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BOOK OF ABSTRACTS

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23rd International Conference on Thermoelectrics

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Honoring H Julian Goldsmid's contributions to thermoelectrics

50 years ago, H Julian Goldsmid published – jointly with R W Douglas – his groundbreaking paper entitled:

"The use of semiconductors in thermoelectric refrigeration"

ICT2004 commemorates this momentous event and honours H Julian Goldsmid's contributions to thermoelectrics.

H Julian Goldsmid

in 1954…

in 2004…

The use of semiconductors in thermoelectric refrigeration

By H. J. Goldsmid, B.Sc., and R. W. Douglas, B.Sc., F.S.G.T., F.Inst.P., Research Laboratories, The General Electric Co. Ltd., Wembley, Middlesex

[*Paper received* 6 *July*, 1954]

In the past the possibility of thermoelectric refrigeration has been considered, but all attempts to produce a practical refrigerator have failed owing to lack of suitable thermocouple materials. In this paper it is proposed that semiconductors should be used and the factors governing their selection are discussed. It is concluded that the semiconductors should be chosen with high mean atomic weights and that they should be prepared with thermoelectric powers lying between 200 and 300 μV. $^{\circ}C^{-1}$. Preliminary experiments have led to the production of a thermocouple consisting of bismuth telluride, Bi_2Te_3, and bismuth, capable of maintaining 26° C of cooling.

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Solid Solutions of Binary Skutterudites as a Means of Reducing Lattice Thermal Conductivity

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Forming solid solutions, i.e., maximizing the influence of point defect scattering by creating large mass defect and elastic strain at the lattice sites, is a well-known approach how to enhance the thermoelectric figure of merit by lowering the lattice thermal conductivity while leaving the electronic properties substantially intact. Indeed, solid solutions are at the core of all state-of-the-art thermoelectrics. Yet, this approach has not been tried in any systematic way on a new class of promising thermoelectrics such as skutterudites. In this paper we report on measurements made on solid solutions of binary skutterudites of two kinds: $Co_{1-x}Ir_xSb_3$ and $Co(Sb_{1-x}As_x)_3$. In the former case, alloying takes place on the site of a metal atom and involves a large mass defect (M_{Co}=58.9, M_{Ir}=193). In the latter case, in addition to a substantial mass defect (M_{As}=74.9, M_{Sb}=121.8), there is also considerable strain due to the disturbance created on the delicate and sensitive environment of pnicogen rings. In both cases we were successful in preparing single phase solid solutions at least up to x = 0.1. We demonstrate significant reduction in the lattice thermal conductivity in both solid solutions and we provide analysis of the data.

Progress Status of Skutterudite-Based Segmented Thermoelectric Technology Development

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Segmented thermoelectric (STE) unicouples based on combination of state-of-the-art and skutterudite materials are currently being developed at the Jet Propulsion Laboratory (JPL) for potential integration into Advanced Radioisotope Power Systems (ARPS) to be used for future NASA deep space missions. Progress made in the fabrication, characterization, performance and lifetime testing are reported. To date, a maximum conversion efficiency of ~ 14% has been demonstrated for a unicouple operating at a hot-side temperature of 975K and a cold-side temperature of 300K. This result fully validates the predicted performance of the unicouple based on the thermoelectric properties of the materials used in the unicouple. The projected performance and benefits of Advanced Radioisotope Power Systems (ARPS) utilizing these advanced unicouples is presented and compared to state-of-the-art SiGe and PbTe-base systems that been used for a variety of NASA deep space missions. The projected system efficiency o the STE-ARPS is about 10% (~ twice that of state-of-the-art) and the specific power is 7-8 W/kg (~ twice that of state-of-the-art). Future development plans and challenges are also briefly reviewed.

Some Peculiar Features of Plastic Deformation and Diffusion Processes In Hot Extrusion of N-$Bi_2(Te,Se)_3$ and P-$(Bi,Sb)_2Te_3$

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Extrusion was effected through conical dies with high elongation ratio (k=64, 289 and 361). It has been proved that in isobaric conditions the plastic deformation rate (έ) and temperature (T) relation in lg έ - 1/T coordinates is described by Arrhenius' equation έ ~ exp(-Q/RT), where Q is apparent energy of the activation of plastic deformation, R is the Rydberg constant. Q value changes from 1.45 eV (the zone of minimal rates) to 0.79 eV (zone of maximal rates). For the investigation of the peculiarities of diffusion a combined Bi_2Te_3 and Sb_2Te_3 cylinder-shaped billet was used with a flat boundary between them, along the billet axis. Concentration curves characterizing Bi and Sb distribution in press-residue and extruded rods were obtained with a help of the MS-46 ("Cameca") device. The proportional growth of the diffusion coefficient (D) with the increase of the plastic deformation rate: D ~ έ was proved. .

Bi2Te3 Film Synthesized through a Co-reduction Method

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Thermoelectric materials aimed to thermoelectric cooling at room temperature or low temperature have attracted much attention because of their potential applications in super conductor and electronic apparatus. Recent years, thermoelectric nanostructures, quantum wells, quantum wires and quantum dots, have been proved possessing much higher thermoelectricity than bulk materials by theoretical and experimental investigations. Chalcogenides, $(Bi,Sb)_2(Se,Te)_3$, has been extensively investigated during the past 40 years because of its good thermoelectric cooling at room temperature and high ZT. For getting advanced thermoelectric materials, several groups prepared $(Bi,Sb)_2(Se,Te)_3$ films with quantum well structure by sputter or other physical methods. Although the experimental results has provided a bright foreground for preparing advanced thermoelectric materials which could be integrated in some microelectronic or superconductor devices, but the high cost and long-time process will be the great obstacle of the widely application of it. During the past decade, low-cost and timesaving chemical methods are widely used to synthesize some functional oxide film, such as ferroelectric films, ferromagnetic films and semiconductor oxide films. However, up to now, there is no report about thermoelectric film and quantum well synthesized by chemical method.

In this paper, Bi_2Te_3 film has been synthesized on silica glass substrate by a chemical-solution-co-reduction method. The film several nanometers to several hundreds nanometers in thickness grew directionally on the surface on the substrate at some special reaction conditions. X-ray diffraction (XRD), scanning electron microscope (SEM), atomic force microscope (AFM), transmission electron microscope (TEM), high resolution transmission electron microscope (HRTEM), and energy-dispersive x-ray spectroscopy (EDS) were performed to characterize the film synthesized at different condition. Formation mechanism of the film was suggested

Synthesis of Indium Doped PbTe by Powder Metallurgy

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Lead telluride based compounds are known for their favorable thermoelectric properties in the 50-600^{o}C temperature range. Indium doping offers the promise of significantly improving the thermoelectric properties of the *n*-type PbTe compounds.

The present communication puts forward the potential for achieving high thermoelectric efficiency in the In-doped *n*-type PbTe based thermoelectric compounds [1].

The experimental processing steps, involved in the use of a powder metallurgy approach for fabrication of PbTe compounds displaying a high figure of merit up to 600^{o} are currently being investigated. The preparation techniques include casting of master alloys with the desired composition, comminuting to appropriate powder particles size, cold compacting and sintering. The prepared samples are being examined by SEM, EDS, XRD and transport property measurements. The design, synthesis and characterization procedures for achieving In-doped PbTe compounds with desired compositions and the preliminary results regarding their figure of merit will be reported. The results indicate that doping with In in the 0.5 to 3 at.% range leads to the pinning of the Fermi level and thereby strongly reduces the temperature dependence of the Seebeck coefficient, yielding a broadened maximum of the thermoelectric figure of merit over a wide temperature range.

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Microstructure and Texture Development in Severely Deformed Cast p-Type Bi_2Te_3-Sb_2Te_3

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Multipass, right angle Equal Channel Angular Extrusion (ECAE) was used to severely plastically deform cast p-type Bi_2Te_3-Sb_2Te_3 to refine the microstructure and develop texture. The ranges of independent extrusion variables examined include extrusion temperature: 500°C, punch speed: 7.5–17.5 mm/min, one through four consecutive extrusion passes corresponding to strains of 1.16–4.64, and several different billet rotation schedules. The microstructure is characterized by polarized optical microscopy and SEM; texture is characterized by X-ray diffraction. The Seebeck coefficient, electrical resistivity and thermal conductivity are used to determine the thermoelectric figure of merit. The results presented include thermoelectric properties and microstructural characterization.

Effect of Interfacial Reaction on Thermoelectric Properties of Bi/Te Bilayer Thin Films

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Bismuth telluride, Bi_2Te_3, is commonly used in thermoelectric refrigeration applications due to its excellent thermoelectric properties near room temperature regime. In this study thin film forms of Bi/Te bilayer structures were prepared by a sputter deposition method and the effect of thermal aging on the thermoelectric properties of the Bi/Te composite thin films was investigated. The preliminary results show that the Seebeck coefficient changed from -40□V/K to -200 □V/K, while the resistivity increased slightly from 2.0×10^{-3} □□·cm to 2.3×10^{-3} □□·cm when the Bi/Te bilayer sample was annealed at 200°C for 12 hours. The thermal conductivity of the annealed sample was measured to be 0.9 W/m·K. The Bi-Te compound phase in the annealed Bi-Te bilayer samples was identified to be Bi_2Te_3 by x-ray diffraction technique. The dependence of the thin film deposition parameters, such as substrate temperature and process pressure on the microstructure and the thermoelectric properties of the Bi-Te bilayer thin films will also be discussed.

Transport and Magnetic Properties of Mn-Doped Bi_2Te_3 and Sb_2Te_3

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Recently, diluted magnetic semiconductors (DMSs), which are prepared by substituting transition metals into nonmagnetic semiconductors, have attracted the worldwide scientific interests because of their unique electronic and magnetic properties. V_2-VI_3 compounds such as Bi_2Te_3 and Sb_2Te_3 are good materials for thermoelectric refrigeration and power generation at room temperature**.** It was reported that Fe-doped Bi_2Te_3 had p-type conduction and ferromagnetic ordering at 12 K. We have fabricated Mn-doped Bi_2Te_3 and Sb_2Te_3 single crystals by the vertical gradient solidification method. In this talk, we will present the structural, magnetic and transport properties of $Bi_{1.98}Mn_{0.02}Te_3$ and $Sb_{1.985}Mn_{0.015}Te_3$ single crystals. From θ-2θ powder X-ray diffraction (XRD) studies, we have determined the lattice constants of $Bi_{1.98}Mn_{0.02}Te_3$ and $Sb_{1.985}Mn_{0.015}Te_3$; a = 4.395 Å, c = 30.109 Å and a = 4.251 Å, c = 30.191 Å, respectively, which are smaller than those of pure compounds due to the smaller atomic radius of Mn, indicating the Mn substitution in Bi(Sb) lattice sites. We have investigated the magnetic properties of $Bi_{1.98}Mn_{0.02}Te_3$ and $Sb_{1.985}Mn_{0.015}Te_3$ single crystals using a physical property measurement system (PPMS) (Quantum Design, Inc). Mn-doped Bi_2Te_3 and Sb_2Te_3 compounds have ferromagnetic ordering at T_C = 10 and 17 K, respectively.

Influence of Nonlinearity and Size Effects on the Efficiency of Microminiature Thermoelectric Generators

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Recently novel submicron and nano-composites started to be utilized as effective materials for thermoelectric direct energy converters. The sizes of such thermoelectric generators are comparable with microscopic characteristic lengths of charge carriers and phonons. The traditional methods of calculation of the efficiency of thermoelectric generators should be revised in the studied conditions.

In the present paper the system of equations for energy balance of electrons and phonons with electron-phonon interaction in limited samples was solved. The temperature dependences of all kinetic coefficients were taken into consideration by perturbation theory method. The size effects on the cooling length also were taken into account. Then the nonlinear density of heat flow and the efficiency of thermoelectric generators were determined. The obtained equation for efficiency transfers into classical Ioffe formula in the assumption of bulk sample. The criterion of usage of traditional formulas for efficiency of thermoelectric generators was determined. The changing of the efficiency of thermoelectric generators with real materials due to nonlinear and size effects were calculated.

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Thermoelectric Generation in Medium-Temperature Waste Heat Recovery Applications

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Waste heat recovery can serve as an effective interim strategy to reduce the growing global energy consumption that is expected to reach over 572 quadrillion kJ by the year 2015. For thermoelectrics to play a significant role in this endeavour conversion efficiencies must be markedly increased and thermal regime of waste heat recovery systems (WHRS) optimised. The paper describes the investigation of the thermal regime of a waste heat recovery system using the exhaust gases of a small-scale steam boiler as a heat source and thermoelectric generator from bismuth telluride. The variables investigated included natural gas flow rate on the hot side, water and air flow conditions on the cold side and thermal contact resistance in between. The research shows that appropriate selection of heat sink type is essential in optimising the electrical power output of the WHRS. Also, to obtain lower thermal contact resistances at the heat transfer interfaces in the system, smoother surface finishes at all contacting areas within the WHRS and higher thermal conductivities of the interface media are necessary

Environmental Impact Assessment of Thermoelectric Generation in Automotive Waste Heat Recovery Application

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On the face of it, waste heat recovery using thermoelectric heat-to-electricity conversion can serve as an effective means in reducing both the growing global energy consumption and emissions (particularly greenhouse gases). In automotive applications, this is achievable by replacing the mechanically driven alternator, for example, by a thermoelectric system thereby increasing the thermal efficiency of the engine in proportion to the thermoelectric conversion efficiency. However, this is only part of the picture. This paper investigates the overall environmental impact of replacing an alternator in a passenger sedan with a thermoelectric waste heat recovery system WHRS) by means of a "cradle to the grave" environmental Life Cycle Analysis (eLCA). The analysis shows that the reduction in greenhouse gas emissions is directly proportional to the conversion efficiency of the WHRS and inversely proportional to the energy use associated with the material extraction, generator manufacturing and product retirement (recycling, disposal). It also highlights the need for the compilation of a comprehensive environmental database on the entire life cycle of thermoelectric generators. This is essential to the promotion of thermoelectric energy conversion as a "green" energy source.

Simulation of Thermoelectric Power Generation with Cylindrical Multi-Tubes

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Electric power was evaluated in case of the thermoelectric tubes exposed to two thermal fluids. The output powers of the 6 systems were analytically deduced from heat transfer derivative equations. The results depended on the system designs such as single tube and double tubes system, in addition to Z and the fluid conditions. The output power could be maximized by controlling the tube length and tube radius because the temperature profiles and the internal resistances depend on them. The maximum output was the largest in the ideal isothermal systems. In the other realistic systems, it was the largest for the system of the counter flow with the single tube. The multiplication of thermoelectric tubes can shorten significantly the device area, although the maximum output from the multi-tubes decreases a little. For example, the double helical tubes can generate 96% output by 35% length, compared with the single tube in the counter flow.

Development of the Thermoelectric Generating Modules using Silicide and Bi-Te

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Komatsu is currently participating in the NEDO project "The Development for Advanced Thermoelectric Conversion System", which started in September 2002 and is supervised by Prof. Kajikawa. The project's mid-term target is 12% conversion efficiency in the temperature region between 30 and 580 °C until end of 2004. Finally it is aimed to achieve 15 % by end of March 2007. The final structure will be 2-stage stacked modules using Bi-Te and silicide materials. Beside the module's efficiency one of the major concerns is of course their lifetime and endurance. So relief of thermal induced stress as well as the suppression of diffusion is an indispensable subject in terms of the actual operation. Another very important topic is the reliable characterization of the modules, such as maximum output power and conversion efficiency[1)]. The presentation will be focused on the module's performance, heat cycling tests combined with Finite Element Analysis and the used characterization techniques.

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Synergistic Design of the Thermoelectric Generator with Internal-Axial-Netted TC Modules

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Thermoelectric effect is the coupling field effect between thermal conduction and electrical conduction. Therefore, toward a different heat source, the thermoelectric generator should have the corresponding coupling structure. The heat flow, the temperature difference and the electric circuit should be synergistic designed.

In this paper, the waste heat flow in exhaust-pipe is a heat source, its characteristics are analyzed, and a new gas-liquid structure of the thermoelectric generator is presented. This generator is composed of the axial netted thermocouple (TC) modules, internal multilevel conversion system and separate cold source forced hydro cooling. As a thermoelectric conversion unit, a large number of the small and thin TCs are fixed at the joints of netted wire frame. It makes the heat gas flow to touch directly with every TC on the first module, and lets the flow go through the channels to convert with other TCs on the next modules. The cold source connects to the engine's hydro cooling system and structures an electric circuit loop among its internal joints and the TC modules.

This scheme can make a great temperature difference, reduce the contact thermal resistances and requires to the thermoelectric materials, strengthen the hot exchange form and the integrated level of thermocouples. In the exhaust-pipe, multilevel that modules made of different materials are axial separately arranged and connecting with circuit. This structure can not only meet the needs of output power, but also get a compact form and a high integral efficiency.

Bismuth Telluride: 50 Years and Beyond

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It is exactly 50 years since p-type bismuth telluride was first demonstrated to be a worthwhile material for thermoelectric refrigeration. Soon afterwards, comparable n-type material was produced and a significant advance came with the introduction of the solid solutions, bismuth-antimony telluride and bismuth seleno-telluride. It was shown that a dimensionless figure of merit ZT equal to unity could be obtained. Most of the improvements since that time have been related to the processing of the material and, until recently, there has been little if any advancement in the figure of merit. However, during the past few years, the nanostructure concept has led to values of ZT substantially greater than unity for the bismuth telluride alloys. Thus, in spite of promising results from low-dimensional devices made from other compounds, bismuth telluride is still at the forefront of developments.

