phase sample of NaCo2O4, which has been prepared beforehand from a stoichiometric starting mixture. Comparison with control samples without addition of Ni(NO3)2 reveals that the "substituted" sample shows a significant decrease in the thermopower with keeping the electrical conductivity almost intact, while the "exchanged" sample shows the lower electrical conductivity with leaving the thermopower unchanged. These results strongly suggest that Ni cations occupy different sites in the Ni-doped samples; disturbing Co-Co spin exchange at the Co site, and compensating holes at the Na site.

**A9-Transport properties of nanostructures within porous materials**

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Nanostructures can be obtained by confining a solid or liquid within the nanometer-sized pores of different porous materials. The advantages of such objects are connected with the possibility to produce nanostructures with different geometries (2D, 1D, 0D), with very large range of characteristic sizes (1nm-100nm), with very large total amount of nanomaterial (up to some cubic cm) and from different substances (metals, semiconductors, insulators). Quantum wires of a wide class of materials were prepared in regular set of closely packed parallel dielectric nanotubes of natural chrysotile asbestos mineral (Mg3Si2O5(OH)4) with external diameters of 30nm (this value determines the distance between the centers of neighbour nanochannels), and with internal diameters of 2-10 nm depending of the origin of the mineral. A filling of the nanochannels with molten materials (Hg, Sn, In, Bi, Pb, InSb, Se, Te) under high pressure conditions (up to 15 kbars) gives the possibility of obtaining a regular systems
of parallel identical nanowires. The superconducting transitions of a complete series of such samples by the contact method were studied, and a temperature spread that is due to fluctuations which are significant for such thin elements was observed. Critical temperatures vs diameter were measured for mercury, tin and indium nanowires from 2nm to 15 nm. The resistance of metallic nanowires in a normal state increases as the temperature is lowered as \( R/kT = 3/2 \) (1 < \( T < 60 \)K). Such temperature dependence is interpreted as demonstration of weak localization in one-dimension. Electrical resistance and thermopower of nanowires (diameters 5-1 nm) from semiconductors (InSb, Te) demonstrated behavior different from bulk materials that cannot be accounted for in terms of ordinary single-electron theories and exhibits features expected for impure Luttinger liquid.

**Acknowledgments**

*This work is supported by the Russian Foundation for Basic Research, grants 00-02-16887, 01-02-17739, and by MNTP “Physics of Solid-State Nanostructures” (99-1112).*

**A9-Thermoelectric Transport Properties of Bi Nanowires**

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An enhanced thermoelectric figure of merit, ZT, has been predicted for Bi nanowires. The enhancement is based on the sharp features in the one-dimensional density of states of the nanowires, the increased boundary scattering of phonons which results in a lowered thermal conductivity, and the semimetal-semiconductor transition. Transport properties are reported for Bi nanowires, which have been prepared by the filling of an alumina template with molten Bi. Lithographic processes are devised to pattern 4-point electrodes on single Bi nanowires that have been removed from the alumina template. High resistance non-ohmic contacts are attributed to a thick oxide layer formed on the surface of the nanowires. The non-linear 2-point i(V) response of these contacts is understood on the basis of a tunneling model. Techniques are developed for making ohmic contacts to single bismuth nanowires through the thick oxide coating using a focused ion beam (FIB) to sputter away the oxide and then deposit contacts. By combining the FIB techniques with electron beam lithography we achieve contacts stable from 300K to 2K for nanowires less than 100nm in diameter. Annealing in H2 and also NH3 environments is found to reduce the oxide completely. However, the high temperatures required for this annealing are not compatible with the lithographic techniques. A lithographic scheme for measuring the Seebeck coefficient of a single Bi nanowire is devised. The electronic band structure of Bi nanowires is modeled theoretically based on the quantum confinement of electrons. 4-point resistivity data on single Bi nanowires are reported and understood on the basis of the theoretical model of the quantized electronic band structure and considering the wire boundary and grain boundary scattering not present in bulk bismuth.

**Acknowledgments**
The support from MURI subcontract 0205-G-7A114-01, NSF grant DMR-01-16042, and US Navy contract N00167-92-K005 is gratefully acknowledged.

A9- Bi-Te-based thermoelectric nanoalloys and micro-modules

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Bi2Te3-based alloys are currently best-known, technologically important thermoelectric materials near room temperature. In this work, we present synthesis of nanosized Bi2Te3-based particles by a solvothermal process at 100-180 °C, and then microfabrication techniques of thermoelectric micro-modules with size of micrometer order from the nanopowder synthesized.

Acknowledgments
The work is supported by National Natural Science Foundation of China, Grant No. 59825102 and 50072010.

A9- Synthesis and Thermoelectric Properties of Bi2S3 Nanobeads

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We present the results of our investigation of the synthesis, structure and thermoelectric properties of bismuth sulfide (Bi2S3) nanometer-scale particles. Particles of Bi2S3 were chemically synthesized by co-precipitation from organometallic precursors of bismuth and sulfur in a high-temperature organic solution. Including additional capping and stabilizing organic molecules in the solution controls the particle growth and prevents aggregation of the nanoparticles. We are able to produce elongated nanoparticles with an aspect ratio of ~ 5, typically ~10 nm wide and ~50 nm long. Characterization by x-ray diffraction and electron microscopy shows that the nanoparticles exist in a single orthorhombic phase and possess high crystallinity. Optical absorption data show a shift of the band gap to higher energies due to confinement of the carriers. Thermoelectric properties of sintered films formed from the bismuth sulfide nanoparticle colloids were also measured and will be discussed in comparison to commercial, bulk bismuth sulfide materials.

Acknowledgments
This work is supported by the U. S. Defense Advanced Research Projects Agency through Army Research Office Grant No. DAAD19-99-1-0001.

A9- Using Optical Measurements to Improve Electronic Models of Bismuth Nanowires
When a porous anodic alumina template is filled with bismuth, the bismuth forms a self-assembled array of aligned single crystalline nanowires. The bismuth nanowires are quantum confined in two dimensions and hence are one-dimensional conductors. The quantum confinement in the nanowires cause subbands in the electronic band structure to form. Each subband forms a singularity in the density of states. This singularity enhances the Seebeck coefficient without decreasing the electrical conductivity, and thus relaxes the trade-off between a high conductivity and a high Seebeck coefficient which is usually found in bulk materials. However, the theoretical models for the bismuth electronic structure are accurate only to 0.1 - 0.01 eV. Since critical features in the electronic band structure (ex. band gap, band overlap) are on the order of 10s of meV, first principles theoretical calculations are not precise enough to accurately simulate the electronic structure of bismuth nanowires. In addition, experimental values of the band parameters, especially at room temperature, are poorly established. Therefore, theoretical models for the thermoelectric properties of bismuth nanowires have limited accuracy. This research seeks to quantitatively measure the effects of quantum confinement in bismuth nanowires as a way to refine these electronic models. Once refined, these models can be used to find the nanowire diameter, doping concentration, and doping type that will give the largest enhancement in the thermoelectric figure of merit.

Acknowledgments
This work is supported by MURI subcontract 0205-G-7A114-01, NSF grant DMR-98-04734, and US Navy contract N00167-92-K005

A9- Experimental Investigation of Thermoelectric Properties of Bi1-xSbx Nanowire Arrays

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Bi1-xSbx alloy nanowires constitute a promising 1D system for thermoelectric applications. Bi has numerous favorable transport properties, such as small electron effective masses and high carrier mobilities, and the band structure is highly tunable when alloyed with Sb, where the band structure engineering concept can be readily implemented to optimize ZT. The Bi1-xSbx nanowire arrays are fabricated by a template-assisted approach within anodic alumina membranes. Seebeck coefficient measurements of these nanowire arrays show enhanced Seebeck coefficients compared to bulk Bi both as a result of Sb alloying and of a reduction in wire diameter. The resistance of Bi1-xSbx nanowire arrays shows an unusual trend as the Sb content varies, which is attributed to the unique wire-dependent semimetal-to-semiconductor transition in Bi-related systems. These experimental results will be discussed and compared with our modeling calculations.

Acknowledgments
This work is supported by MURI/UCLA subcontract 0205-G-BBBB853, NSF Grant DMR-01-16042, US Navy Contract N00167-98-K0024, and DARPA-HERETIC/Caltech-JPL Contract number 1237157.

**A9- Peculiarities of Size Effect Manifestation in Thermopower and Resistance at Electron Topologic Transitions Induced by Doping And Elastic Stretch in Bismuth Based Nanowires.**

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In the present work, by elastic stretch, electron topologic transitions (ETT) of different kinds were realized in nanowires of pure and doped bismuth, and anomalies accompanying them in kinetic characteristics (thermopower and resistance) were investigated. In the nondoped state the size effect in thermopower of pure bismuth wires was shown in sign inversion (from (-) to (+)) in the temperature range 80-150 K and formation of positive maximum achieving the maximum value for wires with minimal diameter (100 nm). At the ETT caused by stretch the sign inversion occurs again, from (+) to (-) in this case. The thermopower maximum value in the negative region significantly depends on wire diameter d. A combined influence of doping and deformation of bismuth wires of different diameters allowed to observe peculiarities of thermopower and resistance at different kinds of ETT in conditions of the size effect manifestation.

**Acknowledgments**

This work is support by Civilian Research and Development Foundation for the Independent States of the Former Soviet Union (CRDF) # MP2 – 3019.

**A9- Some Problems of Improvement of Thermoelectric Parameters of Bismuth and its Alloys**

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The main purpose of the present report is to pay attention to a number of the most important problems to be solved for increasing thermoelectric of bismuth based structures.

Due to concentration and temperature anomaly in behaviour of thermopower S in bismuth and bismuth-antimony alloys under strong doping with donor and acceptor impurities, it is difficult to find conditions for increasing and optimization of thermoelectric parameters, especially alloys and structures for p-branch.
In bismuth and bismuth-antimony alloys due to low density of states of the charge carriers in actual energy extremes, even relatively low concentration of impurities can lead to an appreciable “local” deformation of the Fermi surface topology. In totality these factors determine the upper limit of possibility to improve thermoelectric parameters of bismuth and bismuth-antimony alloys under direct doping with donor and acceptor impurities.

In bismuth based structures with limited dimensions at rather low temperatures the thermopower has positive sign and achieves its maximum value up to $S_{100}$ V/K. Under optimal doping with acceptor impurities it is possible to increase thermoefficiency $Zp$ almost by an order in narrow temperature interval. However, it is insufficient for practical purposes.

Acknowledgments
This work is supported by Civilian Research and Development Foundation for the Independent States of the Former Soviet Union (CRDF) # MP2 – 3019.

A9-20 Segmented Nanowires: a theoretical study of thermoelectric properties
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Low-dimensional systems, such as quantum wires and superlattices, have attracted extensive attention as promising thermoelectric materials due to their expected superior performance relative to their bulk counterparts. Here we propose a novel nanostructure for thermoelectric applications by combining the advantages of both superlattices and nanowires. This new structure is a segmented nanowire consisting of a series of interlaced nanodots of two different materials. Segmented wires have been fabricated by electrochemical deposition and, more recently, by chemical vapor growth. The additional interfaces between the nanodots can reduce the thermal conductivity significantly by limiting the phonon mean free path, while the electronic motion of the carriers along the wire is not as strongly perturbed. Furthermore, this artificial periodic structure alters the dispersion relations along the wire axis, causing the formation of subbands with enhanced density of states near the band edges, thus leading to an increase in thermopower. We will present a generalized theoretical model for the thermoelectric-related transport properties of segmented nanowires. The model will then be applied to segmented nanowires consisting of Bi/Bi$_{1-x}$Sb$_x$ and lead salts to predict their thermoelectric performance in relation to their 1D alloy nanowire counterparts.

Acknowledgments
This work is supported by MURI/UCLA subcontract 0205-G-BBBB853, NSF Grant DMR-01-16042, US Navy Contract Noo167-98-K0024, and DARPA-HERETIC/Caltech-JPL Contract number 1237157.

A9-21 Solvothermal synthesis of SnTe nano-particles and nanowires
In this work, SnTe nano-particles and nanowires were synthesized by a solvothermal process based on the reaction between SnCl2, Te, KOH and KBH4 in N,N-dimethylformamide (DMF) at 100-180 °C for 24 h. KBH4 was used as the reductant. The products were characterized by X-ray diffraction and transmission electron microscopy (TEM). The particles are nearly spherical with sizes of 20-40 nm, and the diameters of the SnTe nanowires range from 60 to 150 nm and the lengths above 1 μm. The mechanism of SnTe nanoparticles and nanowires in this solvothermal process is proposed.

Acknowledgments
This work is supported by the National Natural Science Foundation of China under grant No. 50072010 and 59825102.