Will this compound still remain the best material for thermoelectric cooling in the future? There seems little doubt that any further advances will involve nanostructures, though it seems likely that those substances that show the best performance in the bulk state will remain the best choices in the low-dimensional form. Other materials, such as Bi-Sb, look very promising but there seems to be a good chance that bismuth telluride will still be used during the next half-century. In particular, its complex crystal structure and strongly anisotropic mechanical properties, which have been regarded as a handicap in the past, may well be the key to the exploitation of bismuth telluride in the future.

Formation of Nanometerscale Layers of V-VI (Bi_2Te_3 -related) Compounds Based on Amorphous Prestages

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It is commonly agreed that superlattices based on thermoelectric compounds will open the way towards outperforming material and thus towards outperforming devices compared to bulk material based devices. Due to their needed nanometer scale for the individual layers questions concerning their structural stability may arise. The stability of CVD Sb_2Te_3/Bi_2Te_3 superlattices grown on hot substrates was shown recently [1]. Also recently it was reported that starting with amorphous V-VI material grown on substrates at ambient temperature crystallise rather perfectly oriented during a post-annealing process [2]. As for reasonable micro-devices a layer thickness for the thermoelectric material of some 10µm is needed [3] also the question arise, whether it would be possible to keep the superlattice stable during the growth time-typiallly several hours at elevated temperatures- for those some 10µm thick superlattices.

To minimise Bi/Sb interdiffusion during growth, the superlattice may be deposited at ambient temperature and then be optimized by a postannealing. Here we report on studies concerning the growth, stability, and crystallisation of V-VI compounds and superlattices starting with ambient temperature deposited layers. The layers will be structurally characterised using XRD-, SEM-analysis and FT-IR. Also the dependence of thermoelectric transport properties on the postannealing process will be reported. The behaviour will be compared to a MBE-grown $(Bi_2Te_3)/(Bi,Sb)_2Te_3$ nanoscale superlattice.

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Overview and New Directions in Bulk Materials Research for Thermoelectric Power Generation

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There are presently a number of research groups investigating several different materials systems with properties that are deemed useful for thermoelectric applications. Some are studied due to their low thermal conductivity and the effort towards obtaining a PGEC, or "phonon-glass electron crystal", material. Other efforts focus on materials that exhibit high power factors. Still others focus on "engineering" metastable phases that possess properties that are distinct, if not unique, to solid-state chemistry. This paper focuses on bulk materials, and the requirements and strategies for optimization towards improved thermoelectric properties.

A New Synthesis Route to Antimonides and their Properties

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Contrary to the traditional solid-state reaction method to antimonides, such as Skutterudites, $CoSb_3$, and Zinc Antimonide, Zn_4Sb_3, using high purity and expensive elemental powders as starting materials, a wet chemical route to fine antimonides powders, using very cheap compounds as starting materials, is introduced. The composition and microstructure of the powder are characterized, and the thermoelectric properties of the powders after sintering are investigated.

Thermoelectric Properties of Porous $Dy_xFe_yCo_4Sb_{12}$

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To improve the Seebeck coefficient and reduce the thermal conductance porous $Dy_xFe_yCo_4Sb_{12}$ were fabricated by different processing. The phase and crystal structures were determined by x-ray diffraction analysis (XRD). The electric conductivity of samples was measured at 303K by the four-probe technique. The thermoelectric electromotive force (E) was measured upon applying small temperature differences ($\Delta T < 2$ □) between the both ends of the samples. The Seebeck coefficient of the samples was determined from the $E/\Delta T$. The relations between thermoelectric property and the microstructure were investigated.

Magnetic and Thermoelectric Properties of Alkaline-Earth Filled Skutterudites AT_4Sb_{12} (A = Sr, Ba and T = Fe, Ru)

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Alkaline-earth filled skutterudites AT_4Sb_{12} (A = Sr, Ba, T = Fe, Ru) have been synthesized by the spark plasma sintering method. We present the results of magnetic, transport, and specific-heat measurements. The contribution of *d* electrons of Fe and Ru atoms to these properties are studied by the comparison with those of RT_4Sb_{12} (R = La, Ce). The magnetic susceptibilities of AFe_4Sb_{12} follow the Curie-Weiss law with positive Curie-Weiss temperature indicative of itinerant magnetism of Fe 3*d* electrons. By contrast, ARu_4Sb_{12} compounds show diamagnetism. The four compounds exhibit metallic behavior in the electrical resistivity. The thermopowers of AFe_4Sb_{12} increase linearly with increasing temperature above 50 K, and reach 100 μV/K at 500 K, which value is comparable to that of $LaFe_4Sb_{12}$. The large thermopower in AFe_4Sb_{12} can be attributed to ferromagnetic fluctuations of the 3*d* electrons. The room-temperature thermal conductivities of AT_4Sb_{12} are 70 mW/Kcm, which is four times larger than those of RT_4Sb_{12}. The dimensionless figure of merits *ZT* of AFe_4Sb_{12} are 0.05 at room temperature.

Effect of Coating on the Performance of a Skutterudites-Based Segmented Thermoelectric Unicouple

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When operating at hot junction temperatures of up to 973 K (700o C), initial loss of antimony from Skutterudites-based segmented thermoelectric unicouples could be extensive, particularly in vacuum. Recent tests have shown that such a loss could reduce the unicouple performance by more than 40% compared to theoretical predictions. The application of a metallic or metaloxides coating onto the n- and p-legs near the hot junctions could reduce the antimony loss and hence, the degradation in unicouple performance. A good coating material bonds to the surface of the Skutturtides segments while minimizing the decrease in the temperature gradient along the legs and the electrical losses. The resulting effect depends on the materials properties and the thickness and length of the coating. A 3-D thermoelectric model is developed to investigate the effects of coating thickness (3-12 μm), length (3-6 mm), and materials (metallic and metal- 0xides) on the performance of Skutterudites-based segmented unicouple in which the p-leg has segments of CeFe3.5Co0.5Sb12 and Bi0.4Sb1.6Te3 and the n-leg has segments of CoSb3 and Bi2Te2.95Se0.05. This model takes advantage of the extensive meshing and computation and thermal analysis capabilities in ANSYS, finite element thermal analysis commercial software. The analysis is performed at hot and cold junction temperatures of 973 K and 300 K, respectively, for contact resistance per leg of 100 μm-cm2 and both zero and non-zero side heat losses, and accounts for the change in materials properties of the segments in the n- and p-legs with temperatures. Results indicate that the decrease in peak efficiency and peak electric power due to the application of coating could be less than a percentage point. The model predictions are compared with recent test results of a Skutterudites-based segmented thermoelectric unicouple with a sublimation suppression coating. The test is performed at the University of New Mexico vacuum facility in collaboration with the Jet Propulsion Laboratory.

Performance Tests of Coated and Uncoated Segmented Skutterudites / BiTe Thermoelectric Unicouples

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Performance tests of two segmented thermoelectric unicouples in which the p-leg has segments of $CeFe_{3.5}Co_{0.5}Sb_{12}$ and $Bi_{0.4}Sb_{1.6}Te_3$ and the n-leg has segments of $CoSb_3$ and $Bi_2Te_{2.95}Se_{0.05}$ are performed at constant hot and cold junction temperatures of ~ 973 K and 300 K, respectively, for extended periods of time. The two converters are of slightly different dimensions; one (SEP-03) with no antimony suppression coating and the second (JAN-04) has sublimation suppression coating on the n- and p-legs near the hot junction. SEP-03 is tested in argon cover gas at ~ 0.068 MPa for more than 3600 hours, while JAN-04 is tested in vacuum at ~ 1.0×10^{-6} to 6×10^{-7} torr for hundreds of hours. Results demonstrated initial peak conversion efficiencies of 13.0% to 13.8%. The electric heater power to maintain the hot junction temperature for SETP-03 is significantly higher than that for JAN-04, indicating with argon cover gas the side heat losses are higher than in vacuum. Although the argon cover gas has been very effective in suppressing the sublimation of antimony from the n- and p-legs in SEP-03, a decrease of up to 12% in the Seebeck coefficient of the converter occurred within the first 400 hours then remained almost constant for the remained of the test. In addition, the peak electrical power and conversion efficiency of SEP-03 decreased linearly with cumulative test time. JAN-04 showed almost no change in either the Seebeck coefficient nor the peak electric power and peak efficiency for hundreds of hours of cumulative testing. These results would significantly impact future decisions considering Skutterudites and segmented Skutterudites/BiTe thermoelectric converters with sublimation suppression coating in Advanced Radioisotope Power Systems (ARPSs), decreasing the amount of the $^{238}PuO_2$ fuel by > 30 % and increasing the system's specific power in W_e/kg by > 40%.

Electrical Transport Properties of NbCoSn-based Half-Heusler Alloys

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Electrical transport properties of NbCoSn lightly doped with Ti, Fe and Sb have been studied in the temperature range from 80 K to 850 K. All samples were prepared by arc melting from pure metal elements and annealed for 6 days at 1123 K in vacuum. The electrical resistivity, ρ, of NbCoSn shows metallic conduction ($d\rho/dT>0$) below 150 K, which becomes semiconductor-like behavior between 150 K and 400 K. Above 400 K, the electrical conduction of NbCoSn is metallic. Similar temperature dependence is observed for $Nb_{1-x}Ti_xCoSn$ (x=0.01, 0.02 and 0.05) and $NbCo_{1-x}Fe_xSn$ (x=0.01 and 0.02). Their ρ values appreciably increase with increasing x, particularly below 400 K. $NbCoSn_{1-x}Sb_x$ (x=0.01, 0.02 and 0.05) exhibits metallic ρ–T curve between 80 K and 850 K. In contrast to the other half-Heusler alloys, the ρ value of $NbCoSn_{1-x}Sb_x$ decreases with increasing x. All samples have negative Seebeck coefficient, S, and the absolute values of S monotonically increase with increasing temperature. Some enhancement of S on the doping is found only in $Nb_{1-x}Ti_xCoSn$ system. Relatively large power factor, $S^2/\rho=25\times10^{-4}$ W/mK^2 at 850 K, is obtained for $NbCoSn_{0.95}Sb_{0.05}$ due to the reduced ρ value.

Anomalous Electronic Thermal Conductivity in Bi-Sb: A Possible Explanation

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In previous work we have found that the electronic thermal conductivity in a polycrystalline Bi-Sb alloy appears to be far smaller than is predicted by the usual transport theory. The effect seems to exist for both doped and undoped samples. For undoped material, the Lorenz number becomes larger when the grain size is smaller but this may be due to an increase in the bipolar contribution, arising from a reduction in the ratio of the electron to hole mobility. There does not seem to be any anomaly in the thermal conductivity for single crystals of Bi-Sb, so the effect must be associated with the polycrystalline nature of our material. We note that our measurements were carried out using the Harman technique in which the thermal conductivity is obtained indirectly from the figure of merit. We show that the apparent value of the thermal conductivity can differ from the true value if the material is inhomogeneous. Inhomogeneity may arise in polycrystalline material if the thermoelectric properties are anisotropic. It is possible, then, that the observed anomaly in the electronic thermal conductivity is due to the method of measurement that was employed.

Development of a Precise Evaluation Technique for Thermoelectric Modules

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Precise evaluation techniques are needed to realize high efficiency modules for thermoelectric generation systems. Such evaluation techniques are being developed in Japan as a National Project of Development for Advanced Thermoelectric Conversion Systems supported by the Ministry of Economy, Trade and Industry (METI) and the New Energy and Industrial Technology Development Organization (NEDO). For such evaluation, two testing systems that can accurately measure both the heat flux through modules and the generated electric power were constructed. One type is based on bismuth telluride technology and has a heater temperature of around 300ºC. The other type is designed for modules working in higher temperature and thus has a maximum heater temperature of 700ºC. In both types, the heat flux was measured monitoring the temperature change of metal block and cooling water at both the high temperature and low temperature sides of the module. Based on error analysis for these evaluation techniques, we estimated the accuracy of the measurement and investigated the possibility of standardization of the evaluation techniques.

Reliability Testing of Thin-Film Superlattice Thermoelectric Devices

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We have previously reported thin-film superlattice (TFSL) thermoelectric materials with thermoelectric figure of merit (ZT) values of ~ 2.4 in p-type Bi2Te3/Sb2Te3 and ~1.4 in n-type Bi2Te3/Bi2Te3-xSex superlattices. Recently, we have obtained a ZT of ~1.22 in a p-n TFSL couple at 300K as determined by power conversion efficiencies. In the cooling mode, these devices have cooling power densities in excess of 100 Watts/cm2. As a next step, we study device reliability by industry standard methods, including power cycle testing on single TFSL couples. These relatively simple structures exhibited little change in DT after 100,000 power cycles, suggesting the intrinsic reliability of the TFSL materials under large changes in temperature gradients. This is significant, considering that the TFSL elements can thermoelectrically respond to fast current transients which are inevitable in any switching test. In contrast, bulk devices cannot adequately respond and so do not generate rapidly changing temperature gradients. A natural application of modules comprised of high efficiency TFSL couples would be for the thermal management of communication lasers. Telecordia and MIL-STD883E specifications specify the reliability requirements for such cooling modules. We examine TFSL devices when integrated into more complicated multi-couple module structures, identify potential failure modes and the access impact of integration on reliability performance.

Milliwatt Modules and Generators: Design, Fabrication, and Life Testing

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Milliwatt modules for space applications are being fabricated and life tested for long life NASA applications that use Pu 238 as the heat source. Module testing using series circuit and redundant circuitry is in progress while generator testing using vacuum baked out multifoil insulation is just being initiated. Also, a milliwatt generator design, using multilayer quantum well materials, that offer a large gain in efficiency, will be presented.

The Enhancement of ZT for AlPdRe Icosahedral Quasicrystals in Other Element Substituted or Thin Film Samples

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Electronic structure of icosahedral quasicrystals has a pseudogap near the Fermi level. The pseudogap is expected to reveal the large Seebeck coefficient, S, caused by the steep slope of density of state at the Fermi level. Furthermore, the quasicrystals have low thermal conductivity, □, because of the quasi-periodicity. In the last conference, we reported composition dependences of thermoelectric properties of ternary AlPdRe and quaternary AlPdReRu icosahedral quasicrystals, and related them to that of effective mass determined by the balance of bond strength of intra- and inter-Mackay Icosahedral clusters.

In the present study, the above discussion has been developed, and Fe substitution has been predicted and carried out. By the Fe substitution, electrical conductivity, □, increases greatly, S slightly and □ dose not change almost, in consequence ZT enhances by a factor of two. On the other hand, thermoelectric properties of the AlPdRe quasicrystalline thin films prepared by a molecular beam epitaxy have been investigated. The enhancement of ZT in the thin film by a factor of two in compared to the bulk quasicrystals has been observed also. The origins of these enhancements will be discussed.

Mechanical Alloying of $CoSb_3$

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Skutterudite $CoSb_3$ powders were produced by mechanical alloying of elemental powders using a nominal stoichiometric composition. As-mechanically alloyed powders were of metastable state. Annealing of MA powders under specific condition led to a complete phase transformation to a semiconducting δ-$CoSb_3$. Single phase bulk $CoSb_3$ were successfully produced by vacuum hot pressing with or without subsequent annealing. Phase transformations during mechanical alloying, annealing and hot pressing were systematically investigated using XRD and SEM. Thermoelectric properties as a function of temperature were evaluated for the hot pressed specimens and compared with results of analogous studies.

Increase in Power Factor of the Melt Growth P-Type $Cosb_3$ by Post Annealing and Metal Deposition

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Crystal of peritectic compound of $CoSb_3$ was grown using the vertical Bridgman method. Change in growth parameters resulted in the formation the polycrystalline $CoSb_3$ grains surrounded by Sb metal. In order to remove the excess Sb in the as-grown crystals, a post annealing was performed. Thermoelectric properties of the as-grown and post-annealed samples were measured from room temperature to 873 K. Removing of the residual Sb by the post annealing brought about a formation of void in the crystal, resulting in a increase in the Seebeck coefficient values from 40 (as-grown) to 250 to 500 □V/K (annealed). These values are higher than that of the single crystalline $CoSb_3$ that has the corresponding carrier concentration in the samples. But the samples with much higher Seebeck coefficient value exhibited lower electrical conductivity. To improve the lowered electrical conductivity, metals were deposited on the surface of the post-annealed samples. Temperature dependent thermoelectric properties for post-annealed samples showed a slight decrease in Seebeck coefficient and a considerable increase in electrical conductivity over the temperature range from RT to 773 K. This gave rise to an increase in the power factor that was one order of magnitude higher than has been reported so far.

A Model for Calculating the Figure of Merit of Pbte Based Materials over a Wide Temperature Range

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The thermoelectric figure of merit, $Z = S^2\sigma/k$, where S is the Seebeck coefficient, σ and κ, the electrical and thermal conductivities, respectively, is the measure of the thermoelectric quality of materials. Whereas the Seebeck coefficient and the electrical conductivity are determined experimentally with relative ease, accurate determination of the thermal conductivity is difficult and time-consuming. An alternative for the measurement of the thermal conductivity is determination of its value using known physical and transport properties.

Our communication describes an analytical model for calculating the thermal conductivity of thermoelectric materials using measured Seebeck coefficient and electrical conductivity data. The model was checked and calibrated for *n*-type PbI_2-doped PbTe material. We present the principles of the model, the analytical equations and the calculated thermal conductivity values for *n*-type PbI_2-doped PbTe with different dopant concentrations up to 500^{o}C.

Thermoelectric Properties on Porous $(Bi_xSb_{1-x})_2Te_3$

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Porous $(Bi_xSb_{(1-x)})_2Te_3$ were fabricated by different processing. The phase and crystal structures were determined by x-ray diffraction analysis (XRD). The electric conductivity of samples was measured at 303K by the four-probe technique. The thermoelectric electromotive force was measured upon applying small temperature differences ($\Delta T < 2$ □) between the both ends of the samples. The Seebeck coefficient of the samples was determined from the E/ ΔT. The relations between thermoelectric property and the microstructure were investigated. It was found that suitable size and amount of porous structure can improve the thermoelectric properties.

2-Dimensional Mismatch Power Loss Analysis on Thermo-Electric Power Generator Systems

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This paper describes a 2-dimensional power loss analysis on thermo-electric power generation systems. Generally, thermal sources have temperature distribution that causes the mismatch power losses in thermo-electric power generation systems. To obtain the required voltage of the load, many TEM modules should be connected in series, composing the string. When the temperature of each module is much different by temperature deviation on thermal source, each string output shows different voltage. In this case, when each string is connected in parallel, temperature distribution causes the mismatch power loss. In this paper, mismatch power losses by temperature distribution and effect by connection topology of TEMs on the thermal source were evaluated by computer simulation. In addition, the case of DC power bus system including multi DC-DC converter with MPPT (Maximum Power Point Tracker) or constant voltage control were also evaluated.

Thermoelectric Properties of Rare-Metal-Doped $CoSb_3$

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Binary skutterudite $CoSb_3$ doped with a rare-metal such as tantalum (Ta) and niobium (Nb) was prepared by the vacuum induction melting (VIM) and plasma arc melting (PAM) processes. Specimen annealed at 400□ for 24hrs maintained sound microstructure, however, considerable voids and cracks were found after annealing at above 500□. It seems to be attributed to the phase dissociation and thermal expansion due to phase transitions during annealing and cooling. Single phase δ-$CoSb_3$ was successfully obtained by annealing at 400□ for 24hrs. In the case of increasing annealing temperature, phase decompositions occurred. Doping effects on the thermoelectric properties of $CoSb_3$ will be discussed.

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Preparation and Thermoelectric Properties of $CoSb_3$

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$CoSb_3$ compounds were prepared by the arc melting and hot pressing processes and their thermoelectric properties were investigated at 300K-600K. Annealing effects were examined and they were correlated to phase transformation and homogenization. Undoped $CoSb_3$ showed p-type conduction and intrinsic semiconducting behavior at all temperatures examined. Thermoelectric properties were changed with constituent phases because γ-$CoSb_2$, β-CoSb and Sb are metallic or semimetallic phases while δ-$CoSb_3$ is semiconducting phase. Thermoelectric properties were remarkably improved by annealing in vacuum and they were closely related to phase transitions. Thermoelectric properties of the arc-melted and hot-pressed $CoSb_3$ will be discussed and compared.

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Thermoelectric Properties of $CoSb_3$ Cast under High Pressure

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Binary skutterudite $CoSb_3$ doped with a rare-metal was prepared by the squeeze casting under high pressure, and its microstructure and thermoelectric properties were investigated. Microstructure was refined with increasing pressure due to increase in the cooling rate on solidification. It is expected to increase the solubility by high pressure cast. Thermoelectric properties of the squeeze cast specimen were compared with those of the conventionally solidified specimen. Constituent phases were analyzed and phase transformations by annealing were also examined.

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Thermoelectric Properties of Directionally Solidified CoSb3

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Skutterudite compounds $CoSb_3$ were uni-directionally solidified by the Bridgeman crystal growth method.

Solidification conditions for $CoSb_3$ single crystal were investigated by changing growth velocities, temperature gradients of solid/liquid interface, and amounts of doping elements such as tantalum and niobium.

Microstructures of the obtained $CoSb_3$ crystals were characterized and thermoelectric properties were discussed in the conjunctions with solidification conditions and doping effects.

Synthesis and Structural Analysis for Zn-rich Region of $Zn_{4-x}Cd_xSb_3$ Bulk Crystals

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Recently, beta-Zn_4Sb_3 compounds have been identified as a new thermoelectric material with high figure of merit (ZT=1.3 at 670 K). Although substitution of the Cd atoms for the Zn sites is a powerful way to reduce its lattice thermal conductivity, the substitution limit has not been confirmed yet. In this study, we prepared 9 bulk crystals ~~of~~ at the Zn-rich region of $Zn_{4-x}Cd_xSb_3$ (x=0 to 2.00) using vacuum casting method without annealing. The powder XRD patterns for all samples were measured from 10 to 120 degree with a fine step (0.01 deg.) on a Rigaku RINT-2200V diffractometer. These diffraction patterns were analyzed by the Rietveld method using a multi-phases-fitting condition. All reflected peaks of the 9 samples were indexed by assuming a rhombohedral structure with the space group of R-3c as in the Zn_4Sb_3, revealing that the substitution limit of the Cd atoms for the Zn sites in the $Zn_{4-x}Cd_xSb_3$ system is x=2.00 using vacuum casting method without annealing. The relation between preparation method and the substitution limit will be discussed. In addition, the structural parameters for the whole range of the Zn-rich region of the $Zn_{4-x}Cd_xSb_3$ compounds will be presented.

Relation between Solidification Conditions and Chemical Compositions on Vacuum Casting of $CoSb_3$ Compounds

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$CoSb_3$ has been identified as a promising candidate for the thermoelectric conversion and a number of studies have been done to improve the performance. As shown in the Co-Sb phase diagram, $CoSb_3$ is an incongruent-melt compound which has a peritectic point at 1043 K. Therefore, most samples have been fabricated by sintering process using fine powder which has been prepared by quenching or mechanical alloying to prevent formation of impurity phases, $CoSb_2$ and/or CoSb. In this study, the 5 sets of pure elements of Co+3Sb at the stoichometric ratio were sealed in quartz ampoules with 0.01 MPa of high-purity He gas to ensure the heat conduction. These elements were heated at 1273 K for 20 h and solidified with different cooling rates from -400 to -4 K/h in a programmed electric furnace. The powder XRD studies were carried out to determine the quantities of impurity phases in each sample. A multi-phase-fitting condition of $CoSb_3$, $CoSb_2$, CoSb, Co and Sb was realized using the Rietveld profile fitting program RIETAN2000. Our goal is to optimize the cooling rate of the solidification process for vacuum casting method in order to synthesize single-phase $CoSb_3$ bulk crystals. The relation between solidification conditions and the chemical compositions will be reported and discussed.

Preparation and Rietveld Analysis for the Bulk Crystals of (Co, Fe, Ni)Sb_3 Compounds

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$CoSb_3$ compounds with the skutterudite structure have been recently identified as a new thermoelectric material for the intermediate temperatures. However, the thermal conductivity of $CoSb_3$ is much higher than other novel thermoelectric materials. Although filling rare-earth atoms into the cage of the skutterudite structure is a common solution to reduce the lattice thermal conductivity, substitution of Fe atoms to the Co sites is necessary to obtain filled skutterudite compounds. Therefore, the total number of electrons varies with the rare-earth filling ratio. On the other hand, substitution of the same amount of Fe and Ni atoms to the Co sites is another powerful way to reduce the lattice thermal conductivity without rare-earth filling. In this study, we prepared 11 bulk crystals of $Co_xFe_yNi_zSb_3$ (x+y+z=1, x=0 to 1, y=z) compounds using vacuum casting method with long-time annealing. The powder XRD measurements were performed both before and after annealing of the 11 samples. The Rietveld analysis was applied to refine the crystal structure and to determine the quantities of impurity phases in each sample. The refined crystal structure for (Co, Fe, Ni)Sb_3 compounds will be summarized and discussed. The relation between chemical compositions and the lattice thermal conductivity will be also discussed.

Hot Neutrons for the Investigation of Structure and Magnetism in $Eu_{1-y}Fe_4Sb_{12}$

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Novel types of Skutterudites are of large interest for thermoelectric applications. An important design feature of these open cage systems is the amount of filling with heavy elements such as rare earths. This filling leads to additional scattering of phonons and to a concomitant reduction of the thermal conductivity. The mechanism is not fully understood and different contributions are possible such as scattering of phonons on rattling modes or magnetic excitations. Novel concepts such as orbiton-phonon scattering are discussed. The mechanism of magnetic scattering may be separated by Inserting heavy elements with zero angular momentum such as the Eu^{2+} ion. Neutron diffraction is complicated by the large absorption cross section of Eu at thermal energies. Scattering experiments, however, are feasible using hot neutrons. A powder diffraction experiment on $Eu_{1-y}Fe_4Sb_{12}$ using the hot source at the LLB (Saclay) reveals new information on structural and magnetic properties of this compound.

Thermoelectric Properties of Transition-Metal-Substituted Clathrate Compounds

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We have systematically prepared polycrystalline transition-metal-substituted Ge clathrate compounds with the formula $Ba_8M_xGa_yGe_{46-x-y}$ (y=16-3x for M=Cu, Ag, Au; y=16-4x for M=Pd, Pt) and investigated their electronic and thermoelectric properties. In $Ba_8M_xGa_yGe_{46-x-y}$ (M=Cu, Ag, Au, Pd, Pt) compounds, the transition-metal atoms preferentially occupy the crystallographical 6c sites. The room temperature Seebeck coefficient is enhanced by Ag, Au, Pd, and Pt substitution as compared to that for $Ba_8Ga_xGe_{46-x}$ compounds at the same carrier concentration. The effective mass for these compounds is estimated to be larger than that for $Ba_8Ga_xGe_{46-x}$ compounds. The carrier mobility is hardly affected for M=Pd and Pt. On the other hand, the carrier mobility for M=Cu, Ag, and Au is larger than that for $Ba_8Ga_xGe_{46-x}$ compounds. The relaxation times for these transition-metal-substituted compounds are estimated to be larger than that for $Ba_8Ga_xGe_{46-x}$ compounds, suggesting that the local ordering of the transition-metal atoms in the crystal structure may reduce the carrier scattering. The effects of transition-metal substitution on the band structure and the electronic properties are also discussed.

Transport Properties of $Ca_xCo_{4-Y}Ni_ySb_{12}$ Skutterudite Compounds at Low and High Temperatures

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We report on the transport properties of dense polycrystalline partially filled $Ca_xCo_{4-y}Ni_ySb_{12}$ skutterudite compounds synthesized by a conventional metallurgical route. The influence of the Co substitution by Ni on the low and high temperature electrical resistivity, Seebeck coefficient, Hall coefficient, and thermal conductivity is discussed. It is found that the presence of Ni has a beneficial effect on the power factor. The potential for thermoelectric applications of this new family of compounds is also discussed.

High Efficiency in Thermoelectric Materials by Device Size Control

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The efficiency of thermoelectric materials is characterized by the figure of merit Z. Z can be determined by the relationship of $Z=(R_{dc}/R_{ac}-1)/T$ in the Harman method[1)], where R_{dc} and R_{ac} are the dc and ac resistance, respectively. In the present paper thermoelectric properties such as ZT and the temperature distribution in sample have been measured by the Harman method. Accurate measurements reveal that Z is largely dependent on sample size and a non-linear temperature distribution appears as a stationary state in the materials. We show the experimental results that larger ZT observed in $(Bi,Sb)_2Te_3$ appears in the samples with wider cross section and shorter length, and then insist that Z is not a peculiar materials constant, but must be defined as a physical quantity dependent on the size and position in the materials. It is also pointed out that the observed phenomena are important for improving thermoelectric efficiency in practical application.

Fabrication of Equipment for Evaluating ZT by Harman Method

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The figure of merit Z which characterizes the efficiency of thermoelectric materials is conventionally evaluated by Z=□^{2}/□□. Z can be also determined by relationship of Z=(R_{dc}/R_{ac}-1)/T in the Harman method[(1)], where R_{dc} and R_{ac} are the dc and ac resistance, respectively. In this method only resistance measurements are required and measurements are quite simple. Because the above relationship is valid in the sufficiently adiabatic condition, it is quite important in the experiment that this condition can be satisfied. The heat leakage between sample and heat bath due to not only thermal conductance by the lead wire and the gas but thermal radiation must be suppressed to be negligible. We fabricated the equipment in which some contrivances to have a satisfactory adiabatic condition were made and checked experimentally whether the condition is valid or not. In the present paper we explain the fabrication of the equipment in detail and show that ZT can be precisely obtained by the Harman method improved by our equipment.

Feasibility Study of Thermoelectric Power Generation for Stand-Alone Outdoor Applications

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There has always been a great need for a reliable and environmentally sustainable energy source. This paper analyzes the use of commercially available thermoelectric generators to exploit the temperature difference between air and solid structures to generate electrical power. Maximizing the natural temperature difference across the module to increase the open circuit voltage is crucial. The thickness of the thermoelectric generator is an important factor in determining the temperature difference.

The thicknesses of the thermoelectric generators evaluated are 0.651, 0.507, and 0.404 cm. The modules are mounted on a flat surface of a black plastic bar. The temperature difference across the modules, as well as the open circuit voltage is measured over a period of several months.

Thermoelectric generators have a capping layer over the thermocouples. Two of the modules use aluminum, and one uses a ceramic layer. Temperature was measured on the exposed side of the capping layer. A temperature difference of about one to four degrees Celsius was obtained. As expected a heavy dependence on weather conditions was observed. The generated open circuit voltage was a factor of one to two times smaller than what was expected based on the material's Seebeck coefficient. This indicates a non-zero thermal resistance of the capping layers and that much of the temperature drop is not across the thermoelements. Slight wind affects the temperature of the exposed side far more than the temperature of the actual thermoelement. Additional tests when the exposed side of the thermoelectric generator is attached to a heat sink with multiple fins and also when the modules are fully enclosed are also performed.

The possibility of powering a strip of lights using batteries charged by the thermoelectric generators is evaluated. One of the main constraints on feasibility is the efficiency as compared to solar power. This paper compares and discusses the two power options.

Feasibility Study on Electricity Generation Using Commercial Thermoelectric Cooling Modules

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The authors studied the feasibility of electricity generation using commercial thermoelectric cooling modules. The output performances of three standard thermoelectric cooling modules under the electricity generation mode were tested. The reliability of the thermoelectric cooling modules and the economics of electricity generated by thermoelectric cooling modules was discussed. The paper presents some research results. The results have shown that based upon the current price of the Chinese commercial thermoelectric cooling modules the cost of electricity thermoelectrically generated is lower than the normal industrial one. The authors expect that the era which electricity in large scale generated by the commercial thermoelectric cooling modules using surplus heat of industrial boiler, waste heat of vehicle and burn heat of garbage is coming.

Development of Transient Measurement to Investigate Bi-Te Thermoelectric Properties in the High Temperature Region

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It's necessary to investigate thermoelectric properties of the materials at high temperature range if the materials are used for thermoelectric power generator. We developed a measuring instrument based on Transient method[1)] to measure Seebeck coefficient, resistivity, and thermal conductivity simultaneously from room temperature up to 300 ºC. The commercial transient equipment basically focused on the room temperature characterization and it is significantly difficult to investigate the thermoelectric properties above room temperature. This is due to the heat flow from ambient and this becomes more significant with increase of temperature. We improved this method of measurement and reduced heat flow from outside as much as possible by employing the thermal anchor. Moreover, we compensated thermal conductivity having considered heat flow from ambient radiation, wires, air conduction, and air convection. Using n-type Bi_2Te_3 based samples, we compared thermoelectric properties with the result acquired from another commercial conventional measuring equipment. As a result, they showed pretty good agreement among them and the clear evidence in composition dependence of thermoelectric properties could be obtained.

1. Richard J. Buist, CRC Handbook of Thermoelectrics, Ed. Rowe, 1995,CRC press, inc.Chapter 18

Thermoelectric Properties of Co-Sb Systems for Power Generation Module

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$CoSb_3$-based filled Skutterudite systems have been promising as thermoelectric material which shows high ZT value in a middle temperature range. These materials have been investigated to stabilize its thermoelectric property and improve its ZT.

In this work, the thermoelectric material was fabricated by the rapidly solidification technique with a single wheel. The Co-Sb ribbons obtained by this method were sintered with use of spark plasma sintering (SPS). Characteristics of the sintered samples and these thermoelectric properties were evaluated. In addition, performance of the power generation module was also investigated.

Eco21,Inc is joining "The Japanese National Project on Development for Advanced Thermoelectric Conversion Systems".

Development of Skeleton-Type Thermoelectric Module for Power Generation

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We have participated in The Japanese National Project on Development for Advanced Thermoelectric Conversion Systems supported by the Ministry of Economy, Trade and Industry(METI) and the New Energy and Industrial Technology Development Organization(NEDO), and have been developing a low-cost, high-efficiency and high-reliability Bi-Te thermoelectric module for power generation.