A9-22 Thermal Diffusivity Characterization of Bi and Bi2Te3 Nanowires Array in a-Al2O3 Matrix


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Thermal diffusivity characterization has been carried out for Bi nanowires with diameter of 40 nm and Bi2Te3 nanowires with diameters of respectively 40nm and 150nm, embedded in amorphous aluminum oxide templates. The nanowires are highly ordered and oriented parallel to each other. The porosity of the template varies from 16% and 30% for the 40nm channels and 40% for the 150nm channels. The thermal diffusivity measurements of the composite materials were performed along the nanowires axis using a transient thermal characterization technique and one-dimensional heat conduction model. The measured thermal diffusivity of the Bi based composite is 1.18x10-6m2s-1. The measured thermal diffusivities of the 40nm and 150nm Bi2Te3 based composites are 5.7x10-7m2s-1, respectively 5.6x10-7m2s-1. The measured thermal diffusivities of the composite materials are relatively lower than the predicted values based on bulk/ solid properties and volume ratio of Bi or Bi2Te3 and alumina.

Acknowledgments
This work is supported by the D.O.D.-MURI on Low Dimensional Thermoelectrics and D.O.E. grant #6893309.

A9-23 Large Thermopower in Tensile-Strained Bismuth Wires
We report an investigation of the influence of uniaxial deformation \( \lambda = (L - L_0)/L_0 \), on the thermopower \( S \), and electrical resistivity \( \rho \) of Bi wires with the diameters \( d = 0.1 - 1.0 \) _m_.

In the unstrained state (\( \lambda = 0 \)) at 80 K, the thermopower was found to be positive for wires with \( d \geq 0.8 \) _m_ and negative for thicker wires. Elongation of the 1-_m_ wire up to 2% leads to a small increase of thermopower and to 10% decrease in resistivity. Substantial strain-induced effects have been observed in the Bi wires with \( d < 0.5 \) _m_. For these wires, the magnitude of the positive thermopower decreases with increasing strain and changes sign to negative. At high strains the magnitude of the negative thermopower increases and reaches values of about -45 _V/K at \( \lambda = 2.2 \) % for the 0.3-_m_ wire and about -85 _V/K at \( \lambda = 2.6 \) % for the 0.1-_m_ wire. The latter S value represents approximately an 100% increase over the bulk value for \( _T \sim _3 \) and is comparable to that for \( _T \sim _3 \), \( S_b \sim 80 - 85 _V/K \). Note that the dependence \( S(\lambda) \) becomes greater in the region where the Fermi surface has a smaller number of connectivity components. The Fermi surface and its changes under deformation were investigated using the magnetoresistance quantum oscillations.

A9-24 Wigner Distribution Function to Evaluate the Thermoelectric Power Coefficient, \( _T \), in Nanostuctures

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By means of the Wigner distribution function for a quantum well, QW, the thermoelectric power coefficient, \( _T \), is evaluated. The calculations are based on the particle dynamics in the phase space, which allows to determine likely particle trajectories. It is observed that the thermoelectric power value is strongly affected by the height and width of the QW. These parameters are not significant for bulk materials and when it is computed by the Fermi Dirac distribution function or when it is computed by means of the envelope function method. Results are sketched numerically taking into account the QW parameters.

Acknowledgments

This work is supported by Science Faculty, Pontificia Universidad Javeriana, with project “Elipsometry”

A9-25 Temperature Dependencies of the Electric Field Effect Resistivity and Thermoelectric Properties of the Thin Bi-alloys Wires

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The temperature dependencies (4.2 – 300 K) of electrical field effect (EFE) in bismuth monocrystal wires were investigated. The cylindrical Bi crystals ranging in size from 0.1 to 3 μm with glass coating were fabricated by Ulitovsky method. All the samples were similarly oriented: the cylinder axis made an angle of 19.5° with the bisectrix axis in the bisector-trigonal plane. Owing to the coaxial geometry of our samples the highest electric field value about 107 V/cm on the surface of Bi wire was achieved.

The following important features was observed: (1) The value of EFE, _R/R0 reaches the magnitude of about 13%. (2) EFE depends nonlinearly on the gate voltage U in accordance with the theoretical prediction. (3) The value of EFE slope at U = 0 depends on temperature and diameter of the bismuth wire.

From our experiments on EFE the temperature ranges where _n > _p and _n < _p were defined.

Temperature variations the electric field dependence of the Seebeck effect of Bi-alloys wires were investigated.

Probable mechanisms of the observed effects are discussed.

Acknowledgments
This work is supported by Civilian Research and Development Foundation for the Independent States of the Former Soviet Union (CRDF) # MP2 – 3019.

A9-26 Electric and Magneto Thermoelectric Properties Bi1-xSbx Nanowires by Semiconductor-Semimetal Transition Induced by Elastic Elongation

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Search for materials with new properties stimulates development of methods for purposeful change of energy spectrum of solids. The strongest change of physical characteristics of material takes place at qualitative change of the energy spectrum at electron topological transition (ETT) such as semiconductor-metal.

In the work thin wires Bi1-xSbx obtained by the liquid phase casting in a glass coating under elastic deformations up to 2-3% relative elongation in the temperature range 42-300 K were investigated. In the nondeformed state the wires are semiconductor with minimal indirect gap and have a characteristic semiconductor dependence on T. The longitudinal magneto thermopower and magnetoresistance in the weak magnetic field significantly depended on diameter d. Under elastic stretch, the semiconductor-semimetal transition was realized, accompanied by the sample metallization. In the transition region, thermopower and resistance have peculiarities depending on wire diameter d and temperature. Estimation of figure of merit depending on wire diameter, temperature, magnetic field and constantly changing value of the gap induced by stretch was carried out.
A9-27 Arrays of Nanowires on Silicon Wafers

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Nanowires made of thermoelectric-relevant materials were grown in the pores of alumina templates fabricated on silicon wafers. This architecture combines the nanometer-scale, self-assembly nature of the anodic alumina with the micro-scale, versatile nature of the integrated circuit industry. The nanowires can be made by the pressure injection technique, and even more conveniently by electrochemical deposition. The geometry is adequate for 2-point transport measurements on the nanowire arrays, and for fabrication of nanowire-based devices made of several materials and several components. In this context, a fabrication scheme for a thermoelectric device, containing both n-type and p-type legs, will be suggested.

Acknowledgments
This work has been supported by MURI/UCLA subcontract 0205-G-BB853, NSF Grant DMR-01-16042, US Navy Contract N00167-98-K0024, and DARPA-HERETIC/Caltech-JPL Contract number 1237157

A9-28 Effect of Electron Concentration on the Thickness Dependences of the Thermoelectric Properties of PbTe Quantum Wells

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IV-VI compounds are commonly considered to be promising materials for thermoelectric applications. Recently, interest in these materials has grown due to the theoretical prediction and experimental observation of a substantial increase in ZT in IV-VI superlattices. We report here the results on the thickness dependences of the thermoelectric properties (the Seebeck coefficient, electrical conductivity, the Hall coefficient, and thermoelectric power factor P) for PbTe quantum wells (QWs) with different electron concentration n.

PbTe thin films (d = 5-250 nm) were prepared by the thermal evaporation in vacuum and deposition onto (001) KCl surfaces at 550 K. To obtain n-PbTe films with a different n, we used as a charge stoichiometric bulk PbTe and PbTe with 2 at. % excess Pb. To protect the PbTe films from oxidation, we covered them with a 30 nm EuS layer. In films with lower n, extremum values of the thermoelectric parameters in the vicinity of
50 nm are registered, P exceeding the highest values for PbTe bulk crystals. In films with higher n, the d-dependences have an oscillating character, P reaches its maximum at d \_ 100 nm and this value is higher than the maximum value of P in PbTe QWs with lower n. The non-monotonic character of the d-dependences is attributed to size quantization of electron spectra in PbTe QWs. The quantum origin of the oscillations is confirmed by the fact that an increase in n, which determines the number of populated subbands, leads to the appearance of additional extrema.

Acknowledgments
This work is supported by the U.S. Civilian Research and Development Foundation, Grant No. UE-2069.

**A9-29 Thickness dependences of the thermoelectric properties of Bi thin films**

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The prediction of a significant ZT enhancement in Bi quantum wells under decreasing Bi layer thickness d \[1\] draws attention to a detailed studying of the d-dependences of the thermoelectric properties of Bi thin films. The prediction of a significant ZT enhancement in Bi quantum wells under decreasing Bi layer thickness d \[1\] draws attention to a detailed studying of the d-dependences of the thermoelectric properties of Bi thin films. Studies are known in which oscillations in the d-dependences of the galvanomagnetic properties caused by size quantization were detected. However, there are practically no works on the d-dependences of the Seebeck coefficient or studies on films with d<30nm. The goal of the present work is to study the microstructure and thickness dependences (d =7–500nm) of the thermoelectric properties (the Seebeck coefficient S, electrical conductivity \(\sigma\), the Hall coefficient RH) of bismuth thin films prepared by thermal evaporation in vacuum and subsequent deposition onto mica substrates at 300K and 373K. In the S(d), \(\sigma\)(d), RH(d) dependences, there were observed oscillations, which were most pronounced for the films deposited on substrates at 373K. In the range of 5-10nm, corresponding to the transition from films with a channel structure to continuous films, a decrease in S with increasing d was observed. This initial decrease was followed by a sharp increase in S, and then, the dependence exhibited an oscillatory behavior. The influence of various factors, such as the temperature of measurement, the substrate temperature, aging, oxidation, etc., on the behavior of the d-dependences of the properties was studied. The observed results can be used for interpreting the properties and controlling the parameters of thin film structures with Bi as one of the constituents.


Acknowledgments
This work is supported by the U.S. Civilian Research and Development Foundation, Grant No. UE-2069.
A9-30 Seebeck coefficient of p-type PbTe/PbEuTe quantum well structures

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The thermoelectric properties of (111) oriented p-PbTe/PbEuTe quantum well (QW) structures have been investigated with the help of a realistic QW model. The electrical conductivity _ and Seebeck coefficient S were calculated using the iterative method for the solving the kinetic equations, which has been extended to include the multi-subband transport of carriers and the band anisotropy. The carrier scattering by optical and acoustical phonons has been considered. The dependencies of _ and S vs. well width d and hole concentration p were studied. It was shown that for small d=20_ the energy gap between oblique L and _ valleys vanishes and Seebeck coefficient achieves large values even at very high carrier concentration of p~10^20 cm-3. The presence of high mobility degenerate holes in the longitudinal L valley leads to a small decrease of S. The obtained values of the conductivity and thermoelectric power agree well with the experimental data in the concentration range of p<10^20 cm-3.

Acknowledgments

The work in T.U.M. and in UC-Riverside was supported by the U.S. CRDF-MRDA Grant No ME2-3010.

A9-31 Thermoelectric properties of thin semiconductor nanowires

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It is well known that quasi-one-dimensional semiconductors are perspective materials for thermoelectric applications. Unfortunately, it is difficult to produce sufficiently thin and long nanowires. Therefore, thermoelectric properties of short quantum wires (such as carbon nanotubes) or very thick wires (bismuth infiltrated into cylindrical pores of an anodic alumina template) are studied now.

We produce nanowires using the natural mineral chrysotile asbestos. It consists of thin asbestos tubes. The internal diameter of the tubes depends on a deposit of the mineral and varies from 2 to 15 nm. The length can reach 1 cm. Filling of asbestos tubes by melted Bi, InSb or Te leads to a formation of long quantum wire bundle. We have measured the temperature dependencies of resistivity and thermopower of this quantum wires and have shown that those differ considerably from corresponding dependencies of the initial bulk semiconductors.

Acknowledgments
Previous calculations for one of the half-Heusler alloys have indicated that the mean free path may sometimes be greater for phonons than for charge carriers. When this is the case it is likely that the material will display a higher thermoelectric figure of merit in the amorphous rather than the crystalline form. Here we determine the general conditions that must hold for the amorphous form to be superior. The most important quantity is undoubtedly the effective mass of the charge carriers but it appears that this quantity is unlikely to be large enough to make the free path length of the carriers sufficiently small, at room temperature, in any good thermoelectric material. On the other hand, it seems quite possible that amorphous material may be preferred for high-temperature thermoelectric generation.

In many semiconductors such as $\text{Cu}_{3}S$, $\text{Cu}_{3}Se$, $\text{Cu}_{3}Te$ semiconductors and skutterudite materials band edge states can be described well by various simple band models; one-band, two-bands, and four-bands models with the parabolic and nonparabolic nature and the anisotropic effect. Using these various band models, thermoelectric and transport properties such as Seebeck coefficient, electrical conductivity and the hole coefficient are discussed from general points of view. The energy and the number of the acceptor (+) and donor (-) impurity states together with the band parameters such as masses and band gap are the physical parameters which characterize the material. Changing these physical parameters, general properties of the thermoelectric and transport properties are calculated and are discussed. The calculation is performed with two kind of the treatment for the relaxation, i.e., the constant relaxation time approximation and the energy dependent relaxation time treatment. In the latter treatment the microscopic mechanism due to phonons and impurities is taken into account. Present method is applied to some typical thermoelectric materials.
Interfaces play a vital role in semiconductor electronics and solid-state energy conversion devices. Peltier cooling occurs at an interface due to the mismatch in the transport properties on both sides of an interface. This paper examines in detail the energy transport and conversion processes near the interfacial region. The recently established diffusion-transmission interface condition is used to couple transport at an interface consistently with the transport in the two surrounding bulk regions. Solutions for the Fermi energy, electron temperature, and phonon temperature near the interfacial region are obtained and used to interpret the energy conversion processes near a single interface.