For the purpose of reducing the module cost, we have been trying to manufacture skeleton-type modules with electrodes formed by atmospheric plasma spraying. The modules that had different conditions, such as thickness of modules, size of thermoelectric elements, density of thermoelectric elements and thickness of electrodes, were prepared. Power generation efficiencies and internal electric resistances of these modules were measured, and the optimum conditions for power generation were considered.

In manuscript, the effect of module thickness and electrode thickness on properties of thermoelectric module for power generation will be mainly discussed.

The Analysis of a Heating System based on Thermoelectric Heat Pump

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The paper consider an autonomous heating system which is based on the thermoelectric heat pump (THP) with the environment as a heat source. A mathematical model of THP which takes into account the conditions of heat exchange on junctions of the thermoelectric elements is employed. The main requirements for the construction of thermoelectric modules and heat exchange systems are set. We show that the highest effectiveness is achieved when a scheme with countercurrent flow of heat-transfer agents is considered. The paper conducts an analysis of the effectiveness of thermoelectric sources of heating for Ukrainian climate conditions. The potential of employing the heating scheme under consideration as an energy saving technology and its competitiveness with traditional heating systems is discussed.

Miniature Power Generation Device and its Application to Gas Combustion System

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An all-metal miniature power generation device was developed for the purpose of using in a gas combustion system. A photo-etching technique was adopted to fabricate the device, which consists of 20 pairs of P-N legs with dimensions of 0.5 x 0.1 x 10mm jointed each other with a gap of 0.2 mm. Chromel and Constantan sheets were used as materials for P and N legs.

In a power generation test, the device was placed in the middle of small butane gas flame and a very steep temperature gradient around 700K/cm was produced along the device length despite the large thermal conductivity of the device. This results in an open circuit voltage of 1.15V and an electrical power output of 57mW at 100mA. The device shows excellent durability for a long operation and seems to be promising in supplying an electrical power for small electronics.

Feasibility Study on Electricity Generation Using Commercial Thermoelectric Cooling Modules

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The authors studied the feasibility of electricity generation using commercial thermoelectric cooling modules. The output performances of three standard thermoelectric cooling modules under the electricity generation mode were tested. The reliability of the thermoelectric cooling modules and the economics of electricity generated by thermoelectric cooling modules was discussed. The paper presents some research results. The results have shown that based upon the current price of the Chinese commercial thermoelectric cooling modules the cost of electricity thermoelectrically generated is lower than the normal industrial one. The authors expect that the era which electricity in large scale generated by the commercial thermoelectric cooling modules using surplus heat of industrial boiler, waste heat of vehicle and burn heat of garbage is coming.

Fabrication and Evaluation of an Element for Thermoelectric Generating System

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We designed legs in order to develop a thermoelectric generating system in the temperature range of 300 to 800K. PbTe doped with PbI_2 and $Pb_{0.5}Sn_{0.5}Te$ were used as for n and p-type legs, and Ni was selected for the electrodes of the thermoelectric generating element.

The bonding between legs and electrodes was carried out by silver solder. The interfaces were analyzed electrical, thermal, mechanical, and chemical properties. Thermoelectric generating properties of the fabricated element were evaluated.

High Efficiency Solar Energy System, Thermoelectric-Generators Assisted

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The efficiency of a system based in a photovoltaic solar cell, as best achieves 15 to 20%. Once the photovoltaic solar panel gets a considerable higher temperature input, over 50°C in some stages of the year, the total efficiency of the system drops down considerable.

At this work it has been study a mixture of two sources, as the photovoltaic solar panels and a thermoelectric generator that adds a global increasing inputs. The difference of temperatures is taking as an advantage in some applications, when the location of the photovoltaic solar panels that generates and additional electrical current will damper the effect of lower the efficiency. The accumulation heat effect at the edges is also being control in the metallic structure panel.

The thermoelectric structure is located in the areas that reach the high temperatures in the photovoltaic solar panel, and to obtain the needed temperature difference on the cold side of the thermoelectric devices, this must be in contact with the cold surface of the building were is located.

Power Generation with Fe_2VAl modules using Sodium Heat Source

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A prototype system for thermoelectric power generation using the Heusler Fe_2VAl alloy has been studied by considering the future potential of heat recovery from a liquid metal cooled fast breeder reactor. The modules consisting of 180 pairs using Fe_2VAl cast alloy were mounted on 1.8 meters long of the outer surface of a stainless tube with 34mm diameter which is internally heated by 484-670K liquid sodium flowing at 2 to 8 l/min. The element has a shape of a long cuboid, where one small rectangular end was thermally contacted with the tube surface and the other end was directly cooled by forced air flow to form a counter-type heat exchanger. The internal electric resistances of the modules were nearly same, however, the electromotive force varied widely because of the difference of thermal resistance between the module and tube surface. The output power generated from this prototype system was evaluated to be about 4.2 W/m assuming that all the circumference of the pipe surface is covered by the elements.

Quasi Two Dimensional Correlated Electron Systems as Potential Bulk TE Materials

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Low dimensional materials have been of intense research interest in the field of thermoelectrics over the last decade, but mostly in thin film or superlattice form. Several groups of quasi twodimensional *bulk materials* have also been investigated as potential thermoelectric (TE) materials over this same period. These include several transition metal chalcogenide systems such as the CsBi4Te6 system investigated by the researchers at Michigan State University and the pentatellurides, MTe5, (where M = Zr, Hf, Ti), in our research group at Clemson University. The Bi2Te3 state of the art TE materials are also of this class of materials. In addition, several other materials of this class of low-dimensional bulk materials have also been investigated.

Recently a group of materials know as ceramic oxide TE materials has received much attention and they are also this class of quasi- 2D correlated electron systems. An overview of selected quasi-2D TE materials, their distinctive characteristics as well as their attributes and challenges for their use in potential thermoelectric devices will be given in this paper. One characteristic is that these materials are typically layered systems with strong electron correlation within their planes. They typically possess very high power factor values at their optimum temperature, where the power factor, PF, is given by: PF = a2sT/r > 1.0 Wm-1K-1. They are usually semimetallic systems, with high values of their thermopower (a > 150 mV/K) and low resistivity values (r < 1 mW-cm). However, these materials also tend to possess high in-plane thermal conductivity (k) values, on the order of 4-10 Wm-1K-1. The challenges for these materials include the need to grow large single crystals, the ability to tune the thermopower and ways in which to minimize the lattice thermal conductivity. This can be more of challenge in this type of materials due to their largely anisotropic crystal structure. An overview of some of the various research directions and subsequent successes will be highlighted. Some of our recent results on rare earth doping in the pentatellurides and our work on some of the ceramic oxide materials will be presented.

Nonequilibrium Electron-Phonon Transport Near Sharp Potential Barriers

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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 of sharp potential barriers. 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.

Thermoelectric Bi_2Te_3 Nanotubes and Nanowires Prepared by Hydrothermal Synthesis

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Bi_2Te_3 nanoparticles have been prepared via hydrothermal synthesis by using Te powder and $BiCl_3$ as the reactants and $NaBH_4$ as the reductant. XRD, TEM, EDX and HRTEM have been applied to investigate the morphology and microstructures of the products. The results showed that novel quasi-one-dimensional Bi_2Te_3 nanotubes and nanowires with diameters of less than 100nm and lengths of up to 10 □m have formed during the reactions. The nanostructured powders were used as the additives of hot-pressed Bi_2Te_3 based alloys. The thermoelectric transport measurements indicate that the thermoelectric properties of these nano-composite bulk samples have been remarkably increased and the maximum figure of merit ZT of about 1.2 was achieved.

Cross-Plane Seebeck Coefficient Anomaly in a High Barrier Superlattice with Miniband Formation

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We have measured the cross-plane Seebeck coefficient of short period InGaAs/InAlAs superlattices with 5nm wells and 3nm barriers with different doping concentrations. Contrary to the conventional bulk III-V materials, Seebeck coefficient did not decrease monotonically with doping concentration. A semi-classical model is established to study the thermoelectric transport in superlattices in miniband formation regime. After performing detailed numerical calculation base on this model, we were able to explain the thermopower anomaly measured for superlattices with doping concentrations varying from $2x10^{18}$ to $3x10^{19}$ cm^{-3}. Based on this model, we proposed a structure for an n-type material with a positive Seebeck coefficient. N-type semiconductors have normally a negative Seebeck coefficient. It is shown that in a suitable superlattice structure it is possible to selectively emit "low" energy electrons from the anode to the cathode. Thus, the heat transferred from the anode to the cathode is equivalent to a material with a positive Seebeck coefficient. This will be very useful in cascading thermoelements because changing the doping material during the growth is not necessary.

High Performance Multi Barrier Thermionic Devices

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Thermoelectric transport in multiple barrier superlattice structures is investigated in two limiting cases of no-scattering and strong momentum scattering. In a strong scattering regime when lateral momentum is not conserved, the number of electrons participating in thermionic emission will dramatically increase. Calculations show that even at this regime, a small barrier height on the order of k_BT does not give much improvement in the effective thermoelectric power factor for heterostructure thermionic coolers compared to bulk materials. To have a high coefficient of performance, one should use tall barriers and high doping densities to achieve a large number of electrons moving in the material. In this paper the latter regime of transport is investigated in detail. The current-voltage characteristics and the cooling power density are calculated using Fermi-Dirac statistics, density-of-states for a finite quantum well and the quantum mechanical transmission coefficient. The resulting equations are verified with the experimental dark current characteristics of multi quantum well structures in a wide range of temperatures and electric fields. Our detailed numerical calculations lead to the conclusion that in the metallic based superlattices with tall barriers (>10 eV), one can achieve a large effective thermoelectric figure-of-merit (ZT>5 at room temperature) with a moderate lattice thermal conductivity of 1W/mK [1]. This significant improvement in ZT is due to the increase in the thermionic cooling power density. This can be combined with the other methods to reduce the phonon thermal conductivity in superlattices and thus obtain higher ZT factors.

[1] D. Vashaee and A. Shakouri, Improved Thermoelectric Power Factor is Metal-Based Superlattices, accepted for publication in Physical Review Letters, December, 2003.

Electric and Thermal Conductance of Porous Thermoelectric Materials with Hollow Quantum Structure

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The concept of Hollow quantum structure was proposed in 2002. Here the model on the function of hollow quantum structure on electric and thermal conductance of thermoelectric materials were established and was used in analysis of the properties of thermoelectric materials.

Electrodeposition of Highly Dense, Ordered Bismuth Telluride Nanowire Arrays

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Polycrystalline Bi_2Te_3 nanowires with diameter about 50 nm have been assembled into the nanopores of alumina template by electrodeposition in the solution containing Bi^{3+} and $HTeO_2^+$ with porous alumina template as cathode. X-ray photoelectron spectroscopy (XPS) , high-resolution electron microscopy (HREM) and selected area electron diffraction (SAED) investigations indicate that the nanowires are polycrystalline Bi_2Te_3 with hexagonal structure. Transmission electron microscopy (TEM) and environmental scanning electron microscopy (ESEM) are used to characterize the morphology of the Bi_2Te_3 nanowire arrays. The results indicate that the nanowire arrays are highly dense and ordered.

Development of a Thermoelectric Power Generation System in Industrial Furnaces

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This paper discusses the development of a thermoelectric power generation system which is conducted in the Japanese national project / Development for advanced thermoelectric conversion systems supported by the Ministry of Economy, Trade and Industry (METT) and the New Energy and Industrial Technology Development Organization (NEDO).

The thermoelectric power generation system is designed to use the waste heat of electric resistance heating industrial furnaces and assumed to be exposed to the radiation from a hot wall of 700K - 900K and to a water-cooled cold wall. The system is designed as a unit composed of thermoelectric modules, a hot-side radiation-receiving part and a cold-side part attached to the cooled furnace wall. Materials with high emissivity have been selected for the radiation-receiving part.

In order to carry out the analysis of the performance of the thermoelectric generation unit installed in the industrial furnace, where the heat transmission mechanism is mainly radiation combined with solid heat conduction and minor convection, a simulation tool has been developed. Models of the power generation unit with cascade-type thermoelectric modules have been designed.

Analyses of the thermoelectric performance of models and units have been carried out and are reported.

Thermoelectric Power Generation with Rectangular-Fin Type Elements and Its Applicability in Micro Systems

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A rectangular-fin type thermoelectric device having a simple module structure suitable for micro fabrication was newly proposed as a micro- to milli-scale electric power generator. A simple half-fin model was introduced to examine the basic characteristics of thermoelectric power generation with the module. The power density and conversion efficiency were given theoretically by solving one-dimensional heat and current flows of the half-fin model. It was found that there exist optimum fin aspect ratios to achieve maximum power density and conversion efficiency. The optimum values for each are almost the same and depend on thermoelectric properties, flow and thermal conditions of working fluids, and aspect ratios of flow channels between the fin-type elements. Power density becomes larger when the module is proportionally downsized keeping its optimum fin aspect ratio, while conversion efficiency remains constant, i.e. smaller devices show better performance. Finally, comparative analysis with a conventional pi-type module was also conducted to emphasize the superiority of fin-type module in micro systems, when convective heat transfer resistance is taken into account.

A New Model of Thermoelectric Micro-Power Generator with Parallelly Arranged p-legs and n-Legs Fabricated by Electrodeposition

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Miniaturized solid-state devices are of interest for variety applications. To meet the promising requirement, we designed a new model of thermoelectric micro-power generator, Which is composed of a great deal of parallelly arranged p-legs and n-legs. According to the structural design, the parallelly arranged p-legs and n-legs were fabricated by electrodepositing p type and n type thermoelectric materials into the micro-tubes of a porous polymer template. Then, the p legs and n legs were connected in series with conductive metal layers. The new thermoelectric micro-generator possesses a coin like configuration and its thickness is about 1mm.

Using of a Ring-Radial Generating Thermoelectric Module for the Systems of Uninterrupted Emergency Power Supply

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The problem of searching electric energy sources of low power, being able to realize in an independent mode an uninterrupted power supply for Users, is very actual.

A direct converting of heat energy into electric, under realizing certain temperature difference, enables to solve this problem.

Gas fuel vessels are usually used to heat cottages. Using of a discharged heat both from circulating heat system and vessel's exhaust pipe as well as from running water, enables to form a temperature difference sufficient for obtaining required electric power using thermoelectric generators based on the Seebeck effect.

A generating thermoelectric module (GTEM) is the main part of the installation.

It is a pipe heat exchanger, on which external surface the thermoelectric ring-radial batteries are mounted (TEB). Heat supply can be realized through heat-transfer agent and by direct heating. Heat dissipating is instrumented by the use of heat-transfer medium.

Implementing certain technology makes possible to obtain a reliable, heat resistant, high effective construction and eliminate drawbacks inherent to existing analogs.

This enables to use the supplying heat more effective, to gain higher special heat and electric power values as well as to utilize some exceed heat to obtain added electric energy for saving it.

Evaluation of the reliability of Thermoelectric Generator Modules Considering Elastic and Plastic Deformation and creep effect of the Solder Layer

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Reliability is a key problem of thermoelectric modules for power generation. Usually these modules electrodes are made by sprayed metal. Generally these modules reliability is better than modules constituted by solder.

However, these modules don't achieve the full potential of their performance, because the electrical resistance of the interface between electrode and semiconductor increases.
Addressing this problem, we investigated the properties of thermoelectric modules with contacts constituted by Pb base solder with a melting point of 305□.

The electrical resistance of a 40 pair Bi2Te3 module was measured in a heat cycle experiment and the fatigue damage of the electrical contacts were analyzed. Several modules were investigated with varying parameters like constrain condition, electrode material, element heights and ΔT.

Additionally we carried out numerical Finite Element Analysis of the structure considering elastic and plastic deformation and creeping effect of the solder layer under the heat cycle test condition. Experimental and theoretical results will be compared and discussed regarding the reliability of the thermoelectric modules.

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Thermoelectric Generator Utilizing Boiling and Condensation (Improvement of System Characteristics)

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In this study, an experiment on an improved thermoelectric generator utilizing boiling and condensation heat transfer was carried out using FC5312 as the thermal medium at a wind-tunnel test bench. In order to increase the temperature difference between electrodes, the hot side electrodes of the module were processed into a low-finned condensing surface and a ceramic thin film was used as the insulation between the cold side electrodes and water jacket. A new material thermo-element with high performance at high temperature was used. Further, a new type boiler with pipes of varied diameter in the direction of gas flow was chosen. Experimental parameters were the temperature of the cooling water, the velocity and the temperature of the heated gas. As the results, the distribution of the temperature on the hot side electrodes was improved and the thermo-resistance between the cold side electrodes and water jacket was greatly improved. And the efficiency of the absorbing heat for the boiler reaches 58% and the efficiency of the thermoelectric conversion reaches 5%. Finally, it is confirmed that the experimental results agree with the prediction results by one-mention model.

Acknowledgement: It is gratefully acknowledged that this research have been subsidized by the Ministry of Economy, Trade and Industry (METI) and the New Energy and Industrial Technology Development Organization (NEDO) as a member of Japanese national project for “the development for advanced thermoelectric conversion systems”

Thermoelectric Materials & Technology for Future High Power Deep Space Science Missions

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Thermoelectric power sources have consistently demonstrated extraordinary reliability and longevity for deep space missions (25 U.S. missions to date, with some lasting more than 30 years). This is a truly outstanding track record. Key advantages of this technology include no moving parts, high intrinsic redundancy, excellent scalability, no electromagnetic interference or vibrations, and a well documented graceful degradation over extended periods of time.