Acknowledgments
This work is supported by DARPA HERETIC, DOD-MURI project.

**B2- Phonon and Carrier Spectrum Modification in Quantum Wires and Quantum Dot Arrays and its Effect on Thermal Conductivity**

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Arrays of semiconductor quantum dots and wires have been recently proposed for thermoelectric applications. The predicted ZT improvement in such structures should have come from the decreased lattice thermal conductivity due to additional boundary scattering and acoustic phonon spectrum modification, as well as quantum confinement of carriers with corresponding change in the density of states. At the same time the current understanding of the confined transport in such thermoelectric structures is far from complete, specifically in issues such as how carrier confinement in quantum dots leads to increase in ZT or how much of the lattice thermal conductivity drop is due to phonon spectrum modification and how much is due to boundary scattering. In this paper, we present a model for calculation of the lattice thermal conductivity in quantum wires, which uses actual phonon density of states instead of Debye approximation, and includes phonon frequency dependence in the boundary scattering treatment. We also examine electron and phonon dispersion in three-dimensional regimented Ge/Si quantum dot arrays. We argue that in order to achieve “electron transmitting – phonon blocking” regime it may be helpful to use quantum dot arrays where carrier transport is facilitated by mini-band formation, while acoustic phonons are subject to additional resonant scattering.

Acknowledgments
This work is supported in part by the U.S. CRDF-MRDA project ME2-3010 on Low-Dimensional High Performance Thermoelectric Structures and NSF CAREER Award to A.B.
B2- A Unified Wave-Particle Treatment for Phonon Transport in Superlattices

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Past studies on heat conduction in superlattices treat phonon transport in either totally coherent or totally incoherent regimes. The phonon transport in real materials should include both coherent and incoherent mechanisms. In this paper, a unified theoretical model, which considers the superlattice phonon dispersion relation, the bulk phonon dispersion relation, and interface scattering, has been developed. The phonons are rationally divided into bulk-like and superlattice-like modes according to the mean free path and the minimum number of periods required to form superlattice bands. The model results are used to explain the thermal conductivity data in both the cross-plane and in-plane directions of various superlattices, including their temperature and thickness dependencies.

Acknowledgments
This work is supported by DoD/ONR MURI on Thermoelectrics, DARPA HERETIC project.

B2- Contact Thermopowers Ordin

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The investigation of thermopower arising on a contact with a temperature drop created on it are carried out. As the basic object of study there were used p-n-junctions of the big area formed on Si-wafers. It was discovered that according to the polar symmetry of p-n-junction there arise in it longitudinal and transverse thermo-electric effects. The longitudinal thermo-electric effect corresponds to the bias of the volt-ampere characteristics of the cold diode in area of positive currents and negative voltage. At that big longitudinal thermopower (approximately 5 mV/K) are the results of exception of a bipolar diffusion. The transverse thermo-electric effect in a p-n-junction, at zero bias, has the same sign, as photoelectric force. In contrast to photoelectric force, the transverse thermopower increases at negative biases as well as at positive biases having changed its sign. The model qualitatively explaining the dependence of transverse thermopower on a bias by increase of one of currents (diffusion or drift one) is offered. It is shown that for the full description of p-n-junctions both in equilibrium and in a nonequilibrium condition, the introduction of an additional parameter which was not taken into consideration in the framework of quasistationary consideration is necessary.

B2- A Relativistic Thermoelectromagnetic Theory
A new set of dynamical thermoelectric and thermomagnetic equations will be derived from Maxwell’s Electromagnetic Theory reinforced by a Maxwell-Boltzmann-Einstein-Fermi based physical coefficients. The new set of equations is invariant to gauge transformations and coordinate transformations. This renders a set of equations that can be called “relativistic” in the most general sense. The special case of steady state reproduces the currently acknowledged phenomenological equations. The extreme special case of non-dissipative and steady state reproduces the Onsager linear system.

The absence of a rigorous dynamical theory of thermoelectric phenomena is a current fact. The guideline today is the linear response theory of Onsager, which is non-dissipative and non-generative and describes a passive transport of energy and charge in the steady state. Phenomenological equations only describe quasi-static behaviour and all new discoveries must be “patched” in. The need has arisen for a time variable thermoelectromagnetic theory with simultaneous transformation and transmission of energy, charge and momentum for real time application in both science and industry. Here is a candidate!

Acknowledgments
This work is partially supported by the Icelandic Science Research Fund (RANNIS), the Icelandic Industrial and Technological Foundation (ITI), the Icelandic Ministry of Industry and the Agricultural Productivity Fund of Iceland. Pro%Nil Systems has provided additional funding. Invaluable theoretical discussions and feedback with and from Mr. Kristjan Einarsson, M-Sci, US-Naval Forces and Mr. Sigurur Gunnarsson for philosophical input and Dr. Gunnar Benediktsson, the Royal Technical University of Stockholm (KTH) and Mr Egill Egilsson M-Sci.

B2- Modeling of the Thermoelectric Properties in Quasi-One-Dimensional Organic Semiconductors

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Thermoelectric properties, such as the electrical conductivity _σ_, thermo-power (Seebeck) coefficient S, electrical thermal conductivity _κ_e_ and the thermoelectric figure of merit ZT are theoretically determined for quasi-one-dimensional (Q1D) nondegenerate semiconductors that consist of linear conducting chains of molecules. Two main electron-phonon interaction mechanisms are considered simultaneously. One mechanism is related to the fluctuations of the electron transfer energy from one molecule to another and the second one – by the fluctuations of the polarization energy of molecules surrounding the conduction electron. It is shown that for certain values of the physical parameters the
interference between these two interaction mechanisms can occur. As a result, the relaxation time \( \tau(E) \) as a function of the carrier energy \( E \) takes the form of a Lorentzian peak. This peak can be very sharp provided that the crystal is sufficiently pure and its Q1D properties are rather pronounced. The increase of \( \tau(E) \) leads to the increase of \( \sigma \) and the sharp dependence of \( \tau(E) \) on \( E \) ensures, simultaneously, the growth of \( S \), at relatively low values of thermal conductivity. Theoretically, the values as high as \( ZT \sim 20 \) are possible in such Q1D organic semiconductors. The conditions of realization of such high-ZT quasi-1D organic semiconductors are analyzed.

Acknowledgments
This work is supported by the U.S. CRDF-MRDA project ME2-3010 on Low-Dimensional High Performance Thermoelectric Structures.

**B2- Minority-Carrier Thermoelectric Devices**

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Traditional Peltier coolers employ majority carriers within doped semiconductor regions to transport heat energy between metal contacts. An alternative approach to using such coolers in an external fashion to cool electronic devices is to optimize the thermoelectric performance of the electronic devices themselves. Recognizing that minority carriers play an important role in many electronic and optoelectronic devices, we have developed a general theory for thermoelectric effects in a p-n diode (a prototypical electronic and optoelectronic component) where diffusion of minority carriers is essential to the device's operation. Differences with the traditional Peltier effect are highlighted. It is also shown that the heat energy can be transported from the diode junction to the side contacts, producing temperature gradients within the device and internally cooling the junction. Analytic expressions for quantities such as the effective ZT are derived, as well as optimization conditions for doping, region width, and current density. Predicted heat gradients over micron-scale devices are approximately 7 degrees for InGaAs and 30 degrees for HgCdTe under optimal heat-sinking conditions. Other numerical results are given for several common material systems.

**B2-20 A Transition-State Approach to Understanding and Simulating Cooling at Semiconductor Heterojunctions**

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A semiconductor heterojunction cools when vibrational energies of the adjoining lattices are absorbed by a flux of charge carriers in transition between the dissimilar lattice structures. This system of charge carriers and lattice vibrations defines a transition state that can be expressed in terms of the occupancies of electron and phonon energy
levels at and near the interface region. The evolution of this state and any resultant cooling of the lattice are governed by conservation of energy and momentum. For example, when electrons leave one lattice region and appear in another lattice region, any changes in their aggregate energies and wavelengths are complemented by changes in the aggregate energies and wavelengths of the phonons. To simulate this process, the reported discrete model considers: the electron and phonon band structures of the lattices; the electron and phonon occupancies that determine the actual electronic-vibrational state; the role of external applied fields in supplying electrons to and removing electrons from the interface region; and the ability of the vibrational motion of the lattice to supply phonons to and remove phonons from the interface region. In this manner, the simulation can address highly nonequilibrium junction processes.

Acknowledgments
This work was supported in part by a DoD/ONR MURI Grant on Thermoelectrics (N00014-97-1-0516).

B2-21 Peculiarities of Thermoelectric Phenomena at Large Temperature Gradients

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The results of development of theory of thermoelectric phenomena at large temperature gradients are given. The results of classical thermoelectric effects at large temperature gradients are indicated. The possibilities for increasing the efficiency of energy conversion under conditions of large temperature gradients have been established. A scheme for the accomplishment of such conditions is given. A survey of the book dealing with this problem that has been published this year is presented.

B2-22 Information-Energy Theory of Thermoelectric Sensors

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Institute of Thermoelectricity

The results of creating information-energy theory of thermoelectric sensors of radiation, UHF-fields, alternating currents are given. New quality criteria of thermoelectric materials for such sensors, physical and technological methods for their optimization are found. A series of measuring instruments for metrology, production automation is developed. The relevancy of such results is high in the context of general tendencies of increasing importance of information systems.

B2-23 ROLE OF NONEQUILIBRIUM CARRIERS IN FORMING OF THERMO-E.M.F. IN BIPOLAR SEMICONDUCTORS. TWO-TEMPERATURE MODEL.

Yuri Gurevich, Georgi Logvinov, Oleg Titov, Antonio Ortiz
In [1,2] it was shown that in bipolar semiconductors and semiconductors of p-type the correct research of thermo-e.m.f. is impossible without accounting of nonequilibrium carriers of charge. In the cited papers we restricted ourselves by the one-temperature model which assumes the equality of nonequilibrium temperatures of all quasiparticles taking part in the charge and heat transport.

In the paper [3] it was obtained that recombination of nonequilibrium electrons and holes in bipolar semiconductors is changed when the two-temperature model (different electron and phonon temperatures) is used in comparison with the one-temperature approximation. It is changed also when the sample is inhomogeneous including the inhomogeneous created by the temperature field.

In the present work we report about the thermo-e.m.f. generated in the bipolar semiconductors when both temperature mismatch and nonequilibrium carriers occur. We present new general equations and the boundary conditions to them describing the process of forming thermo-e.m.f. It is obtained some special cases for thermo-e.m.f. and thermoelectric current.

References.

B-3 New original technique for the determination of ZT of PN thermoelectric couples

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In this work we use the thermoelectric coupling between Peltier and Seebeck effects to determine the ZT of a bismuth telluride thermoelectric couple. This coupling acts as thermal induction and produces a voltage drop induced by the Peltier thermal gradient in addition to the resistive voltage. In sine wave current excitation, the relative contribution of these two terms depends on electrical and thermal properties of materials as well as the current frequency. The use of a lock-in amplifier allows to separate the Peltier contribution at the current frequency from the Joule one at twice the current frequency.

We have developed two original models to simulate the electro-thermal behavior of the thermoelectric couple. The first one is based on thermal quadrupole and allows a semi analytical resolution. The second one uses an electrical simulator as SPICE.
In order to control ambient temperature and boundary conditions, we have designed a specific sample holder for such kind of measurement. An optimization procedure allows the identification of electrical and thermal conductivity and thermoelectric power. From this we can determine with a good accuracy the ZT of the couple by a simple electrical measurement, this method is suitable for lot of kind of samples.

Acknowledgments
This work is supported by the Netsu-Denshi Company Japan.

**B3- A Scanning Probe Microscopy based Measurement Tool for Thermoelectric Studies of Nanostructures**

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Enhancement of thermoelectric properties has been predicted for materials of small dimension such as nanowires and quantum dots. The evaluation and measurement of the net thermoelectric properties of nanostructure arrays can be difficult, but quantitative or comparative evaluation of individual nanostructures is particularly challenging due to their size. A scanning probe microscopy based measurement tool has been developed that incorporates sensors and structures to allow for temperature, heat flux, and electrical measurement capability. Work is being done on nanostructures such as high aspect ratio 40-300 nm diameter bismuth telluride nanowire arrays. Aspects of the probe design and thermoelectric measurements made on nanostructures will be presented as part of this work toward a quantitative tool for thermoelectric study of nanostructures.

Acknowledgments
This work is supported by the DOE and DARPA.

**B3- Measurement of Seebeck coefficient perpendicular to SiGe superlattice layers**

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Seebeck coefficient is a very important parameter to understand and evaluate the performance of thermoelectric micro coolers. However, it is very difficult to directly measure Seebeck coefficient perpendicular to thin film devices because of the difficulty
of creating a temperature gradient and measuring localized temperature and voltage change simultaneously. In this presentation, a novel method is described and it is used to measure the effective Seebeck coefficient of SiGe superlattice material perpendicular to the layers. Successful measurement was achieved by integrating a thin film metal wire as a temperature sensor and heat source on top of the SiGe superlattice micro coolers. Extensive thermoreflectance imaging characterization was performed to ensure uniform temperature distribution on top of the thin film device. Details of the experimental set-up and measurement technique will be introduced. Experimental Seebeck coefficient for various device sizes and superlattice thicknesses will be analyzed and compared. Use of the integrated heater sensor offers the possibility to measure the Seebeck coefficient in a wide temperature range down to cryogenic temperatures.

Acknowledgments
This work was supported by the DARPA HERETIC program and the Army Research Office.

B3- Measurement of Bi2Te3 Nanowire Thermal Conductivity and Seebeck Coefficient

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Theoretical predictions suggest that the thermoelectric properties of nanowires could be greatly enhanced compared with the bulk materials. To investigate these predictions, bismuth telluride nanowires are synthesized by electrodeposition into the cavities of porous alumina templates. Individual nanowires are then isolated, and subjected to measurements of both thermal conductivity and Seebeck coefficient over temperatures ranging from 10K to 300K. All measurements are made using a microfabricated device consisting of two suspended membranes with integrated heaters and resistance thermometers. Platinum films are locally deposited at the wire and the heater pad junctions to enhance the contact conductance. Results reveal that the thermal conductivity of polycrystalline Bi2Te3 nanowires is several times lower than the corresponding bulk value and the Seebeck coefficients remains within the range of the bulk value.


B3- Determination of Metal/Si Contact Temperature during Electrical Current Stressing
Interconnect reliability in very-large-scale-integrated (VLSI) circuits is a temperature-sensitive issue. However, it is extremely difficult to measure the temperature at a tiny contact using conventional methods. In this study a method of measuring contact temperature under electrical current stressing is devised using typical Kelvin test structures together with our special designed Seebeck coefficient test structures. The Ti/Si contacts on both p+-Si and n+-Si with different contact area were examined using this method. When applying a current density of 2.8 x 10^4 A/cm^2, the contact temperature is found to increase as much as by 48_C. The temperature dependence of the contact resistance and the contact temperature increase during electrical current stressing will be discussed. The impact of post-implantation annealing and silicide formation on Ti/Si contact resistance and relative Seebeck coefficients (SSi-metal) is also a subject of interest.

Acknowledgments
This work is supported by National Science Council, Grant No. NSC90-2218-E-007-067.

**B3- Thermoelectric device to measure the thermal conductivity of materials**

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A new device for the measure of the thermal conductivity has been developed. This device is very fast in taking measurements and does not need to reach the steady state to do. Therefore, it will be ideal for the quality control of thermal isolating materials.

Right now, it is being built to be able to test samples of different dimensions, ranging from 600*600 to 300*300 mm and thickness within 20 and 250 mm. The measures are taken in less than 30 minutes.

Device configuration: it consists of two plates each of them with 14 peltier pellets. Five of the 14 pellets work as Seebeck effect, that is to say, they measure the heat fluxes coming in and out the device. The other nine pellets work to reach an inside temperature, controlled by a 0.1 ºC precision PID, of 25 ºC up or below ambient temperature.

The sample is sandwiched between the two plates which provide a temperature distribution and heat flux in each side of the sample. This information is then sent to a computer which compares this information (temperature and heat flux) to that given by the numerical model previously defined. The computer continuously modifies both the thermal resistance and capacity of the sample according to the information coming from
the device in order to meet it. All the measures and calculus are automatically made and saved by the system.

The thermal inertia of the device is also considered in the numerical model so as to get more precise measurements during the transitory state. This system requires a calibration once.

In this paper this technique will be discussed and some results plotted.

**B3- A Simple And Sensitive Apparatus For Seebeck Coefficient Measurement Down To 4.2 K**

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A simple and sensitive experimental set-up for low temperature Seebeck coefficient measurement has been fabricated using copper block sandwich type technique (dc) down to 4.2 K. The system can be immersed in a conventional LN2 or helium dewar. The flexibility of the system has been demonstrated by carrying out measurements on different type of samples (Platinum, Ce3 Al, YBCO, and Metallic glass) with different geometry (wire, pellet, ingot and foil). In order to attain better stability and sensitivity, some new techniques are proposed by applying the concept isothermal zone at the junctions of Seebeck circuit (differential thermocouple junctions and copper-sample interface). The effective sample holder design helps for much easier way of sample mounting with better electrical and thermal contacts. The present techniques employed for thermocouple mounting and signal leads contact increases electrical and thermal stabilities of the system with better sensitivity and lesser thermal time constant. The system is sensitive to a change of 25 mK in gradient (YBCO with S=5 micro Volt/Kelvin). We could attain a stability of ±15 nV, ±3 mK and ±1 mK in signal, gradient and temperature respectively.

**B3-21 Rapid Evaluation System of Thermoelectric Properties in Combinatorial Thin Film Libraries**

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We have been utilizing the combinatorial method for the exploration of the thermoelectric materials, which is the way to efficiently fabricate and measure samples at high speed. This method has two important process, fabrication of libraries and rapid screening of the libraries. As for the combinatorial fabrication, we have already developed the composition-spread technique using a moving mask. Here we report on the development of a multi-channel system to measure Seebeck coefficients and resistivity with cooling system (T =50 to 350 K). This system equipped the array of 40 small-pins with springs to contact the sample. The system has the ability of measuring 4-wire
resistance and Seebeck coefficient for 10 pieces of samples on the substrate. We can make the temperature gradient (_T =0 to 3 K) of the pin-array on the two heat sinks with heaters and thermocouples. We used power factor (_S2) as the screening parameter because power factor is considered to be enough for first screening of new thermoelectric materials.

Using this system, we demonstrated rapid characterization of composition-spread libraries using combinatorial pulsed laser deposition. The performance of the screening increased remarkably compared to conventional one-by-one fabrication and measurement.

**B3-22 Improvements of on membrane method for thin-film thermal conductivity and emissivity measurement**

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In this paper, we present a numerical simulation and various test-structure configurations, which enable the Völklein method of measurement of the thermal conductivity and emissivity of thin films to be more versatile and accurate. The capabilities of the Völklein method to measure a broader range of materials are extended by using smaller membranes and accounting of the two-dimensional heat transfer in the membrane. The test-structures are adapted to be integrated in the process flow of a thin-film-based micro thermoelectric generator by putting the thermoelectric material to be measured on the top of the membrane and side by side with the heater. The measurement method is tested on various materials ranging from ceramics, metal and polycrystalline silicon. The accuracy of the measurement method is estimated by numerical simulation for various materials with different thermal conductivity and emissivity. Complementary measurements were carried out for comparison and validation.

**Acknowledgments**

This work was supported by the Jet Propulsion Laboratory (contract 1217092) and DoD/ONR MURI (N00014-97-1-0516).

**B3-23 Characteristic of thermal fatigue on thermoelectric generator with constrained Al heat sink**

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Thermoelectric generation is the direct energy conversion method from heat to electric power. The conversion method is a very useful utilization of waste energy because of its possibility using a thermal energy below 150°C.

This research objective is to establish the thermoelectric technology on an optimum system design method and efficiency, and cost effective thermoelectric element in order to extract the maximum electric power from a wasted hot water.

This paper is considered in manufacturing a thermoelectric generator and characterizing of thermal fatigue properties of thermoelectric module with constrained Al heat sink. It was found that the fatigue life of module with double constrained model was more resist than single constrained model.

**B3-24 An Application of Infrared Imaging for Thermal Conductivity Measurement of Small Sample**

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In research of novel thermoelectric materials, sometimes it is very difficult to grow homogeneous crystal which is large enough to evaluate thermoelectric transport coefficient such as Seebeck coefficient, electrical and thermal conductivity. Among the three parameters, thermal conductivity is the most difficult to evaluate at a good accuracy since the heat losses through the thermocouple wires are not negligible for small size samples.

In this study we applied high resolution infrared imaging camera (Raytheon,Radiance HS) to detect the temperature distribution in small bulk samples which had dimensions of several hundred micrometers. The measurement was performed under vacuum and a steady heat flow condition, and the thermal conductivity was quantified by using two reference samples. The measurement results on small pieces of Bi-Sb-Te (700x700x480um) and Si-Ge alloys (700x700x580um) proved that the accuracy was within 10% at room temperature when the surface was adequately treated. The application of high resolution IR camera to the thermal conductivity measurement is a practical solution to evaluate a very small sample of thermoelectric materials.

**B4- Exploring Mars-The Next Wave**

Mike Sander

Jet Propulsion Laboratory

The planet Mars has been a source of wonder for mankind for millenia. It's red beacon drifting through the sky provoked curiosity and imagination. During the last 150 years, Mars, more than any other other planet, has attracted attention from astronomers, writers, film makers and the public. As NASA's exploration of Mars intensifies and more instruments examine the planet, the new questions continue to multiply faster than the
answers. A whole new generation of rovers is being planned to deepen the study of the planet. One option for enabling this new generation of rovers includes the use of nuclear power. This talk will explore the next steps in the Mars program and the implications of long lived, in-situ rovers on the surface.

**B4- Recent Advances in Thermoelectric Power Generation**

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The development of economic thermoelectric generators for waste heat recovery has become a research focus over the past a few years. In this paper, a review is given of the insights and guidelines proposed recently in an attempt to improve the economical viability of thermoelectric generators. Novel concepts and typical examples of the recent developments in thermoelectric power generation are presented. These include high-power-density thermoelectric generating modules; symbiotic heat-and-power co-generating systems; heat-recirculating thermoelectric-combustion systems and micro-scale thermoelectric converters.

**B4- Energy Conversion Technologies for Advanced Radioisotope and Nuclear Reactor Power Systems for future Planetary Exploration**

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Future exploration of the solar system, particularly the outer most planets will depend on developing robust advanced nuclear power systems capable of providing not only electricity but also co-generation heat for thermal management of the spacecraft while in route, at destination, and for the instrumentation and science missions on board. Going beyond Mars, solar power is not an enabling option due to the weak solar isolation and the prohibitive mass and size of the solar power system. Conversely, advanced radioisotope and nuclear reactor power systems are enabling for future planetary exploration and science missions, requiring various power levels from a few mWs to tens or even hundreds of kWe. The nuclear electrical propulsion initiative announced in February 2002, to move NASA’s exploration effort from “the buggy and horse era to the railroad age” is aimed to:

(a) Develop advanced radioisotope heat sources for radioisotope power systems (RPSs) to enable deep space exploration where there is little or no solar energy, and to provide electrical and thermal powers for long duration surface and subsurface exploration missions on Mars and further away planets in the solar system; and

(b) Develop Nuclear Reactor Power Systems (NRPSs) to enable interplanetary nuclear electric propulsion missions to reduce the flight time by 50% or better, increase delivered cargo, remove dependency on gravity assist maneuvering, and facilitate multiple destination missions.
Unlike RPSs, nuclear reactor power systems could operate at different power levels and are capable of multiple restarts. They can also provide high electrical power in the order of tens to hundreds, or even thousands of kilowatts electric, both on-board and at destination, for increased data transmission rate, house keeping and science experiments while in flight, and for surface and subsurface operations at destination. RPSs and NRPSs operate typically at a source temperature of 1200 – 1300 K, however, the temperature of the heat rejection radiator and total mass of the system will depend on the type of conversion technology used.

This talk will review the recent advances in energy conversion technologies being considered for use in RPSs and NRPSs for NASA’s future missions. These include skutterudites Segmented Thermoelectric (STE), Alkali-Metal Thermal-to-Electric Conversion (AMTEC), Free Piston Stirling Engine (FPSE), and Brayton Engine. While a high conversion efficiency reduces the mass of either the radioisotope heat source or those of the nuclear reactor and radiation shield, it may result in a heavier power system because of the high mass of the converter and/or of the heat rejection radiator. Other parameters that affect the choice of the suitable conversion technologies for these power systems include redundancy, modularity, no single point failures, integration with the nuclear heat source, size and mass of the heat rejection radiator, load-following characteristics, power management and distribution requirements, and radiation hardness. These parameters for the different energy conversion technol.