Near term high temperature thermoelectrics are currently one of two power conversion technologies being considered for the proposed Jupiter Icy Moons Orbiter (JIMO) 2015 mission, a high power (100 kW_e class) deep space science mission planned to explore three of Jupiter's moons using electric propulsion. Development of advanced thermoelectric materials and technology is also underway for possible application to future high power electric propulsion missions beyond JIMO.

Application of thermoelectric energy conversion to large scale power systems requiring low mass, long life and high levels of reliability and redundancy, present unique challenges in terms of system design and analysis, materials synthesis, component fabrication and converter assembly. Near term approaches have recently focused on Si-Ge alloys and converters conductively coupled to the heat source, while more advanced segmented and cascaded materials combination with conductively or radiatively coupled schemes are being developed for future programs. Some of the key challenges are presented and recent technical progress is discussed.

The Influence of Tin Content on the Structural and Physical Properties of $Pb_{1-x}Sn_xTe$ Solid Solutions

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The figure of merit Z ($Z=S^2\sigma/k$, where S is the Seebeck coefficient, k and σ are the thermal and electric conductivities, respectively) is a measure of the performance of thermoelectric materials.

The IV-VI compounds, the best known of which is PbTe, are a family of materials for thermoelectric applications on account of their high figure of merit Z over a wide temperature range. PbTe compounds are mostly (but not exclusively) used as n-type materials and efforts are being made in order to find an optimal p-type material to be used as a positive pellet in a thermoelectric battery.

The present work is concerned with optimizing the p-type material system $Pb_{1-x}Sn_xTe$. Specimens with $0 \le x \le 0.6$ were synthesized from elemental powders and homogenized. Segments from all specimens were taken and ground into fine powder, silicon powder was then added as reference material, and mixture examined by XRD. The XRD results were computer processed (peak searches in APD and lattice parameter calculations in CELIZ) and the composition dependence of the lattice parameters was determined, showing a linear relationship over the investigated composition range.

Among the transport properties that have to be determined, we measured the Seebeck coefficient, using the hot probe technique. The Seebeck coefficient deceases with increasing tin content. Electrical resistivity and Hall effect coefficient were determined by the four probe technique. The results of these measurements will allow determining the distance of the Fermi level.

Influence of Alloy Scattering on the Electron Mobility in Extruded $(Bi_{1-x}Sb_x)_2(Te_{1-y}Se_y)_3$ Thermoelectric Materials

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We present the effect of Se and Sb on the electron mobility of polycrystalline n-type $(Bi_{1-x}Sb_x)_2(Te_{1-y}Se_y)_3$, for $0 \leq x \leq 0.125$ and $0 \leq y \leq 0.07$, obtained by mechanical alloying and extrusion. The introduction of Se as well as Sb in pure Bi_2Te_3 is of interest because of their strong effect on the reduction of the lattice contribution to the thermal conductivity, thus allowing a marked increased in thermoelectric performance of the (pseudo-binary) alloy. The electrical transport properties were measured in the range from 20 to 300 K, where we observed a systematic decrease of the mobility with increasing Se and Sb incorporation. We analyze this decrease compared to what would be expected from alloy scattering, and conclude that the effect of Se is more drastic than that of Sb because the electronegativity difference between Te and Se is much larger than between Bi and Sb. The quantification of the alloy scattering mechanism is important for the development of new thermoelectric materials.

Optimum Power Factor of Films in the Bi-Te System

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The deposition conditions for co-evaporated Bi-Te films, namely the material and crystal structure of the substrate, evaporation rate of individual species, and substrate temperature T_s, were varied, and the thermoelectric properties of the films were measured. The substrates were glass (Type II Soda Lime), Al_2O_3, MgO, mica, and Pt. The deposition rates were varied such that the tellurium composition changed from 55 At% to 70 At%, and T_s ranged from 130°C to 280°C. The Seebeck coefficient, electrical resistivity, and carrier concentration, were measured (except for films grown on Pt). Chemical composition and crystal structure of the films were compared with a standard Bi_2Te_3 single crystal sample.

The measured Seebeck coefficient, electrical resistivity, and carrier concentration varied from -34 μV/K to -280 μV/K, $0.23\text{x}10^{-5}$ ohm-m to $4.1\text{x}10^{-5}$ ohm-m, and $-2.3\text{x}10^{19}$ cm^{-3} to $-1.96\text{x}10^{19}$ cm^{-3}, respectively. The power factor increased with T_s, ranging from 0.16 mW/K^2-m (T_s = 130°C) to 4.1 mW/K^2-m (T_s = 260°C). At high substrate temperatures, the control of the film stoichiometry was difficult, due to re-evaporation of Te from the substrate. Films with 60 At% of Te had the highest power factors.

Thermoelectric Properties of Bi_2Te_3 Thin Film Produced by High Density Plasma Deposition Process

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The high density plasma deposition process was used to prepare Bi_2Te_3 thin film on a silicon wafer substrates. The Bi_2Te_3 target was firstly made by squeeze casting method from Bi and Te pellets with a purity of 99.99%. The thickness of Bi_2Te_3 thin films was 500 nm. X-ray diffraction studies revealed that the crystal structure of the as-deposited film is the same with Bi_2Te_3 target. The Seebeck coefficients S, electrical conductivities □ and thermal conductivities □ of Bi_2Te_3 thin film were measured in the temperature range from room temperature to 430K and compared to those of bulk Bi_2Te_3 material.

Experimental results show that the thin film sample has a obviously lower thermal conductivity, but only less decrease the electrical conductivity and Seebeck coefficient. These results illustrated that the ZT value of thermoelectric materials have a chance to be enhanced by reducing the size of materials.

Heat Rejection Alternatives for Lamp-Top Thermoelectric Generator

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The main objective of this research work is to enhance the performance of thermoelectric (TE) generator by developing an effective heat rejection method for the cold side of TE modules. Commercial TE modules using bismuth telluride based alloys and consisting of 127 coupling were used. A compact device was then designed incorporating two modules with the metal sheet at the top of lamp acting as the heat source. Two types of heat rejection alternatives were considered: a rectangular fin heat sink (RFHS) and a closed-end oscillating heat pipe (CEOHP). The effect of temperature difference between the hot side and the cold side was analyzed. The maximum electrical power is 1.4 W for the RFHS and 0.3 W for the CEOHP at the hot side temperature of 150 °C. It has been concluded that, the RFHS is better than the CEOHP in terms of heat rejection rate and economic.

Passivation-free Thermoelectric Power Generation Module Using Textured P/N Oxides

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Thermoelectric oxides have inherent potential of highly reliable thermoelectric power generation modules as they can hold both chemical stability and mechanical strength in the high temperature atmosphere. We have fabricated a thermoelectric module using the oxide materials: n-type Ca-doped $(ZnO)_3In_2O_3$ and p-type $Ca_3Co_4O_9$. To optimize thermoelectric performance in these layered oxide materials, the reactive-templated grain growth process was taken to realize their highly textured ceramics. The figures of merit were evaluated to be ZT~0.3@1000K in air for both materials. A bridge-type thermoelectric module was designed to minimize any contact problem under thermal cycling. Seven p-n pairs were connected in a series using the noble-metal paste and the In paste for the high- and low-temperature contacts, respectively. The module gave ΔT=630K and output an open-circuit voltage of 1.1 V with an exposure of the alcohol lamp, which corresponded to the calculated value from the Seebeck coefficients of the materials. The stability without any passivation demonstrated a practical potential for high-temperature thermoelectric applications.

Micro-thermoelectric Power Generator Fabricated by Nanowire Array Thermoelectric Material

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Miniaturized solid-state devices such as MEMS, micro-electrical system and even "system on a chip" are of interest for variety of space and terrestrial applications. For those micro-systems, micro-power sources with low power, high voltage output are necessary. To meet the promising requirement, we combined the high thermoelectric performance of nanowires with the advantage of IC fabrication process and designed a new type of micro-thermoelectric power generator which is comprised of n-type and p-type Bi_2Te_3 nanowire array thermoelectric materials. The nanowires are embedded in the alumina nanoporous film and the unique laminar structure of the micropower generator makes thermo-electricity conversion more effective. A high voltage output can be obtained by connecting the nanowire array micro-zones in parallel and then in series electrically. The designed micropower generator possesses a film like configuration and its thickness is less than 100μm. An important aspect that distinguishes our device from the conventional one is that thermoelectric nanowire arrays are firstly used to fabricate thermoelectric micro-generator.

Fabrication of Thermoelectric Oxide Devices

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Different versions of a thermoelectric unicouple composed of *p*-type $Ca_3Co_4O_9$ (Co-349) and *n*-type $LaNiO_3$ (Ni-113) bulks were constructed using Ag paste containing *p*- and *n*-type oxide powders, prepared from the same bulks, for connection of the *p*- and *n*-legs, respectively. Open-circuit voltage (V_o) of the unicouple connected using Ag paste containing 6 wt.% of the oxide powders reaches 100 mV at a hot-side temperature (T_H) of 1073 K and a temperature difference (T_{diff}) of 500 K in air. Internal resistance (R_I) of this unicouple is 26.2 mOhm at 1073 K in air and decreases with increasing temperature. Maximum output power (P_{max}), evaluated using the formula $P_{max} = V_o^2/4R_I$, is 94 mW at 1073 K (T_{diff} = 500 K) and increases with temperature. This value corresponds to a volume power density of 663 mW/cm^3.

Potential for Improvement in Thermoelectric Properties of Hexaborides

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We reported that divalent hexaborides (CaB_6, SrB_6, BaB_6) are of n-type and have relatively high ZT values compared with those of other boron-rich solids. The power factors of the hexaborides were large enough, which exceeded 10^{-3} W/Km over the entire temperature range measured (from room temperature to 1100 K), but their high thermal conductivities cause the ZT values to be moderate. To improve thermoelectric properties of the hexaborides, we have tired to reduce their thermal conductivity by substituting part of metal atoms with other element while maintaining their high power factor. We found that the substitution even with lighter element reduced lattice thermal conductivity. But in some cases, power factor decreased due to unexpected change in carrier concentration. The carrier concentration in the divalent hexaborides appears to be related to defects or deficiencies in the crystal. We have therefore performed electronic structure calculations on the divalent hexaborides to elucidate the origin of the carrier and to discuss the further improvement in the thermoelectric properties of the hexaborides. Detailed results and discussions will be presented at the conference.

High Temperature Thermoelectric Properties of RE-B-Si Higher Borides

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Boron-rich inorganic compounds such as YB_{66} have been extensively studied but mostly for their structural or mechanical properties. These compounds are typically attractive as materials for their high hardness and great stability in extreme environments originating from the strong covalent bonding of boron. However, striking physical properties (electronic, magnetic) had not been found in such compounds.

Recently we have been able to develop new functionalities, namely magnetism, in novel boron-rich compounds focusing on the role of the B_{12} icosahedra. Magnetic transitions at moderate temperatures have been discovered for rare earth B_{12} icosahedral cluster compounds despite their being magnetically dilute, semiconducting f-electron systems.

In this work, we focus on the thermoelectric properties of novel B_{12} icosahedral borosilicides $REB_{44}Si_2$ (RE=Gd-Lu). Since these materials are stable to temperatures over 1700 K, they can be promising for high temperature thermoelectric application since the thermoconductivity in the higher borides are typically very low. Seebeck coefficients in excess of 200 □V/K are observed at temperatures above 1000 K. And figures of merit ZT of 0.06 were estimated at 1000 K for unmodified $REB_{44}Si_2$, with the temperature dependence of ZT sharply increasing as temperature increases. Possibility of using or modifying these novel B_{12} icosahedral compounds for high temperature thermoelectric application will be discussed.

The Effects of Addition of the Other Elements on Thermoelectric Properties of α- and β-Rhombohedral Boron

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α-rhombohedral boron(α-boron) and □-rhombohedral boron(□-boron) are representative crystalline structures of boron-rich icosahedral cluster solids(BRICS) which consists mainly of B_{12} icosahedral clusters. In the BRICS, a slight change of the structure or environment of B_{12} icosahedral cluster can cause metallic-covalent bonding conversion, which can cause that the electrical conductivity σ and the Seebeck coefficient S can be as high as those of metals and semiconductors, respectively. Five-fold symmetry of the icosahedral cluster does not match with the translational symmetry of a crystal, consequently makes lower thermal conductivity κ with complex structure. For these reasons, BRICS are promising candidates for high temperature thermoelectric materials. In the last conference, we reported that Vanadium(V) doped □-boron had the largest ZT for n-type among several metal doped ones ($M_{1.0}B_{105}$).

In the present study, V composition dependence on thermoelectric properties of □-boron has been investigated and we have found out that $V_{2.0}B_{105}$, which including some of dispersed metallic second phase(VB_2), had agreeable improvement of ZT mainly due to high σ. On the otherhand, Carbon(C) and Phosphorus(P) was doped into α-boron. C doped α-boron (Boron Carbide) has higher σ and even lower κ than P doped one(Boron Phosphorus), thus has larger ZT for p-type.

Electronic Properties of Semiconducting Rhenium Silicide in Respect to its Thermoelectric Properties

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The pure and Al-doped single crystals of semiconducting rhenium silicide ($ReSi_{1.75}$) of a high perfection have been grown by the zone melting technique in order to investigate the thermoelectric efficiency of this compound and, therefore, its potential for thermoelectric application. Theoretical calculation of the electronic and thermoelectric properties was also performed. The electrical resistivity of the crystals was measured with conventional *dc* four-probe technique in the temperature range of 77 – 800 K simultaneously with the measurement of the thermoelectric power. The slope of the high temperature portion in the temperature dependence of resistivity for the undoped crystal yields the value for the band gap of 0.14 eV. This is in good agreement with our theoretical calculations. The comparison with the undoped $ReSi_{1.75}$ shows a threefold decrease of the resistivity as the result of doping. Undoped crystals show in the thermoelectric power both types of conductivity. The Seebeck coefficient of Al-doped $ReSi_{1.75}$ is positive in the whole temperature range studied and reaches the maximum value of 100 μV/K at about 800 K.

Theoretical calculation of the charge carrier mobility is based on the effective masses, which are estimated from the *ab initio* electronic band structure and classical scattering mechanisms. The effective mass tensor for electrons and holes was calculated along the principal axes at the conduction band minimum and valence band maximum, respectively. As the most important feature we find a strong anisotropy in hole effective masses. The mobility as well as thermoelectric properties estimated in the wide temperature range confirmed the experimental data for both doped and undoped $ReSi_{1.75}$ crystals.

Thermoelectric Properties of Ba_xC_{60} Compounds

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We use two different methods to synthesize barium fullerides powders. The obtained barium fullerides powders were sintered by Spark Plasma Sintering (SPS) technique yielding bulk specimens. We report Hall effect at room temperature and electrical resistivity in the temperature range of 110K-850K. Thermopower and thermal conductivity are measured in the temperature range of 300K-850K and 300K-1000K respectively. These barium fullerides have low lattice thermal conductivity, close to the value of amorphous SiO_2. The potential of these fullerides for thermoelectric applications are discussed.

Preparation of Boron-Carbide ($B_{13}C_2$) Thin Films and Thermoelectric Devices by Intense Pulsed Ion Beam Evaporation

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Crystallized $B_{13}C_2$ thin films were fabricated by intense pulsed-ion beam evaporation (IBE). IBE is an instant thin film deposition method using ablation plasma which was produced by irradiation of intense pulsed ion beam on a target. Electrical conductivity of the thin films were 10^2 [1/□m] at room temperature and 10^4 [1/□m] at 1000 [K]. Seebeck coefficients of the thin films were approximately 200 [□V/K] from room temperature to 1000 [K]. Thermoelectric (TE) properties of obtained films were as comparable as those of bulks. The IBE method allows fabrication of $B_{13}C_2$ films without substrate heating. For the application of the $B_{13}C_2$ film, we developed "in-plane" type TE device using solid-state bonding with n-type SrB_6 thin film prepared by pulsed laser deposition (PLD). Generation of thermo-electromotive force and electrical power could be confirmed from the TE device fabricated, and the sample was worked as a TE device. To the best of our knowledge, this is the first demonstration of the TE device composed of only boron-rich solids. Details of the results and improvement in the TE properties of the $B_{13}C_2$ films using the IBE method will be presented at the conference.

High Performance Heat Exchanger for Thermoelectric Cooling with Large Heat Loads

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Commercial viability of high heat-load thermoelectric cooling applications is critically undermined by grossly inadequate heat dissipation mechanisms currently used in conjunction with Peltier modules. This paper discusses the design considerations and development strategies of a novel micro-scale heat exchanger technology that significantly promotes heavy-duty thermoelectric refrigeration.

Presented heat exchanger concepts incorporate the excellent heat transfer characteristics of fluid flow through very narrow channels (micro-channels). Simulation models and theoretical analyses are developed to describe the influence of critical parameters such as fluid channel geometry, thermal conductivity and fluid flow rate on heat transfer rates and pumping power of the micro-heat exchanger. Predicted thermal performance of the heat exchanger is experimentally verified while identifying optimised parametric combinations for thermoelectric applications.