**B4- Advanced Thermoelectric Power System Investigations for Light-Duty & Heavy-Duty Vehicle Applications**

Terry J. Hendricks & Jason Lustbader

NREL

Many recent exciting developments in new, next-generation thermoelectric (TE) materials has created some interesting opportunities for energy recovery and power production in light-duty and heavy-duty vehicles. The new, next-generation TE materials offer the promise of much higher performance and lower device and system cost. These new TE materials include two classes of materials being investigated by government and industry researchers, skutterudites and quantum well materials, which can be further categorized into quantum wires, quantum dots, and thin-film superlattices. This discussion will cover what new energy conversion and power production opportunities appear possible in light-duty and heavy-duty vehicles, quantify the potential power possible in light-duty and heavy-duty vehicles for different drive cycles, and show the system optimization and design tradeoff results generated to date. We will also discuss the thermoelectric system analysis software and its connection with NREL's ADVISOR vehicle analysis package.

**B4- Simulating the Thermoelectric Power Generated by a Temperature Gradient Characterized by a Non-Analytic Phonon Distribution**

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Thermoelectric energy generation can involve steep temperature gradients. When such large temperature differences occur over small distances, it may not be appropriate to use analytic (Bose-Einstein) distribution functions to characterize the phonon distributions. As a consequence, calculating the electric potential generated by the diffusion of charge carriers may be hindered by miscalculations of carrier lifetimes. Instead of relying upon equilibrium temperature distributions when calculating carrier lifetimes and mobilities, the reported effort provides an alternative solution: use the actual phonon populations to simulate electron-phonon scattering. To this end, a discrete object-oriented simulation of coupled thermoelectric transport has been constructed. Two coupled automatons, one for electrons and one for phonons, track the classical diffusion of the electrons and phonons. Coupling between these flows is provided by ‘golden rule’ quantum mechanical scattering events. These events are determined by actual phonon and electron occupancies. Averaging in time and space defines mobility, conductivity and charge flux. These outputs are properly sensitive to details of band structures, coupling strengths, and temperature gradients. Techniques used in this simulation are applicable: to simulating thermopower generation modules; and to understanding and predicting degraded performance of electronic and optoelectronic devices operating under high thermal loads.

Acknowledgments
This work was supported in part by a DoD/ONR MURI Grant on Thermoelectrics (N00014-97-1-0516).

B4- Solar Thermoelectric Generators based on Advanced Thermoelectric Materials

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During past years, considerable efforts have been spent to identify new classes of thermoelectric materials with better characteristics as compared to established thermoelectric materials. Among the most promising materials discovered, compounds with the skutterudite structure have received a particular attention. N- and p-type materials have been synthesized and measured with higher figures-of-merit than the more standard Si-Ge based alloys, making them very attractive for high temperature applications. In this communication, we report on the use of these advanced thermoelectric materials in a solar thermoelectric generator (STG). The performance, dimensions and weight characteristics of different STG designs, obtained from theoretical simulations, are presented in detail. The design has been optimised for an operation at a distance of 0.45 AU from the Sun and to produce a minimum of 400 W of electrical power. It is shown that the skutterudite-based STGs could be used advantageously as primary or auxiliary power source for spacecraft in near Sun missions.

Acknowledgments
This work was supported by ESTEC/ESA, contract N° 15071/01/NL/PA.

**B4- Numerical Modeling of Diode-like Structures for Energy Conversion**

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Numerical model for diode-like structures used for energy conversion was developed on the basis of extended Boltzmann equation. The model included energy-dependent relaxation time. Abrupt junctions model for injected current gives non-trivial results. Experimental results track model predictions. Comparison with material thermoelectric performance and model predictions for existing and future experiments will be discussed.

**Acknowledgments**

This work is partially supported by the U.S. Defense Advanced Research Projects Agency.

**B4- Optimization of Segmented Thermoelectric for Maximizing Conversion Efficiency and Electric Power Density**

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Segmented Thermoelectric Unicouples (STUs) are being considered for terrestrial and space electric power generations at different hot and cold side temperatures. For high temperatures (> 700 K), skutterudite alloys have been developed at the Jet Propulsion Laboratory (JPL) in Pasadena, CA, with ZT ranging from ~0.92 to 1.48 for temperatures up to 973 K. In addition, a number of STUs have been fabricated using p-type CeFe4CoSb12, and Bi2Te3-based alloys and n-type CoSb3 and Bi2Te3-based alloys, and tested at cold and hot side temperatures of 300 K and up to 970 K, respectively, demonstrating conversion efficiency to date of ~ 10%. The thermoelectric materials of the segments in the n- and p-legs of STUs, each has highest ZT within a certain temperature range. Therefore, not only the cross-sectional areas of the legs, but also the number and the lengths of the segments in both the n- and p-legs need to be optimized. Such an optimization could be for maximizing the conversion efficiency or for maximizing the electric power density. In this work, a global optimization methodology is developed for optimizing the dimensions of the segments in n- and p-legs of STUs. This methodology is coupled to a 1-D analytical model of STUs that is capable of handling up to five segments in each of the n- and p-legs. For a specified hot and cold side temperatures and the proper selection of thermoelectric materials, the lengths of the segments as well as the values of the interfacial temperatures in the n- and p-legs are calculated, for either optimizing the conversion efficiency or the electric power density of
the STUs. The calculated results also include the axial temperature distribution in the various segments in the n- and p-legs, the terminal voltage, optimum conversion efficiency, electric power output, and input and rejected thermal powers or heat fluxes, as functions of operating current. Results indicate that for hot and cold side temperatures of 973 K and 300 K, respectively, when optimizing STUs for maximizing the conversion efficiency, the interfacial temperatures between the various segments in the n- and p-legs are same as those at the intersection of the ZT curves of the thermoelectric materials in the segments. This is not the case, however, when the dimensions of the various segments and number of segments in the n- and p-legs of STUs are optimized for maximizing the electric power density. When optimizing the STUs for maximizing the power density, the interfacial temperatures could be 50-198 K lower than at the intersections of the ZT curves of the segment’s materials. For maximizing the power density, the calculated interfacial temperatures are the same as those at the intersection of the curves of the power performance parameter, _, of the thermoelectric materials of the segments in the n and p-legs. The power performance parameter curves for the different thermoelectric materials will be presented in the paper.

Acknowledgments
This work is supported by NASA Cross Enterprise Development Program, Grant No. NAG3-2543

B4-20 A Ladder Thermoelectric Parallelepiped Generator

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A thermoelectric generator is constructed from a large number of series connected parallelepipeds of some thermoelectric crystalline material. The hot and/or cold reservoir is made of some electrically conductive metal, and the fluid is to some extent conductive to the ground. This topology generates a number of small capacitors formed by two metalized parallelepiped crystal faces and the usually grounded thermal reservoir. We analyze the frequency behaviour of such a thermoelectric generator, which typically contains thousands of parallelepipeds, each generating few milliwatts.

Electronic network theory of linear circuit elements has a strong connection to the mathematics and the algebra of Polynomials in the Complex Domain. This is due to the fact that a dynamical differential equation can be Laplace transformed from the time domain into the frequency domain, and in the process, is turned into a polynomial in the complex variable “s = _ + i_”, where (\_) is the angular frequency “f = /2_” and (\_) is the dissipative (or generative) time-constant. A thermoelectric generator consisting of a large number of small crystals connected serially together can be considered as a naturally occurring network of lumped elements, and is ideally suited to network analyses in the frequency domain.

Acknowledgments
This work is partially supported by the Icelandic Science Research Fund (RANNIS), the Icelandic Industrial and Technological Foundation (ITI), the Icelandic Ministry of
B4-21 Predictions of Segmented Thermoelectric Unicouples Performance at Hot Temperatures < 873 K and a Cold Temperature of 293 K

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The different thermoelectric materials commonly used and those newly developed, each possesses a high Figure-Of-Merit or ZT within a certain temperature range. Extending the use of these materials outside their respective temperature range results in low conversion efficiency and/or low electric power density. In order to achieve high conversion efficiency, Segmented Thermoelectric Unicouples (STUs) for hot side temperatures < 873 K (600 oC) and a cold side temperature of 298 K (25 oC) are being considered for a host of terrestrial applications. Examples include conversion of exhaust heat to electricity in light and heavy-duty vehicles and trucks and in armed personnel vehicles, and electrical power generation in undersea and marine vessels, in remote areas, and for environmental sensors. The n- and p-legs of STUs are made up of a number of segments of different thermoelectric materials. These materials have the highest ZT within the operating temperature difference of interest for each segment. Other consideration in selecting the appropriate thermoelectric materials of the segments are chemical and mechanical compatibility with minimal interfacial resistances and minimal or no mass diffusion across the common interfaces. Although the appropriate materials of the different segments could be easily identified for an exiting database, the dimensions and number of segments as well as the interfacial temperature of the segments need to be optimized. In this paper, three STUs are optimized for maximizing the conversion efficiency and the electrical power density, using a global optimization methodology described in a companion paper in this conference. The optimized STUs operate at same cold side temperature of 298 K and hot side temperatures of 873 K, 773 K and 673 K. The composition, number, and the dimensions of the segments in the n- and p-legs typically change as the hot side temperature decreased. The optimized designs and the calculated operation parameters, such as the conversion efficiency, electric power, and input and rejected thermal powers, and the interfacial temperatures, although have similar dependences on the operation current, their actual values vary with the materials database used and with the assumed contact resistance per leg. Two data sets are used in the analyses, one is credited to JPL and the other to Hi-Zi, Inc., and the contact resistance per leg is varied from zero to 150 _cm2. Preliminary results for a hot side temperature of 873 K, indicate that with a zero contact resistance, as a reference case, the STU designed to maximize the conversion efficiency has a peak efficiency of 15% versus only 13.6%, when designed to maximize the electric power density. When
the contact resistance increases to 150 __-cm2, these peak efficiencies decrease to 13.3% and 11.3%, respectively.

Acknowledgments
This work is supported by NASA Cross Enterprise Development Program, Grant No. NAG3-2543.

B5- Thermoelectric QW Device
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Hi-Z is developing new thermoelectric materials that are expected to yield conversion efficiencies several times that of present day materials. Based on on-going DOE funded experimental work, Hi-Z anticipates conversion efficiencies of 20-30% at a TH of 700°C and a TC of 300°C. These materials are in early stage development for low temperature waste heat applications, plus the payoff will be in higher efficiency systems that can operate at higher temperatures.

The breakthrough that makes large increase in efficiency is made possible by the use of quantum well (QW) structures. Hi-Z has generated power and efficiency data demonstrating a QW couple efficiency of 14%. These measurements were made recently on a small couple that combined a multilayer QW of P type B4C/B9C with a QW of N type Si/SiGe. This couple operated between 70°C and 250°C and was fabricated on a 5_m Si substrate with ~ 11_m film thickness. The efficiency was calculated by dividing the power out of the couple by the power in. The 14% efficiency was obtained with no correction for an extraneous heat losses, such as the Si substrate.

B5- Energy Conversion Using Diode-like Structures
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Diode-like structures having n*/n/p doping of various semiconductors showed increased thermoelectric performance. Suspected mechanisms allowing increased performance include carrier injection from highly doped emitter (n*) with abrupt concentration profile and blocking of the ohmic return current on the collector side. Best results so far were obtained in the temperature range 500-600K and correspond to efficiencies more than 35% of ideal Carnot cycle. Experimental results for different diode designs will be discussed.

Acknowledgments
This work is partially supported by the U.S. Defense Advanced Research Projects Agency.

B5- Electron Tunneling Through Large Area Vacuum Gaps
We have obtained tunneling currents of over 10 A through the vacuum gap between conformal electrodes having area on the order of 0.1-1 mm². Large area vacuum gap is obtained using surface replication method allowing exact matching of shapes of two electrodes. We regulate vacuum gap width in the range of 30-100 Åo using piezoelectric actuators. The same actuators are used to regulate angles between the electrodes. Measured I-V characteristics show that overall current through the system could be represented as sum of tunneling current and current running through the shorts between electrodes and that tunneling current becomes dominant at distances greater than 30 Åo. Capacitance and conductance dependence on the distance between electrodes is also in good agreement with simple model of electrodes separated by vacuum gap. Such a device could be used for cooling and power generation.

B5- Non Steady-State Operation of Thermoelectric Generators

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The theory of ultrafast thermoelectric conduction has been applied to study the pulsed operation of commercially available bismuth telluride electricity generating modules. According to this theory a power output equal to that of a thermoelectric module operated under stationary conditions at matched load can be obtained with an output load below and even well below the matched impedance. Experimental work has confirmed this phenomenon. The effect of the frequency and the duration of a quasi-square pulse is studied experimentally in order to maintain the output power equal to that of a steady-state operation. Theory shows that as the electric current increases then one may be able to exceed the DC power output, but this remains to be confirmed experimentally. Various types of TE modules that exhibit this effect have been analyzed, like two Altec 1010 modules, as well as two others specially designed. The consequence is that cost per watt of electricity will decrease providing the output power is increased. A brief description of the switching device is given, with overall (thermoelectric plus electric conversion) efficiencies of operation to obtain DC and 5-20 kHz AC.

B5- The Study for Substrate Temperature effects on Thermoelectric Properties of the Amorphous Si-Ge-Au Thin Films

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We have already reported the anomalously large thermoelectric power of the Si-Ge-Au amorphous thin films. Amorphous thin films were prepared by the alternate deposition of Ge doped heavily with Au and Si in ultrahigh vacuum chamber. In this paper, we show the thermoelectric properties of amorphous Si-Ge-Au thin films deposited on the substrate at 77 K to 650 K. Substrate temperature have large effects on the thermoelectric properties and degree of crystallinity (or "degree of amorphous") of samples. The samples deposited on the substrate at 77 K have the largest thermoelectric power (up to 100 mV/K), but electrical resistivity is also largest (up to 10 ohm-m). The samples deposited on the substrate at 650 K have the thermoelectric properties, which is almost same as conventional bulk Si-Ge crystals. We intended to control the thermoelectric properties through the 'degree of amorphous' by changing the substrate temperature.

**B5- Efficiency Testing of Modules Containing Segmented Thermoelectric Couples**

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Teledyne Energy Systems

Teledyne Energy Systems has a long history of making high reliability thermoelectric generators. At the system level, modeling of the thermoelectric performance and the overall thermal balance is necessary to ensure a successful generator design. Part of this process includes predicting the performance of the completed thermoelectric module when operated at the hot and cold temperatures of interest. This paper describes efficiency measurements made on a complete module of multi-segmented thermoelectric couples. The module is a bonded assembly of 20 couples. The P-leg of the couples consists of Bi$_2$Te$_3$, TAGS and PbSnTe while the N-leg contains Bi$_2$Te$_3$ and PbTe. The construction of the module and the efficiency test setup is described. The overall system has been modeled and the predicted results are compared with measurements. Couple efficiencies of 7.9 - 9.5% were measured at various hot and cold junction temperatures. The measured data agree well with the predictions.

**B5- Development of a High Efficient Thermoelectric Stack for a Waste Exhaust Heat Recovery of Vehicles**

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Applications of a thermoelectric generator to vehicles have been recently renewed according to the desire of fuel saving and environmental issues, primarily due to advantages for a waste exhaust heat recovery. In the last couple of years, we have intensified a broad research to develop a high efficiency thermoelectric stack, which is an united system of thermoelectric modules and a heat exchanger. The developments of advanced thermoelectric materials and devices are the key to improving the practicability. The thermoelectric materials under investigation are mainly filled skutterudites
RM4Sb12 (R=Yb, Ce; M=Co, Fe, Ni). In order to maximize the conversion efficiency of the devices operating in the 350 -800K temperature range of exhaust heat gas, the p-, n-legs segmented with these skutterudites and state-of-the-art Bi2Te3 have been used to build up the devices. We could obtain valuable data showing a validity of installing the thermoelectric stack in vehicles, but much problems still remain to be solved in a practical level.

**B5- Performance of a Ground-source Thermoelectric Generator**

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This paper describes a prototype ground-source energy harvesting system using an off-the-shelf thermoelectric module to generate very small amounts of electricity from the diurnal temperature fluctuations in the air. The prototype was instrumented and measurements to characterize the performance of the device were collected over a twenty-seven day period. The average attenuation and phase lag of the ground temperature relative to the air temperature were calculated from measured temperatures. The available total temperature difference between the air and the ground, and the temperature difference available at the thermoelectric module were correlated and analyzed. Three different operating regimes were identified. From measurements, it was found that the device generated electricity at a relatively constant rate despite large changes in the weather. The majority of the generation occurred during a four-hour period in the afternoon. The thermoelectric module, while designed for a much different application, performed without any problems or performance degradation over the short test period. Direct solar insolation on the air-side heat exchanger had a significant effect on the performance of the device. It was estimated that improved matching of the thermal resistance between the heat exchangers and the thermoelectric module could increase the generation by a factor of approximately nineteen.

**Acknowledgments**

*This research was supported by the Defense Advanced Research Projects Agency and the Army Research Office, Grant No. DAAG55-98-1-0307.*

**B5- Small Thermoelectric Generators**

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Thermoelectric generators with combustion heat sources are being developed for the U. S. Army, TACOM-ARDEC, by Hi-Z Technology, Inc., for battery replacement in the field and for powering lightweight portable battery chargers. These small generators range in output power from 0.3 watts to 20 watts. The main thrust of the development
work is to demonstrate utilization of diesel or other military logistics fuel as the heat source. The thermoelectric generating modules being used operate at relatively low hot side temperatures and with modest power conversion efficiencies. Nevertheless, the concept shows potential advantage over batteries in watts per pound and watt-hours per pound, thus addressing the “battery problem” and the need for lightening the soldier's battery burden, and doing so at reasonable costs. The thermoelectric material used in this application is current state-of-the-art. However, Hi-Z is also developing advanced thermoelectric materials and devices that promise significantly improved performance in the near future.

Acknowledgments
The work reported is sponsored by the U. S. Army, Tank-Automotive and Armaments Command, Armament Research, Development & Engineering Center, Picatinny Arsenal.

**B5- Optimisation of the Thermal Regime of Thermoelectric Generators in Waste-Heat Recovery Applications**

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A thermoelectric generator is a device, which directly converts heat to electricity. These generators have been receiving renewed interest in recent years in a wide range of applications such as domestic wood heating, remote area power generation, automotive applications and power supply in interplanetary space flights. Applied as waste-heat recovery systems (WHRS), these generators can reduce fuel consumption and greenhouse gases such as carbon dioxide in stationary and mobile power plants.

The aim is to build a prototype system for a passenger car with the purpose of providing electrical power to replace or supplement the alternator. But first, estimation of the thermal contact resistances in the system and optimisation of the heat transfer surfaces of the heat source and heat sink. Manufacturers of thermoelectric elements normally quote the temperature difference across the element for optimum operation and the temperature on the hot sides for durability. The research has shown that when the thermoelectric elements are assembled four thermal contact resistances are introduced. These occur at the metal-to-metal interfaces that are filled with thermal compound. Good estimates of these resistances need to be made in order to regulate the thermal regime between the heat source (exhaust gases) and the heat sink to provide the required conditions for optimum operation of the element.

The paper will describe analytical and experimental investigation of the thermal regimes at the various interfaces in a typical thermoelectric generator assembly and present a model to estimate thermal contact resistance at these interfaces with different electrical insulators.

**B5- Fabrication and Testing of Advanced Thermoelectric Unicouple for Power Generation Applications**

J. Sakamoto, J. Snyder, and T. Caillat
**B5- On the Research and Developments of Institute of Thermoelectricity of Ukraine**

Anatychuk L.I.

Institute of Thermoelectricity

The basic results are given concerning ITE achievements in:
- theory of thermoelectric energy conversion;
- development of generalized theory of thermoelectric energy conversion;
- creation of computer methods for discovery of new thermoelement types.

The results of such discoveries, namely: acicular, layered anisotropic, gyrotropic thermoelements, are given. The advantage of such thermoelements over conventional thermocouples is demonstrated, namely, enhanced reliability and efficiency of thermoelectric modules for generators and coolers.

The results of module developments utilizing waste heat of industrial and heat engines, etc. are given.

The results of creating enhanced reliability modules for space systems, microgravitation and generator modules of space purpose are given. The results of creating enhanced reliability modules for generators used in deep space flights, development of air-conditioners for rooms and transport, generators for gas turbines of up to 800 kW power, various stand-alone generators are described. Special emphasis is given to the results of creating generators using the heat of soils, the results of creating reliability theory of thermoelectric systems are given. In the new context reliability and methods of its determination are described, concrete solutions are given to increase reliability of thermoelectric modules and systems, including other directions of thermoelectricity application, i.e. measuring technique, metrology and especially medicine for treatment of oncological diseases, etc.

**B5-22 Reliability Investigations in Thermoelectricity**

Anatychuk L.I., Luste O.J., Malyshko V.V.

Institute of Thermoelectricity

The results of development of reliability theory of thermoelectric systems are given. Contemporary reliability theory of thermoelectric systems is created. New reliability parameters and characteristics are proposed. The ways to improve considerably the reliability of sophisticated thermoelectric devices are found. Experimental information on the regularities and mechanisms of thermoelectric module degradation is obtained.

**B5-23 Thermal Generators Utilizing Heat Flows in Soils**

Anatychuk L.I., Mikityuk P.D.

Institute of Thermoelectricity
The results of research to develop theory and technology of thermal generators utilizing heat flows in soils are given. The results of creating durable sources with service life over 30 years for power supply to various independent apparatuses are obtained.

**B5-24 A Study of Heat Sink Performance in Air and Soil for Use in a Thermoelectric Energy Harvesting Device**

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A suggested application of a thermoelectric generator is to exploit the natural temperature difference between the air and the soil to generate small amounts of electrical energy. Since the conversion efficiency of even the best thermoelectric generators available is very low, the performance of the heat sinks providing the heat flow is critical. By providing a constant heat input to various heat sinks, field tests of their thermal conductances in soil and in air were performed. A prototype device without a thermoelectric generator was constructed, buried, and monitored to experimentally measure the heat flow achievable in such a system. Theoretical considerations for design and selection of improved heat sinks are also presented.

**B5-25 Comparison of Maximum Power Point Control Methods for Thermoelectric Power generator**

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When the thermoelectric module is connected to the load, its operation point is determined by the intersection of the source and the load characteristic curves. The dc bus thermoelectric modular systems and the battery-based thermoelectric power generator systems require a voltage matching interface with a maximum power tracking control or a constant voltage control, which is inserted between the thermoelectric module and the load. The constant voltage control method is usually used for the thermoelectric power generator. On the other hand, the maximum power tracking control method shows wide matching ability compare to the constant voltage control method and automatically optimizes an operating voltage. This paper describes a comparison of the controlling algorithm and the matching efficiency between two methods.

**B5-26 Fabrication and performance of an oxide thermoelectric power generator**

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A box-type thermoelectric power generation module was fabricated using polycrystalline oxide materials, -Na$_{0.70}$CoO$_2$ (p-type) and Ca$_{0.92}$La$_{0.08}$MnO$_3$ (n-type). This module (25mm x 25mm x 15mm) includes two p-n couples connected in series and supplied the maximum electric power of 7.6 mW to an external load resistance under the condition of hot side temperature, Th=345°C, and temperature difference, 281°C. The module was sufficiently tough for repeated heat cycles up to Th=345°C in air. After a continuous operation at Th=345°C for 10 days, the maximum electric power decreased by about 17% due to the increase in the internal resistance of the module.

Acknowledgments
This work is supported by Research Foundation for Materials Science.

B5-27 The design of adding heat reflective emitter coatings on the cold region of infrared thermopile
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Followed by the great development of microelectronics and micromanufacture technology, thin film thermopile sensors develop very fast. Recently, many attempts have been made to increase the output of thermopile detectors. Most of these improvements are mainly designed to decrease the sensor’s thermal conduction. In this paper, a new design of infrared thermopiles based on closed membrane with additional reflective layers is demonstrated. The thermopile fabrication process combined with MEMS technology is fully compatible with CMOS processes. The additional reflective layers, which are made by deposited metal or metal-dielectric coatings, increase the sensor’s sensitivity and detectivity by reflecting and transferring the heat absorbed in the cold region to the surrounding air. On the other hand, this design also largely improves the system reliability. It decreases the sensor’s parameters’ disturbance resulting from ambient temperature drifting, and thus improves the anti-jamming ability of the whole system. Using the system model described in this paper, we are able to calculate the sensor’s performance results, which are exactly consistent with those from experiment.

B6- Challenges in Thermal Management of Microprocessors
Ravi Mahajan
Intel Corporation

In this paper, the evolution of microprocessor power and the impact on thermal management is traced. It is shown that thermal management is rapidly becoming one of the key challenges in microprocessor packaging. The evolution of thermal solutions and the impact of technical and business
constraints is traced. It is shown that cooling of microprocessors involves technical, integration and business challenges. Current strategies and some future needs are traced. A case is made for the need to address thermal management along a number of fronts including device, package and system innovations. Some of the future areas of focus are discussed to stimulate thought among the technical community.