As indicated by exhaustive testing, the developed micro-heat exchanger delivers unprecedented levels of thermal performance with modest fluid flow rates setting a new industry benchmark for thermoelectric cooling threshold. The enhanced thermal efficiency and very low fluid pumping power of this new design greatly improves the coefficient of performance of thermoelectric refrigeration and will enable the design of commercially viable refrigeration systems.

Thermoelectric CPU Cooling Using High Efficiency Liquid Flow Heat Exchangers

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The inevitable rise in cpu heat generation has sparked intense interest in active cooling devices. A dramatic increase in the number of commercial cpu coolers, including water blocks with and without thermoelectric modules, has occurred in the past 18 months. Some of these coolers use sophisticated jet impingement and microchannel designs, while others are relatively primitive.

This paper discusses the major design issues for this application and the challenges of high heat flux loads for thermoelectric solutions. The most successful designs are described and experimental performance testing of several of the best in class models is presented.

The Peltier-Actuated Microvalve

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A microfluidic valve is formed by creating a flow channel past a Peltier junction. Fluid flow through the channel is stopped when the Peltier junction causes the fluid to freeze, forming a solid plug in the channel. Traditional valves operate by moving solid objects to obstruct the flow path. This requires sealing against a valve seat, and leads to complicated geometries that are difficult to manufacture on the MEMS scale. Other issues with traditional valves include large dead volumes, materials for valve seats, contamination, and small actuation forces. In the new concept, a Peltier junction cools the fluid sufficiently to freeze it. The valve is opened by reversing the current in the Peltier junction. A valve operating on this principle has no moving parts and has a straight, smooth-walled flow path with constant cross-section across the valve. It is able to withstand differential pressures in excess of 2 MPa across the valve, has essentially zero leakage, and is unaffected by particulate contamination. Prototype valves have been built and tested, demonstrating actuation times under one second. Analytical and finite-element models of the valve have also been developed to explore performance and scaling issues.

High Cooling Power Density Silicon Microrefrigerator

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We fabricated a silicon microrefrigerator on a 500μm-thick substrate with the standard IC fabrication process. The cooler achieves a maximum cooling of ~ 1.2 ^{0}C, below ambient at room temperature. A 3D electrothermal model is developed to analyze the device and its material intrinsic properties. Simulations show that the cooling power density for 40x40μm^2 device exceeds 500 W/cm^2. The device has a unique 3D geometry and the current and heat spreading, distinguishing it from the conventional 1D thermoelectric devices. The 3D geometry contributes to large cooling power density, which is less dependent on substrate thickness as compared with the conventional 1D structure. Another important benefit from this geometry is that the maximum cooling exceeds the theoretical prediction in 1D geometry, $\Delta T_{max}=0.5ZT_c^2$. This 3D silicon microrefrigerator will be very useful in removing the localized hot spots thus reducing thermal design requirements for the integrated circuit chips.

Design and Simulation of Thermoelectric Heating System by Electro-Thermal Model and Graphic Diagram

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This research was aimed at designing of utilization graphic diagram for a thermoelectric heating system and simulating of operation of this system by electro-thermal model, which same as in designing and simulating of a transistor amplifier. In the design phase, the graphic diagram was simulated by PSPICE program using an electro-thermal model. In system, the heat load can be selected for designing and determining the heat exchanger value of cold side in this graphic diagram. The temperature and heat load at both cold and hot side for operation of the system at design could be simulated by electro-thermal model. The performance of the prototype system for designing and simulating was evaluated the using Melcor, CP 1.4-127-045L and varied the current input and heat exchanger at cold and hot side of the system. The results are close to the simulation of operation of this system.

Solid State Micro Climate Cooling System for Personnel Working in Indian Desert

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The physiological mechanism of human body heat dissipation triggers the central control, giving rise to increase blood flow to extremities and increased rate of sweating for cooling by sweat evaporation. At higher ambient temperature (55^{o}C); prolonged sweating causes dehydration and if auxiliary cooling is not provided the sustained dehydration leads to hyperthermia, which becomes life threatening if body temperature is not controlled. Realizing the intensity of the thermal problems faced by persons working in Indian desert regions during summer, suffer from heat disorders. R&D Division of MECON, Ranchi together with DIPAS, Delhi took up the development Solid State Micro Climate Cooling system for controlling body temperature under such conditions. Earlier attempts to develop such a device had not been successful. This paper reports technical details and performance of Solid State Micro Climate Cooling system, based on Peltier Effect and thermal impedance matching principle. The system developed is liquid based in which fluid (water) is chilled in a TE-assembly, circulated through a body suit stitched for such applications to provide adequate cooling to the body and then returned to the TE-assembly. This system operates in a closed loop. The performance of the system has been ensured by careful matching of components in an innovative design and parameters optimized through our software based on mathematical modeling of the total integrated system.

TEM Cross-Section and Planview Preparation of Bi_2Te_3 Thin Films Epitaxially Grown on BaF_2 Substrates

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Multiquantum well structures of Bi_2Te_3 are predicted to have a high thermoelectric figure of merit ZT. Structural and chemical investigations by transmission electron microscopy (TEM) are necessary and can be related to the thermoelectric properties of the material. We present preparation methods of cross-sectional and planview multilayer Bi_2Te_3 thin films and of cross-sectional BaF_2 substrates for TEM. The samples consist of 1 μm thin Bi_2Te_3 thin films or $Bi_2Te_3/Bi_2(Te,Se)_3$ superlattices epitaxially grown on BaF_2 substrates. Both preparation methods include mechanical polishing and conventional ion milling. The main problems for TEM preparation are the brittleness of the BaF_2 substrate and the weak bonding between the Bi_2Te_3 thin film and the BaF_2 substrate. Therefore, all of our cross-sectional and planview samples consist of composite structures. Cross-sectional samples of the BaF_2 substrate consist of a composite of BaF_2 glued between a silicon and $BaTiO_3$ ceramics dummy. For the preparartion of samples of Bi_2Te_3 thin films for the TEM we first glue a silicon dummy on the Bi_2Te_3 thin film and then removed the BaF_2 substrate completely. Planview samples consist of a composite of Bi_2Te_3 glued on a silicon dummy. Cross-sectional samples consists of a composite of Bi_2Te_3 thin film glued between two silicon dummies. A few results of the structural investigations by TEM are shown.

Quantitative EDX Analysis of Bi_2Te_3 in the TEM

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The chemical composition of p-type $(Bi,Sb)_2Te_3$ and n-type $Bi_2(Te,Se)_3$ Peltier devices was investigated by energy-dispersive X-ray spectroscopy (EDX) in a transmission electron microscope (TEM). The advantage of EDX analysis in the TEM is the higher lateral resolution of about 50 nm compared to a resolution of 1µm by wavelength-dispersive X-ray spectroscopy (WDX) in an electron probe microanalysis (EPMA). However, a large Bi fluorescence radiation was dedicted by hole count measurements. The chemical composition determined by the EDX analysis yielded on average 41±2 at% of Bi. The mole fraction ratio for Bi was to high and the accuracy of the measurements was not acceptable. We introduced a stray aperture to absorb the stray radiation and yield a high-precision quantitative chemical analysis. With this aperture inserted we obtained local mole fraction ratios of 40±0.5 at% for Bi. The scatter of the data decreased by a factor of 4.

Also, our investigations showed a slightly changing stoichiometry on the micrometer scale and thus confirmed the inhomogeneous chemical composition found by WDX. Our former investigations by WDX in an EPMA showed a substitution of Sb for Bi in p-type material with a large variation in stoichiometry of about 1-1.5 at%. The same behaviour was found for Se and Te in n-type material. Variations in stoichiometry on the sub micrometer scale might yield structural modulation in Bi_2Te_3 and therefore have an influence on the thermoelectric and elastic properties of Bi_2Te_3.

Electrodeposition of Bismuth Telluride Nanowires in Porous Alumina Templates

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Dense and uniform nanowire arrays of bismuth telluride (Bi_2Te_3) have been successfully electrodeposited into porous alumina templates, which have been optimized for thermoelectric performance. A pulse-potential deposition technique has been employed, resulting in increased length uniformity of the nanowires and greater control of growth rate. In this poster we present the morphology and structure of nanowires characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The Bi_2Te_3 nanowires have a high nucleation percentage, are continuous, and are highly oriented. Pristine alumina templates are critical for the control and manipulation of dense, high aspect-ratio nanowire arrays during the electrodeposition process, while thick templates are desired for practical integration into current electronics technology. Porous alumina templates have been fabricated with minimum defects, as evidenced with SEM, using a double anodization procedure and other optimized parameters. Defect-free templates 120 micrometers thick and with 40 nanometer pore diameters have been produced without the need for mechanical polishing.

Substrate Temperature Dependence of Recrystallization Process of Si-Ge-Au Amorphous Thin Films Evaluated by using PAS

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Photoacoustic spectra of the Si-Ge-Au amorphous thin film have been measured as functions of substrate temperature and annealing cycles. The Si-Ge-Au amorphous thin film was prepared by the alternating deposition of Si and heavily Au-doped Ge in ultrahigh vacuum which have intended artificial superlattice structure as deposited. The Si-Ge-Au amorphous thin films show the anomalously high thermoelectric properties such as nondimensional figure of merit ZT ~ 1000. The artificial superlattice structure of sample deposited on to room temperature substrate defuses by anneal of only 500 K-15 min. Even after degradation of the superlattice structure, thermoelectric properties change slowly with repeated annealing cycles of 900 K-10 min. Although there are no apparent differences in X-ray diffraction profiles for the amorphous thin film in this region of annealing cycles, we have successfully detected the apparent differences in photoacoustic spectra as a function of substrate temperature and annealing cycle.

Thermoelectric Properties and Thermoelectric Devices of Inn and Inon Thin Films Prepared by Reactive Radio-Frequency Sputtering

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For fabrication of thermoelectric power devices using III-nitrides, we have studied their thermal and thermoelectric properties. The III-nitride thin films of amorphous structure have been produced on SiO_2 glass substrates at 100°C using N_2 and Ar gases by reactive radio-frequency sputtering method. In particularly, for InN, the thermal diffusivity and the power factor at room temperature (RT) were 6.6×10^{-7} m^2/s and $3.5x10^{-4}$ W/mK^2, respectively. The thermal conductivity was estimated to be 2.0 W/mK using the value of the thermal diffusivity and mass density.

We also present on the devices using nitride films (~1□m). The devices are composed of a)AlInN-Chromel of 20 pairs on SiO_2 glass, b) InN-Chromel of 20 pairs on SiO_2 glass, and c) InN-Chromel of 20 pairs on polyimide film. The polyimide film substrate is suitable for the flexible devices. The maximum output power and the open output voltage of the three devices were a) $1.6x10^{-6}$W and 0.21V at the temperature difference from RT, □T = 345K, b) $3.9x10^{-6}$W and 0.22V at □T = 332K, and c) $0.33x10^{-6}$W and 0.089V at □T = 280K, respectively.

Enhancement of Seebeck Coefficient of InN Thin Films by Liquid Nitrogen Cooling Sputtering

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With the aim of fabricating a thermoelectric power device using III-nitride semiconductors, we have studied the thermoelectric properties of InN thin films prepared by reactive radio-frequency sputtering. InN films were prepared on SiO_2 glass substrates using N_2 and Ar gases. During the preparation of the samples, the substrate was cooled using liquid N_2 (LN_2) and its temperature T_s was set 140 K. The thickness of the samples was about 1 □m. Their electrical resistivity and Seebeck coefficient (□ were measured in the temperature range from 373 K to 873 K. All samples showed n-type conductivity. InN prepared by the conventional sputtering (namely, T_s = 473 K) showed at most a typical □ value of 50 □V/K with post annealing, while InN prepared by LN_2 sputtering showed a □ value of over 100 □V/K with post annealing even at 373K and 130 □V/K at 873K. The power factor was $1x10^{-5}$ W/mK^2 at 873K for InN with the conventional sputtering and $3.5x10^{-4}$ W/mK^2 at 873 K for InN with LN_2 sputtering.

Thermoelectric Properties of Insb Thin Film Grown by Metalorganic Vapor Phase Epitaxy

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We present the thermoelectric properties of InSb thin films grown by metalorganic vapor phase epitaxy (MOVPE). The MOVPE method is the supreme one to produce the devices using compound semiconductors. The InSb films (1□m) were grown on a) semi-insulating GaAs substrate, b) sapphire substrate, and c) SiO_2 glass substrate. We have targeted a new type thermoelectric device hybridized by using wide gap semiconductors of nitrides and a narrow gap one of InSb. InSb film grown on SiO_2 glass showed 150□V of Seebeck coefficient (□) and $2x10^{-3}$ W/mK^2 of power factor (P_f) at 400°C. For InSb film on sapphire, the □ and P_f were 150□V and $3.2x10^{-3}$ W/mK^2 at 400°C, respectively. For InSb film on GaAs, the □ and P_f were 190□V and $1.5x10^{-3}$ W/mK^2 at 100°C, respectively. Electron mobility of InSb grown on SiO_2 glass was 18000 cm^2/Vs at room temperature. When GaAs was used as substrate, the highest mobility of our InSb films were over 50000 cm^2/Vs at RT. Although the thermal conductivity (□) of InSb bulk single crystal is relatively high, the □ of our InSb thin films is expected to be reduced since they are thin and partially polycrystalline.

The Boundary Scattering of Phonons and the Maximum Thermal Conductivity of Bi-Sn Nanowires

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We study the electronic topological transitions of quantum Bi wire of diameters in the range 100nm-3μm doped with Sn. These transitions are induced by stretch (negative pressure) and doping.

The thermopower of these Bi nanowires show peaks of up to 80μV/K at around 40K. These peaks are related to diffusion thermopower under strong electron- and holes – boundary scattering. The thermal conductivity has not being measured. We study the prospect of Bi nanowire arrays as thermoelectric materials under conditions of long-wave phonon freezing caused by phonon-boundary scattering at the nanowires interfaces.

Seebeck Coefficient Anomaly Due to the Electron Topological Transition in Bi-Sb Wires

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This work is devoted to the investigation of the thermo- and magneto-thermoelectric properties of single Bi1-xSbx nanowires (200nm < d < 5μm) in glass coating under elastic deformations of up to 2.5% (relative elongation) in the temperature range 4.2-300K and magnetic fields of 14 T. The motivation of this work is to demonstrate the Seebeck coefficient anomaly caused by the Electron Topological Transition (ETT).

Nanowires of Bi-6at%Sb and Bi-8at%Sb are narrow gap semiconductors with Eg ~ 4meV.

Under stretch we observe a semiconductor-to-semimetal transition (ETT). This transition is monitored with Shubnikov-de-Hass oscillations, a very well known probe of the Fermi surface. We present calculations of the thermoelectric Power factor of these materials. The Seebeck coefficient exhibits a peak at low temperature that is associated with the ETT. The mechanizm for the enhancement of the Seebeck coefficient is discussed.

The work was stimulated by previous work on the low temperature thermoelectric properties of Bi1-xSbx by Red'ko N.A. in proceedings of the 14 International on Thermoelectrics. A.F. Ioffe Physical-Technical Institute. St. Petersburg. 1995, p. 82-84.

Characterization of Individual Bismuth Telluride Nanowires by Transmission Electron Microscopy

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Transmission electron microscopy (TEM) has been used to examine the structure and composition of electrochemically deposited nanowires for use in thermoelectric devices. The nanowires are doped and undoped Bi_2Te_3, and $Bi_{1-x}Sb_x$ alloys. TEM is essential for the characterization of these samples because it affords versatility in imaging, diffraction and spectroscopy at a spatial resolution appropriate for the nanoscale. This poster will present the TEM results. The nanowires are 40 nm in diameter, generally cylindrical, and have very high aspect ratios. Dark field images show that the nanowires are polycrystalline with small grains. Energy dispersive spectroscopy gives quantitative composition determination and chemical continuity along the wires. Using TEM to characterize these samples is a useful feedback method for the optimization of electrodeposition conditions.

Thermoelectric Properties of Y-Doped Polycrystalline $SrTiO_3$

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Thermoelectric properties of Y-doped polycrystalline $SrTiO_3$ ($Sr_{1-x}Y_xTiO_3$) are measured from 10K to 900K. It is found that the Y-doped polycrystalline samples show a low resistivity, $\sim 1\times10^{-5}$ ohm m and high Seebeck coefficient, ~150 μV/K at room temperature. Consequently they have a high power factor, 1.2×10^{-3} W/mK^2, defined as $PF=S^2/\rho$, where S is the Seebeck coefficient and ρ is the resistivity. Furthermore, we have observed the reduction of the thermal conductivity of $SrTiO_3$ due to the phonon scattering by Y dopant.

Thermoelectric Properties of Bi-Based Rhodium Oxides

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$NaCo_2O_4$, Ca-Co-O and Bi-Sr-Co-O have high performance thermoelectric properties, which have hexagonal CoO_2 layers as a common unit. Recently Okamoto *et al.* reported $Sr_xRh_2O_4$ with RhO_2 layers, which is isostructural to $NaCo_2O_4$. We expected a Rh oxide isomorphic to Bi-Sr-Co-O, and successfully synthesized polycrystalline samples of Bi-Sr-Rh-O. were prepared by solid-state reaction. The X-ray diffraction pattern indicates that the structure of this compound is the same structure as Bi-Sr-Co-O. The thermopower and the resistivity are 100 □V/K and 48 m□cm at room temperature, respectively. The temperature dependence of thermopower and resistivity is similar to that of Bi-Sr-Co-O. In the conference, we will also report on the doping effect on Bi-Sr-Rh-O system.