**B6- Thermoelectrics for Environmental Control in Automobiles**

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**B6- Use of Thermal Isolation to Improve Thermoelectric System Operating Efficiency**

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It is shown that thermal isolation of sections of individual thermoelectric elements, modules and arrays of modules can be used to progressively heat and cool a working fluid so as to increase system efficiency when compared to that of standard TE modules with isothermal hot and cold sides. Equations for performance in heating and cooling modes of operation are derived for steady state conditions with one-dimensional, temperature independent material properties. Analytical approximations with closed form solutions are given for COP in cooling and heating. The analytical results are compared with precise numerical solutions for several cases of interest. Efficiency is shown to increase up to 120% over that of conventional TE modules for certain important applications that involve cooling or heating of fluids and solids, such as air conditioning and heating and the like. Limitations of the technology are discussed. It is shown that no benefit occurs for steady state refrigeration usage. Predicted performance of air conditioning systems using thermal isolation, in combination with advanced TE materials with ZT of 2 to 3 are shown to have system efficiency comparable to that of refrigerant 134A.

**B6- Increased Thermoelectric System Thermodynamic Efficiency by Use of Convective Heat Transport**

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The thermodynamic efficiency of thermoelectric systems is shown to increase in geometries where convective heat transport can be used to effectively reduce internal heat conduction losses within the thermoelectric elements themselves. For the case of one-dimensional, temperature independent material properties exact analytic solutions are given. Equations for maximum COP and cooling power are presented, as are equations
for maximum COP in heating and maximum efficiency and power output for power generation.

Comparisons with standard thermoelectric systems show efficiency gains of 20 to 60% for certain important cooling applications. For heating, 10 to 40% gains are shown to be attainable, and for power generation benefits and gains are presented. Methods of achieving convective transport are discussed briefly, as are applications to air conditioning, heating and temperature control. Convective heat transport is shown to provide efficiency gains and other advantages in co-cycle power generation.

**B6- Classical and Modern Feedback Controllers for Thermoelectric Coolers**

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This paper is concerned with the design of feedback controllers for thermoelectric coolers. The system under consideration is modeled as follow: an aluminum block is used as the object to be cooled by the thermoelectric device. A heatsink and fan are provided to dissipate the heat removed from the aluminum block. Two temperature sensors are also provided to measure the aluminum block and heatsink temperatures.

A set of two nonlinear differential equations describing the dynamics of the system is obtained by applying the law of conservation of energy to the system. Analytical expressions defining the aluminum block and heatsink equilibrium temperatures are determined from the dynamic equations and verified by experimental measurements. All relevant system parameters are evaluated using experimental data. A small-signal linear model is developed to approximate the dynamics of the nonlinear model around neighborhoods of the equilibrium points. From the linear model, we develop the mathematical tools needed for the control design such as the state space and transfer function descriptions of the linear model.

Classical and modern feedback controllers are designed to monitor the amount of cooling provided by the thermoelectric device. The classical design is based on a variant of the PID controller. We observe that by properly adjusting the gains of the classical controller, accuracy of the order of ±10 mK can be achieved. However, as the system parameters drift from their nominal values, the classical design deteriorates. The modern controller, on the other hand, is based on the H2/H∞ robust control synthesis and proved to be robust to system parameters change.

**B6- Discreet variables obtainment that determine the behavior of a thermoelectric cell**

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Universidad Politécnica de Cataluña (UPC), Barcelona, Spain

The objective of this work is discreet variables obtainment that govern the behavior of a thermoelectric cell through a uC that it permit to implement a discreet system. It is intended, moreover, to implement a compact system that could measure coefficients so important to know the performance of the cell as the coefficient of
Seebeck. Through a discreet characterization of the thermoelectric cell is possible to simulate their behavior through an adequate software.

**B6- SOME ASPECTS OF PHASE TRANSITIONS CONTROL BY THERMOELECTRIC METHOD**

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Very small temperature change is required to reach phase transition (both for the 1st and the 2nd types). The temperature change comes to fractions or to units of degrees. In the case of the 2nd type of a phase transition there is no latent heat transfer. A thermoelectric heat pump is an ideal instrument for a temperature management of an object for phase transition control and gives a possibility to extract or to introduce very small quantities of heat. In the conditions of the thermoelectric control of phase transition the coefficient of performance and the heating coefficient reach the values much more than 1.

Three aspects discussed in the paper:

1. Possible physical problems that could be solved by the thermoelectric control of phase transitions. They are connected with the change of aggregative state of materials (the 1st type of phase transition) and with changes of resistance, optical, magnetic and dielectric behaviors of materials (the 2nd type of phase transition).

2. The thermoelectric method as an instrument for investigation of material properties near the transition point.

3. Parameters of specific thermoelectric devices for phase transition control.

**B6-19 Injection Current Internally Cooled Light Emitter**

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Heat management has an important bearing on the performance of a semiconductor laser due to the strong temperature dependencies of critical parameters such as threshold current, wavelength stability, efficiency, and lifetime. Traditionally, an external Peltier cooler is used for thermal control; however, this can be unfavorable for integration. Here we present a model for thermoelectric cooling which is internal to the device itself. By designing the heterostructure band offsets appropriately, we can create thermoelectric cooling sources in the laser's active region. This is due to the change in carriers' average transport energy as they go across heterojunctions under diffusion against built-in fields. While a conventional double heterostructure laser typically causes
thermoelectric heating at the cladding/core interface, a structure with Type-II heterointerfaces and appropriate doping can produce thermoelectric cooling near the active region without sacrificing carrier and optical confinement. Heat is thus shifted to the contact regions, where it is more readily conducted away. Through self-consistent drift-diffusion/Poisson equation simulation, we show that the cooling power of this mechanism can be similar in magnitude to other heat exchange processes in the laser, and then show that this effect can have a significant impact on the active region temperature of long-wavelength lasers such as those found in the GaInAsSb system.

**B6-20 Control in sliding manner for a thermoelectric cell**

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The technique of control in manner slide defines a commutation surface and consist in obtaining that the trajectory of the system through a commutation surface to reach a balance. In a thermoelectric system can guarantee the stability of some variable as for example the temperature in the thermoelectric cell before untimely disturbances. In this work is developed a system of control by sliding manner that guarantees the stability wished in all the state space.

**B6-21 Temperature Field Irregularity of Thermoelectric Device Elements**

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The account of irregularity of temperature fields is especially important for thermoelectric devices which are characterized by high thermal fluxes values. For this purpose the program for calculating of three-dimensional temperature fields was designed on the base of known numerical algorithms. By using this program it is possible to obtain the real values of thermal resistances of such thermoelectric devices elements as module’s ceramic plate, heat-sink base etc. In article some calculations results, including the results of ceramic plate optimization, are given.

**B7- Thermoelectric Micro Devices: Current State, Recent Developments and Future Aspects for Technological Progress and Applications**

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Due to their unique expected properties thermoelectric microdevices, thermogenerators as well as Peltier coolers, are of high demand for different applications namely for telecommunication purposes. Thus worldwide efforts are undertaken to expand the technology for thermoelectric devices into the field of typical microsystem technologies including aspects of advanced low dimensional high ZT materials. Favourite
material systems are up to now the bismuthtelluride (V-VI) compounds and the silicon/germanium (IV-IV) alloys. Recent results proof the capability to implement low dimensional material of both material systems into microsystem devices and show the possibility to adapt typical wafer based microelectronic technologies for the fabrication of thermoelectric devices even for the non CMOS bismuthtelluride related materials.

Thus this survey will present the state of the art, a summary of recent results together with the intended applications, as well as expectable technological aspects for microsystem fabrication. An attempt will be presented to compare strength and weakness of the different technological concepts.

**B7- Thin-film Superlattice Thermoelectric Devices for Power Conversion and Cooling**

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Thin-film nanostructured materials offer the potential to dramatically enhance the performance of thermoelectrics and offer new capabilities ranging from microelectronics cooling to thermochemistry-on-a-chip to miniature power sources. We have recently demonstrated a significant enhancement in thermoelectric figure-of-merit (ZT) at 300K, of about 2.4 in p-type Bi2Te3/Sb2Te3 superlattices and ~1.2 in n-type Bi2Te3/Bi2Te3-xSex superlattices.

For power conversion, it is also of interest to evaluate the ZT at higher temperatures. The ZT of the p-type superlattice material appears to increase from 2.45 at 300K to 2.92 at 400K. We will also discuss the progress in n-type Bi2Te3/Bi2Te3-xSex superlattices and our initial understanding on the reasons behind the less-than-dramatic performance of these materials compared to the p-type superlattices. We will discuss approaches to achieve an average ZT of ~2.5 with both p- and n-type superlattice couples through the temperature range of 450K to 300K, to achieve a power device conversion efficiency of 11.4% with a temperature differential of only 150oC. We have begun fabricating thin-film power device modules utilizing the p and n-type superlattice materials. We have achieved current densities in the range of 3.3A/cm2 in mini-modules with a _T across device of only 25K; bulk thermoelectric modules, for similar _T, offer 16 mA/cm2. Similarly, we have obtained an order or more larger power conversion levels with thin-film superlattice devices compared to commercial thin-film devices for similar _T. These material developments are projected to lead to thin-film power conversion device modules with an intrinsic (excluding fuel mass and other system components like thermal management) specific power in the range of 571 W/gm. This can be compared to a potentially achievable 4 W/gm using bulk modules. The thin-film devices, resulting from microelectronic processing, also allow cooling devices with ability to remove high heat-flux levels. We have obtained 32K and 40K sub-ambient cooling at 298K and 353K, respectively, in single p-type superlattice micro-thermoelements with potential localized active-cooling power densities approaching 700 W/cm2. In addition to high-performance and large cooling power densities, these thin-film microdevices are also extremely fast acting, within ~10 _sec or about a factor of 23,000 faster than bulk thermoelectric
technology. We will describe progress in p-n couple and module fabrication. We will discuss cooling module development including early demonstrations of a 2.5 cm x 3.5 cm large-area thin-film thermoelectric module with about 630 elements.

We will discuss outstanding issues such as heat removal from the heat sink towards the full exploitation of this technology for both power conversion and cooling. Our approach is to develop thermal management compatible with the concept of High-Active-Flux, Low-Input-Output-Flux device. Thermal modeling data will be presented that indicates that it is possible to couple two orders of magnitude larger active heat-flux through the thermolements, by having low packing fraction of active thermoelectric devices on a high-efficiency heat spreader. Thus, while we operate with heat flux levels in the range of 500 to 1500 W/cm² through the elements, depending on cooling or power conversion, heat flux levels in the range of 5 to 15 W/cm² are expected at the heat sink.

**B7- Thin film based thermoelectric energy conversion systems**

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Up to now thermoelectric materials used in commercial energy conversion devices like infrared sensors, Peltier-coolers or thermogenerators do not take advantage of the enormous potentials provided by low dimensional structures. Scope of this presentation is the experimental verification of the predicted increase of the thermoelectric figure of merit $Z^*T$ in low dimensional systems above values of bulk materials. Concepts for the realisation of devices using low dimensional structures based on the classical thermoelectric materials (V-VI-compounds for temperatures around 300 K (bismuthtelluride) and IV-VI-materials for temperatures up to 600 K (leadtelluride, PbTe), silicides for high temperature applications) were made. Low dimensional films of these systems are prepared and their structural and electronic transport properties are determined. An important part is the theoretical modelling of these new thin film devices. The results were used to determine the best suited geometrical dimensions and to compare the calculated device performance with the experimental results.

We will resume the preparation and thermoelectric properties of IV-VI and V-VI superlattice structures grown by molecular beam epitaxy as well as on Si-Ge SL structures grown by faced target sputtering. Concepts for the realisation of devices were developed and optimum device dimensions for thermoelectric energy converters were determined. We will report on the technological realisation and the characterisation of these novel thin film devices. A comparison of calculated and measured device characteristics will be presented. The obtained results will be discussed with respect to the rising industrial interest in high performance thermoelectric thin and thick film devices.

**Acknowledgments**

*This work is supported by the BMBF, Grant-No. 03 N2014A/5.*
B7- Development of Wafer-scale Cooling/Heating Thermoelectric Arrays using Thin-film Superlattice Devices

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Here we report on the fabrication and characterization of 2-inch wafer scale thermoelectric modules with 7 x 9 thermoelectric arrays of cooling/heating locations. These modules employ a promising thin-film thermoelectric device technology that exhibits a significant enhancement in the thermoelectric device figure of merit (ZT) at 300 K, cooling/heating power densities in excess of 100 Watts/cm², and cooling/heating response times significantly faster than bulk devices. The cooling/heating spot size is in the range of 100 square microns to a square millimeter.

In order to power and characterize these modules, we have developed a high-speed computer controlled power supply with integrated real-time infrared imaging of the micro-array. The precise current supplied to each discrete device controls the device temperature. The current control system uses an embedded high-speed microprocessor under the supervisory control of a PC running LabVIEW®. The embedded processor uses a high-speed serial link to control a dedicated current source for each device. This method of control allows the creation of individual temperature control profiles, and exploits the rapid response time of the thin-film device. Using this system, we compare the response times of bulk and thin-film devices in the same format.

We discuss the use of thermoelectric micro-array modules to provide temperature control of the chemistry in so-called “lab-on-a-chip” applications, such as DNA and Proteomic micro-arrays. Many interesting reactions are thermally sensitive, so integrated cooling/heating arrays can be used to start, control and stop the reactions with precision and consequently reduce the variability of experimental results. Independent temperature control of this type allows simultaneous experiments to be run under multiple conditions and temperatures, enriching the informational yield, and decreasing number of required experiment repetitions.

B7- Cascade Thermoelectric Micro Modules for Spot Cooling High Power Electronic Components

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Many power electronic and electro-optic components constitute high density localized heat sources. This creates a severe thermal problem during their operation. To ensure safe action and high performance of such elements, the miniature thermoelectric coolers (TECs) with compatible cooling power density have to be used. Thus the development of short-legged TECs having increased cooling capability is an important problem. Recent experiments with single-stage TECs showed that rather high performances can be retained with TE leg length down to 0.2 mm. The paper represents farther progress in this direction. Development of cascade TECs with TE leg length
below 0.5 mm is undertaken to create devices having not only enhanced cooling power density but also possessing increased attainable temperature differences. No experience existed up to now with such cascades. In addition to technological problems, a potential difficulty to obtain good performance lays in the fact that cascade TECs are much more sensitive to irreversible losses at electrical and thermal contacts than single-stage ones. Theoretical analysis of the influence of these factors is given. Estimations are made to define attainable temperature differences, when various kinds of substrates are used including Al2O3, AlN and diamond ceramics. Experimental researches are undertaken to validate theoretical predictions. The samples of two-, three- and 4-stage micro modules with TE legs 0.2 and 0.3 mm long are manufactured using AlN ceramic. The temperature differences achieved are compatible with those obtained in traditional long-legged coolers.

**B7- Electrochemically Fabricated Thermoelectric Microdevice**

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**B7- Design and Characterization of Cold Point Thermoelectric Coolers**

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We describe structured point-contact thermoelectric devices that confine the thermal gradients and electric fields at the boundaries of the cold end, and exploits the reduction of thermal conductivity at the interfaces, tunneling properties of point contacts, and the poor electron-phonon coupling at the junctions. We propose a simplified theory of quantum cold point metal-semiconductor contacts and detail the design of cold point thermoelectric coolers. Temperature and electrical measurements of prototype cold point coolers using bismuth chalcogenides in vacuum indicate doubling of the thermoelectric figure-of-merit ZT values to the range of 1.4-1.7 at room temperature. Analysis of the underlying transport effects at single point junctions using vacuum STM experiments suggest performances that could yield ZT > 3 at room temperature.

**B7- Low Temperature Thermoelectric Modules**

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Optimization of the new low temperature thermoelectric material CsBi4Te6 has been investigated. Recent progress in improving the thermoelectric properties of these materials and the development of prototype modules will be reviewed. These materials have shown very promising thermoelectric properties for cooling applications in the 100-300K range, however doping and alloying optimization is essential toward developing
high efficiency coolers. Our progress in this optimization procedure, and further developments of prototype modules will be presented along with thermoelectric measurements on the individual module legs, and performance measurements on the modules.

Acknowledgments
This work is supported by the U. S. Office of Naval Research, Grant No. N00014-01-1-0728.

**B7- Experimental Results Confirming Improved Performance of Systems Using Thermal Isolation.**

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Results are presented of a design verification study demonstrating the system efficiency increase in thermoelectric systems that utilize thermal isolation. Three devices ranging from 40 to 2500 watts of electrical input power are described. Test results for these devices are compared to the theoretical best values for conventional thermoelectric systems.

Demonstrated performance gains are at least 50% greater than the theoretical best coefficients of performance (COP) for conventional systems. Measured performance ranges from 60 to 90% of the theoretical COP for thermal isolation geometries. Loss mechanisms that reduce the performance from theoretical values are discussed.

**B7- Peltier Cooling System Utilizing Liquid Heat Exchanger Combined with Pump**

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Peltier cooling systems utilizing liquid heat transfer directly with thermoelectric modules are adopted in fridges for hotel-use, home-bar and so on. For the decrease of electric power consumption and a cost reduction, the high efficient and high capacity liquid heat exchanger in which a thermoelectric module is installed is developed. In the heat exchanger, a high efficient round thermoelectric module with 62mm in diameter is used and liquid heat transfer on the surface of the thermoelectric module is enhanced by using the rotation of impeller for liquid pumping. The cooling system utilizing the heat exchanger achieves equal cooling capacity with COP of 2.1 times in comparison with the cooling system for the conventional manifolds with three thermoelectric modules with 40mm square.

**B7- Characteristics of Peltier current lead systems for half-wave-rectified current.**

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Evaluation of Peltier current lead (PCL) was performed experimentally and numerically. Calorimetric measurements were performed at direct current (DC) mode and half-wave rectified current (HWRC) mode in the experiments. The experimental results showed the reduction of the heat leaks at both DC and HWRC mode. One dimensional heat conduction equations at thermal equilibrium were solved numerically. In the calculation for the HWRC mode, the time average method was used because the thermal behavior is slow and temperature in any parts the system are nearly constant in a cycle of HWRC. When we used the time average method, the performance of the Peltier cooling in HWRC mode was found to be reduced to be $2/\pi$ time of Seebeck coefficient for the DC mode analytically. The calculation results matched with the experimental one at low current. Furthermore, the calculation results showed that the difference between the current dependences of the heat leak in DC mode and HWRC mode are not large and that the current dependence of the temperature difference in HWRC mode are smaller than that in DC mode.

**B7- Reliability of Thermoelectric Modules Soldered to a Base Plate Undergoing Temperature Cycling**

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Installing a thermoelectric module (TEM) into a cooling assembly via soldering offers advantages over the conventional mounting method using thermal grease and screws. Soldering can reduce the assembly complexity, provide for a lower thermal interface resistance, and eliminate the need for screws that otherwise create a thermal shunt within the assembly.

However, soldering a TEM to a plate can seriously affect reliability. If the substrate of the TEM has a coefficient of thermal expansion (CTE) that is different than the base plate to which it is soldered, the substrate will distort as the assembly’s temperature is changed from the temperature at which the solder solidified. This, in turn, mechanically stresses the solder junctions within the TEM. Thus, even the act of soldering the assembly together and then returning it to room temperature can induce mechanical stresses. When subsequently temperature cycled, fatigue failure at the solder junctions can occur quickly.

Since there is little data for the reliability of soldered assemblies, a matrix of tests was implemented to determine when or if a soldered assembly can provide acceptable reliability. The variables in the tests included the physical size of the TEM, the CTE of the base plates, and the range of temperature cycles to which the assemblies were subjected. Results of these experiments have provided some very important guidelines for various combinations of TEM size, mounting plate CTE and certain relevant properties of the solder.
**B7- Thermoelectric Air Conditioner for Railways - Modifications, Results, Prospects**

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Brief review of the situation with air conditioning for railways is reported. Results of air conditioning unit modification and trials are shown. The description of basic prototype subassembly developed at RIF Corp. was presented at the XIX International Conference on Thermoelectrics. The comparison with the basic prototype and improvements, concerning hot side liquid loop modification, water-to-air heat exchanger enhancement, and thermoelectric unit structure correction, are described. Basic air conditioning subunit is of 2 kW cooling power, while overall dimensions are decreased and TE unit efficiency is increased. The results of laboratory tests and of running trials at Russian railways are reported. Economic evaluation is performed and commercial applicability for locomotive driver’s cabin air-conditioning is reported. Topical questions of air conditioner further modifications, including features of switching to heating mode, of electronic control system, various methods of external water-to-air heat exchanger efficiency enhancement, and electronic control circuit improvement, are discussed. The applicability of thermoelectric air-conditioning for the whole railway coach is suggested.

**B7- Thermoelectric Gas Cooling System with Power 150 kW, Putting into Operation Results**

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In article “Gas Cooling System with Power 150 kW”, which was represented on ICT’99, the system from more than 4000 thermoelectric modules was announced. It was designed for radioactive gas cooling from inlet temperature +55 °C till –20 °C, with rate-of-flow 800 m³/hr. Beginning from September 2001 the system operates at the Leningrad nuclear plant. Exploitation of such system significantly increases effectiveness of radioactive agents adsorption in coal adsorbers and, accordingly, allows to keep ecological environment in the region at the requested level, even by the emergency radioactive gas blowout. Article describes the main principles of cooling system design and presents basic characteristics in accordance with exploitation results.

**B7-20 Fabrication and modeling of a thermoelectric micro-generator**

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A thermoelectric micro-generator has been fabricated using compatible standard semiconductor technologies. The active material is a fine-grained polycrystalline silicon material, with the microstructure tailored to decrease the thermal conductivity while maintaining good electrical properties. A simplified analytical one-dimensional model of the micro-generator has been made to find an optimum thermoelectric film thickness and thermoelectric leg length. The optimal geometry of the micro-generator depends on the thermal properties and emissivity of the materials as well as of its working environment i.e. air or vacuum. These results have been extended to a more realistic geometry of micro-generators by a numerical model. The performance of such micro-generators is predicted for various materials and geometry combinations.

Acknowledgments
This work was supported by the Jet Propulsion Laboratory (contract 1217092) and DoD/ONR MURI (N00014-97-1-0516).

B7-21 Experimental analysis of a new heat dissipater that reduces the constriction resistance appearing in the thermoelectric refrigeration.

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As it has already been pointed out in previous works, the problem of heat flux addressing always appear in the thermoelectric applications. At the last international thermoelectric conference, held in Beijing, we theoretically presented a device capable of addressing the heat flux at the time that reducing the constriction resistance.

This work attempts to present such as device together with its experimental analysis. A comparison with the theoretical and flat plate results will also be given in order to see how well the device agrees with the theoretical predictions and how good it is compared with a flat plate.

Some details about some of the components the device consists of will also be briefly presented. With this system we intend to improve the performance of a thermoelectric module which will result in an improvement of the performance of the equipment which the device is assembled.

B7-22 Several Features in Development of Thermoelectric Systems

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Current developments in the field of Thermoelectrics at RIF Corporation, particularly, of systems for cooling air (air-to-air) and liquids (water-to-air), are reported.
The ways of enhancement of thermoelectric system performance are described. Various modes of thermoelectric module operation are considered. The significance of “smart” electronic control for thermoelectric unit is emphasized. Diverse methods of heat rejection by means of air, liquid and bi-phase heat exchangers (heat pipes) are discussed. The finned heat sink efficiency according to the structural features and to forced ventilation aspects are discussed. Several approaches are offered to achieve higher Coefficient of Performance (C.O.P.) of thermoelectric systems. Economical evaluation of said methods is given in comparison. Directions and future of subsequent research and development activities are reported.

**B7-23 Measurements of the Peltier heat at a junction between semiconductor and strongly correlated materials**


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It was suggested recently that the efficiency of a thermoelectric converter could be increased by additional thermal effects, which might appear at the interface between a semiconductor and a material with correlated electrons. Several groups of materials possessing different types of electron correlation have been synthesised. These groups include Kondo materials with a strong interaction between conduction electrons and localised magnetic moments of rare earth ions, manganites, which demonstrate strong electron-phonon interactions and high-Tc semiconductors, whose properties are explained based on either strong antiferromagnetic interactions between electrons or a bipolaron model. Thermocouples comprised of a semiconductor and strongly correlated materials have been fabricated and Peltier heat measured over a temperature range 15–330 K using two methods: a compensation method and measurement of the maximum temperature difference across the thermoelement under operating conditions. The experimental results of the Peltier heat measurement were compared to the results of calculations based upon preliminary measured temperature dependence of the Seebeck coefficient, electrical and thermal conductivity of materials as well as electrical and thermal resistance at the interfaces.

**Acknowledgments**

This work was supported by the EPSRC (UK) grant No. 04003/01.

**B7-24 Some Experimental Results on Electrical Ni/Cr Contacts onto Thermoelectric Materials**

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Ni and Ni/Cr films have been deposited by RF (1.78 MHz) magnetron sputtering method onto glass and n and p BiSb? substrates at low temperatures (<100 °C).
Adherence results were first obtained by scotch test and for the best samples also by soldering and scratch measurements. A maximum value of 120 Kgf/mm² was obtained for a Ni(300nm)/Cr(30nm) sandwich structure onto n? type material. This high value of the adherence force besides their good electrical contact properties recommends this contact structure for further testing in Peltier devices.

**B7-25 Peltier Temperature Controlling Box for Test Circuit Board**

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Peltier temperature controlling box for test circuit board is a compact warmer and cooler with an exact temperature control system. It used thermoelectric cooling modules for cooling and a thin film heater for heating, and adopted SCM for temperature control. Its controlled temperature range is -40 to +55°C the temperature controlled precision is ±0.5°. The paper introduces the design principle, configuration, temperature-control mode and the test results of the Peltier temperature controlling box detailed.