Preparation and Anisotropic Thermoelectric Properties of New Cobaltites A_xCoO_2 (A=Sr and Ca) Thin Films

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New epitaxial thin films of layered cobaltites A_xCoO_2 (A=Sr and Ca) have been prepared on sapphire substrates by rf-planar magnetron sputtering. The grown phase in the A_xCoO_2 films was found to be a monoclinic β-phase of primitive layered-cobaltites structure and the epitaxial orientation of the film could be controlled by the surface plane of the sapphire single crystals. The resistivity parallel to the CoO_2 layers $\rho_{//}$ for the β-Sr_xCoO_2 is as low as 2 mΩcm at room temperature and shows metallic behavior. The ratio of perpendicular resistivity $\rho_{\perp}$ to $\rho_{//}$ increases from 20 at room temperature to 90 at 3K. More isotropic nature was observed in the Seebeck coefficient. Parallel Seebeck coefficients $S_{//}$ of A_xCoO_2 are approximately 60 μV/K at room temperature and the perpendicular $S_{\perp}$ is about a half of $S_{//}$.

Preparation and Thermoelectric Properties of Misfit Layer Sulfides [Ln2S2]pNbS2

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We have prepared a series of misfit layer sulfides $[Ln_2S_2]_pNbS_2$, where *Ln* stands for rare-earth elements. Except for *Ln* = Eu and Lu, nearly single-phase samples are prepared. The compounds consist of an alternate stacking of a trigonal prism-type NbS_2 layer and a double layered NaCl (RS)-type Ln_2S_2 block, parallel to the *c*-axis. Three types of the stacking mode of the NbS_2 layer and the RS block have been found and they can be classified with a (3+1)-dimensional superspace group description. The thermoelectric properties of the samples were also determined. In the case of *Ln* = Yb, the samples exhibit Seebeck coefficient S~ 60 V/K, the electric resistivity = 1.9 mcm and thermoelectric power factor $S^2/$ = 1.9 x 10^{-4} W/mK^2 at 300 K.

Thermoelectric Properties and Electronic Structure of Strontium Ferrites

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Cobalt oxides have large Seebeck coefficient (□) and high electrical conductivity (□), and they are p-type materials. Since n-type metal oxides discovered up to now possess low thermoelectric (TE) properties, intensive studies have been carried out to find good n-type TE oxides. We focus on the ferrite oxide because of their lower toxicity and low cost. We synthesized polycrystalline strontium ferrites with compositions of $SrCo_xFe_{1-x}O_{3-\square}$ (x=0.0, 0.25, 0.5), and measured their □s and □s from 300K to 950K in air. The □s increased with an increasing x, but the□s did not change. On the x=0.5, the □was $1x10^4$□$^1m^{-1}$ and the □ was -20□V/K at room temperature. To discuss the transport properties of the strontium ferrites, we calculated an electronic structure using first principle molecular orbital calculation. According to the calculation, density of states (DOS) at Fermi energy (E_F) for $SrFeO_3$ is composed of Fe-4d and O-2p states. For the Co substituted one, contribution of O-2p states to the DOS at F_E increases. As a results, Co substitution increases carrier density and mobility, which is due to increase in delocalized p state at E_F.

Size Effect of *A*-site Cation on Thermoelectric Properties in n-type $CaMnO_3$ System

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The electron-doped $M_{1-X}Ca_XMnO_3$ is known to show a relatively high n-type thermoelectric performance in oxide materials. The substitution for the Ca-site by Bi presents the best figure of merit Z for X=0.90~0.95. The origin of the high performance has been reported to come from the increase of the carrier mobility due to the larger intersite distance for hopping. However, there have been no systematic investigations as for the size effect of the *A*-site cation of perovskite structure ($AMnO_3$) on the thermoelectric properties including the Ca-site substitution by divalent ions.

In this study, we investigate the relation between the ionic radius r_A of *A*-site cation and the thermoelectricity. The several series with 1.17Å≤r_A≤1.23Å of $RE_{0.10}Ca_{0.90}MnO_3$ (RE=La, Pr, Nd, Sm, Gd, Dy), $La_{0.10}(Ca_{1-y}Sr_y)_{0.90}MnO_3$ ($0.05 \leq y \leq 0.4$), $La_{0.05}(Ca_{1-y}AE_y)_{0.95}MnO_3$ (AE=Sr, Ba: $0.02 \leq y \leq 0.05$) *etc.* were fabricated by solid state reaction. The electrical resistivity □(T), thermal conductivity □(T) and thermoelectric power $S(T)$ for each sample were measured from 10 K to 300 K and the figure of merit Z and the power factor P were estimated. We also measured the Hall effect and estimated the carrier mobility. The size effects of the *A*-site cation on the thermoelectric properties were discussed.

Influence of Co-site Substitution on Thermoelectric Properties in $La_{1-x}Sr_xCoO_3$

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The $La_{1-x}Sr_xCoO_3$ system exhibits the complex magnetism and metal-insulator transition depending on the hole concentration x. Near the metal-insulator transition region (x~0.10), $La_{1-x}Sr_xCoO_3$ shows a large thermoelectric power S with a relatively low electrical resistivity □ which results in the higher figure of merit Z value (=S^2/□□□ □ the thermal conductivity) at 300 K. The Z value is higher than those of layered Co-based oxide polycrystals such as $NaCo_2O_4$ and $Ca_3Co_4O_9$ [1].

In this paper, we study the Co-site substitution by the magnetic and non-magnetic elements for the $La_{1-x}Sr_x(Co_{1-y}M_y)O_3$ system (M=Ga, Ti, Cu, Al, and Sn; x=0.15, 0.20; y=0~0.10). The relation between the magnetism and the thermoelectric properties is discussed from the viewpoint of the ionic radius and the electronic configuration of substituted elements and the average valence of cobalt.

[1] H. Fujishiro *et al.,* Proceedings ICT'03, (2003), pp.235-238 and pp.192-195.

Thermoelectric and Magnetic Properties of Layered Cobaltites: Na_xCoO_2 and $Ca_3Co_4O_9$

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Layered cobaltites have attracted much interest since the discovery of large thermoelectric power in $NaCo_2O_4$. Several layered cobaltites have been discovered and all of these compounds possess a CdI_2-type CoO_2 sheet in their structures, which is considered to be an essential constituent for realizing good thermoelectric performance. Various kinds of structural components called block layers, can be inserted between the CoO_2 sheets to stabilize the structure of cobaltites and to supply charge carriers into the CoO_2 sheets. In the crystal structure of Na_xCoO_2, randomly distributed Na layer can be regarded as a block layer. On the other hand, a block layer of $Ca_3Co_4O_9$ is a series of rock-salt-type $[Ca_2CoO_3]$ layers. In this study, the crystal structures were analyzed using a Rietveld analysis program RIETAN-2000 based upon the x-ray diffraction patterns. The electron density distributions were visualized by an elaborate method, which is a combination of the maximum entropy method (MEM) and the Rietveld refinement. The thermoelectric power, the four-probe dc resistivity, and magnetic susceptibility were measured using a homemade device, a Physical Property Measurement System (PPMS), and a SQUID magnetometer (MPMS). The effective magnetic moments of Na_xCoO_2 decrease with increasing x. This indicates that the intermediate spin state Co^{4+} in the population ratio at the *2a* site decrease with increasing a sodium content.

Temperature Dependent Resistivity and Thermoelectric Properties of $PbPd_{1-x}Cu_xO_2$

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Structure, resistivity and thermoelectric properties of $PbPd_{1-x}Cu_xO_2$ have been investigated. Single phase polycrystalline samples of $PbPd_{1-x}Cu_xO_2$ ($0 \leq x \leq 0.04$) have been prepared by solid state reaction up to x = 0.04. Structural characterization by Rietveld analysis of powder X-ray diffraction data indicates that as the Cu doping content increases, lattice parameters, *a* and *b*, increase whereas *c* decreases. $PbPd_{1-x}Cu_xO_2$ exhibits metal to insulator transition around 100K in temperature dependent resistivity measurement. This compound has a metallic conductivity above this temperature; thus, we have investigated this compound as a new candidate oxide material for thermoelectric conversion. Results from Rietveld refinement of powder X-ray diffraction data, temperature dependent thermopower and Hall effect measurements along with Cu doing effect into Pd site will be presented.

Thermoelectric Properties of $Bi_2Ca_2Co_2O_y$ Polycrystalline Textured Materials

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The texturation of $Bi_2Ca_2Co_2O_y$ (BC222) polycrystalline materials using the hot-forging technique has been investigated. We revealed a partial-melting reaction during the sintering step leading to the growth of very large plate like-grains (up to 50μm in diameter and several μm in thickness). Based on DTA/TGA, X-ray diffraction and SEM analysis, we detailed the mechanisms of reaction during the heat treatment. This liquid phase reaction represents a strongly interesting aspect to promote an efficient stacking and sliding of grains during the thermomechanical treatment. The hot-pressing conditions and grain size were shown to strongly affect the thermoelectric properties. Based on an innovative quantitative texture analysis, we established a clear relationship between the transport properties, the texture strength and the microstructure.

Study of New Thermoelectric Material, CuAlO2 using Ab-inito Calculations

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The development of ab initio calculations enable us to understand the material properties on the fundamental ground and further more to predict new materials. It is interesting to examine these powerful tools to predict and to design novel materials for thermoelectric use. Actually, there are some reports that what electronic structure bring in a good efficiency for thermoelectricity. But there are studies along with these lines. In this work, we studied conventional material, Bi2Te3 compounds and PbTe , and new thermoelectric material CuAlO2 using ab initio calculation(FLAPW).

First of all, we calculate band structure, density of states(DOS) and fermi surface. In the second place, for variable carrier concentration, we calculated carrier conductivity and Seebeck coefficient based on Mott-Jones formula.

In our calculation, we brought out why conventional thermoelectric materials have good thermoelectric properties. In good thermoelectric material, when carrier concentration vary, density of state (and fermi area) varies dramatically. Accordingly these have a large Seebeck coefficient. In our calculation, CuAlO2's Seebeck coefficient is three times as high as Bi2Te3's one.

We report, in this conference, why new thermoelectric material CuAlO2 has high Seebeck coefficient from theoretically.

Thermoelectric and Transport Properties of textured Ca-doped $(ZnO)_mIn_2O_3$ Ceramics

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The Ca-doped $(ZnO)_mIn_2O_3$ (m is an integer) ceramics were fabricated by the reactive templated grain growth (RTGG) method and their thermoelectric properties were examined. Plate-like $ZnSO_4 \cdot 3Zn(OH)_2$ particles were used as reactive templates and mixed with In_2O_3 and $CaCO_3$ powders for a stack of tapes. *In-situ* formation and the subsequent sintering resulted in the highly textured Ca-doped $(ZnO)_mIn_2O_3$ ceramics. The textured ceramics exhibited enhanced electrical conductivity when compared to that of the non-textured ceramics while the Seebeck coefficient and thermal conductivity exhibited a small anisotropy. The Ca doping effectively reduced the thermal conductivity, resulting in the improvement of the thermoelectric properties. The Ca-doped specimen along the *ab*-plane with a composite phase of $(ZnO)_3In_2O_3$ and $(ZnO)_4In_2O_3$ showed the *ZT* value of 0.31 (at 1053 K), compared with 0.23 (at 1053 K) for the non-textured one. The detailed transport properties of $(ZnO)_mIn_2O_3$ will be discussed.

Thermoelectric Properties of $Na_xCo_2O_4$/Ag Composites

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The synthesis of the thermoelectric $Na_xCo_2O_4$/Ag composites was tried by Ag powder addition to $Na_xCo_2O_4$ and subsequent mechanical grinding and sintering. Ag was hardly dissolved in the $Na_xCo_2O_4$ matrix, and the thermoelectric composites composed of the $Na_xCo_2O_4$ and Ag phases could be obtained. The electrical resistivity of the composites was significantly smaller than that of the sample without Ag. On the other hand, the composite samples showed the Seebeck coefficient larger than the sample without Ag. From these results, the power factor was significantly improved by Ag addition. However, Ag particles were coarse, about 10 μm in size in the $Na_xCo_2O_4$ matrix, and the thermal conductivity increased with increasing amount of Ag, resulting in the figure of merits of $Na_xCo_2O_4$/Ag composites almost the same as that of the sample without Ag addition. Thus, dispersion of fine Ag particles should be provided in the future in order to decrease the thermal conductivity.

Enhancement of Electrical Conductivity in Layered Cobaltite Ceramics by Texture Improvement

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We have examined the effect of texture improvement on the thermoelectric and transport properties for ceramics of $[Ca_2CoO_3]_{0.62}[CoO_2]$ (abbreviated as CCO) by applying the reactive-templated grain growth (RTGG) method using □-$Co(OH)_2$ platelets as the topotactic seeds. All the RTGG-prepared CCO ceramics showed high degrees of orientation with the Lotgering's factor reaching ~1. It was found, however, texture differences detected by the rocking curve measurement with respect to the (004) diffraction of CCO significantly affected the in-plane electrical conductivity, □$_{ab}$. An increase in the orientation degree of □-$Co(OH)_2$ templates in a green compact increased that of the resultant CCO ceramic that was formed with the templates by heat treatment. Furthermore, an increase in pressure and duration time of uniaxial pressing during the heat treatment, was found to increase the orientation degree of CCO ceramic. Other types of layered cobaltites were also (00l) textured by the RTGG method and the enhancements of □$_{ab}$ were similarly observed. The enhancement of □$_{ab}$ for the textured ceramics is attributable to the increase in the carrier mobility due to a better grain alignment in the microstructure of CCO.

Thermoelectric Properties of Oxide Added -CuAlO2

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The oxides are famous for thermoelectric materials in Japan in these years. We have investigated delafossite structure of CuAlO2 for thermoelectric material. Originally, this material has been invented as the transparent oxide of p type semiconductor (Kawazoe et al., 1997). The material was formed from Cu2O and Al2O3 by a powder metallurgical method sintered at 1473K for 16 hrs, and we added ZnO (0.01mol %) to CuAlO2. As the results, Seebeck coefficient was measured up to 700K resulting in decreasing with temperature. The values of 870 and 400 micro volts were obtained at 300K and 670K, respectively. And the most lowest electrical resistivity was the order of 0.001 Om which was too high for thermoelectric material. Therefore, the power factor was 1.0E-4. ZnO addition was not effective to improve the thermoelectricity. However, we are going to investigate another oxide and to measure thermal conductivity and Hall coefficient.

Thermoelectric Properties of $Ca_{1-x}Y_xMn_{1-y}R_yO_{3-z}$ (R=Ru, Nb) at High Temperature

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High figure of merit, ZT~1, has been already achieved for some p-type thermoelectric oxide materials, but not for n-type ones yet. Perovskite-type $CaMnO_3$ is one candidate of n-type thermoelectric oxide materials. The electrical conductivity and Seebeck coefficient of $Ca_{1-x}Y_xMnO_{3-z}$ reported for x=0.1 by two groups were scattered each other, and thermal conductivity was not measured. In this study, the electrical conductivity, Seebeck coefficient and thermal conductivity of $Ca_{1-x}Y_xMnO_{3-z}$ (x=0-0.30) were systematically measured in the temperature range from 300 to 1273 K to find the optimum composition and temperature of the highest Z value. Higher doped samples exhibited the metal-insulator transition in the relation between electrical resistivity and temperature, and the transition temperature increased with increasing x. The absolute value of Seebeck coefficient and the thermal conductivity decreased with increasing x content. The highest figure of merit of Z=1.77×10^{-4} K^{-1} was obtained for x=0.15 at 1273 K. Furthermore, the thermoelectric properties of $Ca_{0.85}Y_{0.15}Mn_{1-y}R_yO_{3-z}$ (R=Ru, Nb) measured will be compared with those of other similar perovskites.

Theoretical Investigation of Substitution Effects on the Electronic Structure and Transport Properties of Layered Cobalt Oxides NaxCoO2

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The layered cobalt oxides NaxCoO2 and its analogs have shown to be promising thermoelectric materials. In the attempt to increase the figure of merit, the effects of substitution on different sites of g-NaxCoO2 have been studied extensively by experiments. There are, however, few theoretical investigations, especially first-principles electronic structure calculations to elucidate the substitution effects. In this study, the first-principles density functional theory is employed to investigate the substitution effects on the electronic structures of g-NaxCoO2 in the paramagnetic states. Using the standard kinetic theory the Hall concentrations and Seebeck coefficients were calculated. To further understanding on the contribution of spin entropy, which has been suggested to dominate the thermopower in NaxCoO2, spin-polarized calculations with different sites substitutions, in particular, the non-magnetic element substitutions on Co-sites were also performed.

Spin State Transition in Ca-doped $Na_{0.7}CoO_2$: Muon Spin Rotation and Relaxation in the Layered Cobaltites with the Nominal Covalence below 3.25

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In order to clarify the origin of the transition around 300 K in Ca-doped $Na_{0.7}CoO_2$, magnetism of $(Na_{0.7-y}Ca_y)[CoO_2]$ with y=0.05 and 0.1 was investigated by a positive muon spin rotation and relaxation (μ^+SR) experiment. According to a weak transverse field μ^+SR measurement, it was found that the spin state of the Co ions in $(Na_{0.6}Ca_{0.1})[CoO_2]$ changes around 300 K; that is, the exponential relaxation rate $-vs.-T$ curve exhibited a large maximum around 300 K with an accompanying small change in the muonic Knight shift, whereas no changes in the asymmetry, as in the case of $[Ca_2CoO_3]_{0.62}[CoO_2]$ around 400 K.

Although the spin-density-wave (**SDW**) state exists for Na_xCoO_2 with x>0.75 at low temperatures, zero-field μ^+SR spectra in the Ca-doped samples showed no muon precessions down to 1.8 K but fast relaxations. This is probably because the Ca^{2+} ions in the Na planes alter the charge and/or spin distribution in the CoO_2 planes. As a result, the **SDW** order is strongly hindered, while the nominal Co valence is decreased below 3.25.

Reversible Thermoelectric Nanomaterials

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The central difficulty in the design of high efficiency thermoelectric materials is the proportionality between the electronic thermal and electrical conductivity in bulk materials, given by the Wiedemann-Franz law. We prove that the ratio of the thermal and electrical conductivities vanishes in thermoelectric nanomaterials with delta-function electronic density of states (DOS) subject to finite opposing thermal and potential gradients. In this analytically tractable limiting case it can be shown that the thermopower approaches a theoretical maximum and the efficiency is equal to the Carnot limit in the absence of phonon heat leaks.

Using a simple numerical model, we also show that for constant electrical and lattice thermal conductivity, the higher figures of merit obtained in nanomaterials with delta-like DOS can be attributed primarily to the break-down of the Wiedemann-Franz law, rather than to their increased thermopower, leaving the figure of merit of thermoelectric nanomaterials essentially limited only by finite thermal conductivity due to phonons.

This work may assist in understanding recent high-profile experimental results showing greatly enhanced thermoelectric figures of merit in nanomaterials such as quantum-dot superlattices, thought to have delta-like electronic DOS as a result of quantum-confinement effects.

A Challenge to Create Novel Oxide Thermoelectrics

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Oxide materials had been ignored for a long time in the thermoelectric community, but the discovery of Na_xCoO_2 as a strong candidate material in 1997 lit a fire on the researchers' mind to explore high-efficiency oxide materials. $Ca_3Co_4O_9$, ZnO(Al), $Zn_5In_2O_8$ are some examples so far found, but they still show rather low figures of merit (ZT <1) and remain to be further improved, although they many advantages for high-temperature power generation, such as non-toxicity, thermal stability and oxidation resistance.

Challenges to create novel oxide thermoelectrics have been motivated recently and investigations from various viewpoints of materials design are being carried out extensively. Especially, as it is difficult to control an electronic system and a phonon system simultaneously in a single crystalline field, a complex crystal composed of more than two nanoblocks with different compositions and structural symmetries (we call it a "hybrid crystal") is considered to be effective to control electron transport and phonon transport separately enhancing the total conversion efficiency. Nanostructure control through nanoblock integration would be promising for developing novel oxide thermoelectrics.

Superlattice Thin-film Thermoelectric Material and Device Technologies

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Nanoscale superlattices in the Bi_2Te_3-material system, based on the concept of phonon-blocking-electron transmission, have demonstrated high figure-of-merit (ZT~2.4 at 300K) at the individual thermoelement level as well as very high cooling power density, extremely rapid cooling or heating and also same-or-better functionality, as quantified by heat pumping, with $1/40000^{th}$ of the active-material-usage compared to state-of-the-art bulk thermoelectric technology. The relatively inexpensive but microelectronics-type technologies used for the superlattice thin-film device fabrication also lend themselves suitable for flexible module design as well as for reductions in design cycle time and cost. Thus efficient thermoelectric refrigeration and air-conditioning using these high cooling power density superlattice devices, enabled further by reduced costs for heat-exchanger components, are likely in the long term.

A detailed temperature dependence of the ZT of these materials would be presented in range of 100K to 400K, with a phenomenological understanding of the properties. We will highlight the state of transition of these materials and early device prototypes to module-level performance for both cooling and power conversion. We have determined a ZT>1.3 in fully fabricated p-n couples, using p-type Bi_2Te_3/Sb_2Te_3 and n-type $Bi_2Te_3/Bi_2Te_xSe_{3-x}$ superlattices, from heat-to-electrical power conversion efficiency measurements. A concept denoted as High Active-Flux, Low Input/Output Flux (HAF-LIOF) has been developed and validated for the use of the high heat-flux (>2000 W/cm^2) superlattice devices, with relatively simple heat-exchanger systems for power conversion. The cooling performance of similar devices has been encouraging as well, with cooling power densities in excess of 100 W/cm^2 at the module level. The improvement in cooling performance has involved solving a series of engineering issues related to the intrinsic superlattice thermoelectric couple as well as that between the couple and the system-interfaces. Some of the challenges that remain to be addressed in the full development of this technology will be discussed.

Ideas and progress in transitioning the Bi2Te3-based superlattice materials to 1-dimensional quantum wires would be presented. We will highlight some of our next generation superlattice materials for medium and high-temperature applications. In addition, we will present our approach to applying the Bi2Te3-based superlattice technology with other high-temperature thermoelectric device components for efficient waste-heat-recovery in many systems. Our approach to integrating the high-performance Bi2Te3-based superlattice devices with PbTe-based and SiGe-based devices for obtaining higher overall efficiencies, potentially in excess of 20%, as well as power densities in excess of 5 W/cm2 would be covered.

Standardisation in Thermoelectric Transport Properties Measurements – an Update on the Cardiff NEDO Laboratories, DLR Cologne and University of Aarhus program

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An overview of recent activities in standardising thermoelectric transport measurements between Cardiff, NEDO laboratories (UK), DLR Cologne (Germany) and a commercial Physical Properties Measurement System (PPMS) at the University of Aarhus (Denmark) is described. Both absolute and relative standardisation (through round robin testing) were employed using certified reference materials and samples of thermoelectric materials manufactured in-house. Standardisation of thermal conductivity measurements using the PPMS in particular showed significant deviation from expected values above room temperature. It is appears these deviations may be due to incorrect estimation of sample heat loss corrections (calculated by the PPMS software) and this is demonstrated by external adjustment of the heat loss correction parameters for several different samples using a fixed scaling factor. Such tests are expected to encourage further such standardisation to be carried out between thermoelectric semiconductor research laboratories, thus increasing confidence and traceability of published data.

Thermoelectric Properties of $CaPd_3O_4$-Based Oxides

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$CaPd_3O_4$ is a semiconductor with a small energy gap of less than 10 meV, in which electrons and holes can be doped through partial substitution for Ca. For hole doping, we have found that Li-substituted samples show considerably good thermoelectric properties, whose power factor is comparable to that of polycrystalline samples of Na_xCoO_2. We have further found that Bi substitution can supply electrons, though the mobility still remains low. Most unexpectedly, the band gap can be controlled by a proper substitution for Pd, and the thermoelectric properties are much improved by partial substitution of Co for Pd. The thermoelectric properties and electronic states of $CaPd_3O_4$ will be quantitatively discussed.

Solid-Phase Epitaxial Film Growth of Thermoelectric Oxide Semiconductor, Na_xCoO_2

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High-quality epitaxial films of *p*-type thermoelectric oxide conductor, Na_xCoO_2, were successfully fabricated on a (111)-oriented yttria-stabilized-zirconia (YSZ) and a (0001)-oriented □-Al_2O_3 substrates by solid-phase-epitaxy (SPE) at 700 °C using (111)-oriented epitaxial CoO films grown by a pulsed-laser deposition (PLD) as template and $NaHCO_3$ powder as Na^+-source. Na_xCoO_2 was formed by lateral solid-phase intercalation of Na^+ from $NaHCO_3$ into Co_3O_4 epitaxial layer, which was formed by thermal oxidation of CoO during heat treatment. Epitaxial relationship between Na_xCoO_2 and YSZ, evaluated by high-resolution X-ray diffraction (HR-XRD) and high-resolution electron microscope (HREM), was (0001) $[1\ 1\ \bar{2}0]_{NaxCoO2}$ || $(111)[110]_{YSZ}$. Pendellosung fringes due to interference of X-ray were clearly seen around 0002 Bragg reflection peak of Na_xCoO_2. Electrical conductivity (□), carrier hole concentration (n_h), Hall mobility (□$_{Hall}$) and Seebeck coefficient (S), and power factor (S^2□) of $Na_{0.86}CoO_2$ epitaxial film (25 °C) were 1,200 Scm^{-1}, 4.0 x 10^{21} cm^{-3}, 2.0 $cm^2V^{-1}s^{-1}$, +120 □VK^{-1}, and 1.6 x 10^{-3} $Wm^{-1}K^{-2}$, respectively, which were comparable to those of bulk single-crystalline Na_xCoO_2.

High-Temperature Thermoelectric Performance of N-type Degenerate Semiconducting Titanate; Heavily-Nb-doped SrTiO3

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Degenerate oxide semiconductors composed of transition metals with d-orbitals forming the band edges would be promising candidates for thermoelectric semiconductors because rather large density-of-states of d-orbital generates large thermopower as compared to s- or p-orbitals. In order to examine this hypothesis we have chosen Nb-doped $SrTiO_3$ (STO / CBM: Ti 3d t_{2g} / VBM: O 2p) as an *n*-type degenerate semiconductor and measured its thermoelectric properties at high temperatures.

The carrier concentration increased proportionally with increasing Nb-concentration and reached ~ 2 x 10^{21} cm^{-3} when 10% Nb was doped, while Hall mobility was almost independent of Nb-concentration (~ 1 $cm^2V^{-1}s^{-1}$). The carrier concentration decreased drastically to less than 10^{17} cm^{-3} when the sample was annealed at elevated temperatures above 400^{o}C in air, but remained unchanged when it was annealed under Ar or vacuum at temperatures even as high as 800^{o}C. The electrical conductivity decreased proportionally to ~ $T^{-3/2}$, suggesting that ionized impurity scattering is dominant. The absolute value of Seebeck coefficient increased proportionally from 50 to 150 μVK^{-1} with increasing temperature at 25-800^{o}C, while thermal conductivity decreased proportionally to T^{-1} from 6 to 3 $Wm^{-1}K^{-1}$. The highest ZT value obtained was 0.13 at 800^{o}C for 10% Nb-doped STO.

Texture-Properties-Microstructure Relationship in Highly Oriented $Ca_3Co_4O_9$ Bulk Materials

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The $Ca_3Co_4O_9$ (Co349) phase interests many researchers due to its relative good thermoelectric performance and resistance to moisture and humidity. However, to consider the introduction of this material in power generation, the performances have to be improved. One of the well-known ways for the enhancement of transport properties consists of the alignment of plate-like grains in the bulk materials due to the highly anisotropic properties of the Co349 layered structure. In that case, a quantitative texture analysis is required to establish clearly the texture-physical properties-microstructure relationships for a best understanding and design of improved bulk thermoelectric materials. X-ray and neutron diffraction measurements, based on the acquisition of several 2θ-scans for various χ angles, were used to calculate the orientation distribution and related normal and inverse pole figures. It revealed a real interest to quantitatively determine the fibre texture strength in Co349 textured ceramics. Different processed materials, synthesised by the magnetic grain alignment and hot-pressing methods, were compared in terms of physical properties and texture strength.

Preparation and Thermoelectric Properties of High Oriented $Na_xCo_2O_{4-\delta}$ Ceramics by Spark Plasma Sintering Method

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The preparation of highly-textured $Na_xCo_2O_{4-\delta}$ ceramics and their thermoelectric properties have been reported. Plate-like $Na_xCo_2O_{4-\delta}$ particles were synthesized from the solution consisted of metal salts, citric acid, organic solvents and H_2O. $Na_xCo_2O_{4-\delta}$ ceramics was prepared by Spark Plasma Sintering (SPS) process which is a new type sintering method for this material. Plate-like pure phase $NaCo_2O_{4-\delta}$ was obtained from the solution of Na : Co = 1.4 : 2 by heat treatment at 1173K for 1h in air. A few amount of Na could be realized to form $NaCo_2O_{4-\delta}$ and a large amount of Na was localized at grain boundary or removed from the powder during heat treatment at high temperature for long time. Average diameter and thickness of obtained plate-like particle was 4□m and 1□m, respectively. The grains could be oriented easily by application of uniaxial pressure. The ceramics of a high density (relative density to single crystal 96%) and a high orientation (Lotgering factor 0.71) were obtained by the SPS method at 1073K (SPS temperature) for 1min, 29.4MPa (uniaxial pressure), in Ar atmosphere (atmospheric pressure). These ceramics showed highperformancein thermoelectric properties, that is in-plain resistivity 2.35m□cm, seebeck coefficient 120.7□V/K and power factor 6.20□W/cmK^2.

Relationship between the Structural Dimensionality and the Thermoelectric Properties in Cobalt Oxides

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Recently, a renew of interest in the cobaltites has been motivated by the discovery of superconductivity in $Na_{0.3}Co_2O_3(H_2O)_{1.3}$ [1] and by a large figure of merit in $NaCo_2O_4$, misfit cobaltites and perovskites. The origin of these thermoelectric properties can be explained by the coexistence of Co^{3+} ($3d^6$) and Co^{4+} ($3d^5$) in low spin (LS) state which creates a large entropy and induces a large thermopower (TEP). Due to the fact that cobaltites are strongly correlated electron system, the spin degeneracy of Co^{3+} and Co^{4+} and the ratio between them affect S [2]. Therefore, we have attempted to study the TEP of cobaltites in different structure and dimensionality.

The 1D $A_3BB'O_6$ family exhibits fascinating magnetic properties. The structure consists in chains of alternating prismatic and octahedral sites. The magnetic behaviour in our $Ca_3Co_2O_6$ crystals can be described as ferromagnetic S=2/S=0 chains on an antiferromagnetic Ising triangular lattice. This compound exhibits a large TEP value (S_{300K}~ 450 $\mu V.K^{-1}$) and a resistivity of 50 Ω.cm, 1,000 times larger than that of the misfit cobaltites. To modify the cobalt valency and decrease the resistivity, substitutions of one cobalt per Ir^{4+} or Rh^{4+} have been attempted. We have also replaced the Ca per Sr in order to weaken the AF coupling between chains. The perovskite $LaCoO_3$ presents interesting electronic and magnetic properties. It exhibits a spin state transition from Co^{3+} LS to Co^{3+} IS at 100K. The TEP is positive and very high ~600$\mu V.K^{-1}$ [3] at 300K. Substitutions at the A-site with Ce^{4+} or Th^{4+} have been made to try to generate a n-type cobaltite by creating Co^{2+} in the Co^{3+} matrix. The S values indicate a clear change of the nature of the charge carriers from p-type for $LaCoO_3$ (S~600$\mu V.K^{-1}$) to n-type for $La_{0.99}Ce_{0.01}CoO_3$ (S~-300$\mu V.K^{-1}$). A similar behavior is obtained as we substitute the B-site with tetravalent cations Ti^{4+}, Sn^{4+} and Mn^{4+}. Thus the substitution with a tetravalent cation on the A- or B-site changes drastically the sign of the TEP and the carriers nature. Finally new layered hydroxide cobaltites which belong to the family of the layered Ruddelsen Popper (RP) type phases have been stabilized in the system Sr-Co-O. The perovskite blocks are sandwiched between the $[SrO]_2$ NaCl-type, insulating layers which allows to modify the dimensionnality of the structure. The dehydratation of these new compounds allows to prepare Co^{4+} rich new RP cobaltites which properties will also be shown.

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Physical Principals of Thermoelectric Converter Based on Sorting of Charge Carriers in Energy by Phonon Drag in p-n Junction

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The new mechanism of thermoelectric power generation in p-n junction is suggested. The sorting of charge carriers in energy by electron-phonon drag is the basis of it.

It is well known that phonon heat flux can generate electric current in certain cases due to transmission of direct momentum to the charge carriers in processes of mutual scattering (thermo-e.m.f. caused by electron-phonon drag). Besides, a spatial sorting of carriers in energy appears in the presence of this electron-phonon drag. This effect has to be displayed most strikingly in the semiconductors with the special heat boundary conditions (electron boundary conditions are adiabatic, and phonon boundary conditions are isothermal).

Calculations are carried out in two-temperature approximation with different electron and phonon temperatures. It is shown that the electron temperature difference at the hot and cold semiconductor sample can exceed the temperature difference of external heater and cooler due to the presence of the electron-phonon drag.

Percolation Effects in Impurity Subsystem of Crystal and Controlling of Thermoelectric Properties of Solid Solutions

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One of the basic methods of enhancing the thermoelectric figure of merit of materials is formation of solid solutions. For a number of solid solutions we have experimentally observed anomalies in the concentration dependences of different properties, in particular the thermoelectric properties, in the range of impurity atom concentration of 1-2 %. We have suggested that this phenomenon is of universal character, and in any solid solution there is a critical range in the vicinity of the percolation threshold, where a qualitative change of the solid solution state, associated with the formation of percolation channels, occurs. However, up to now, the existence of such critical phenomena has not been taken into account when developing new thermoelectric materials.

In the present work, new experimental data proving the existence of anomalies in the concentration dependences of the thermoelectric properties in IV-VI-based solid solutions are reported. The behavior of the thermoelectric properties within the critical range is analyzed and corresponding theoretical estimates are made. It is shown that one can significantly enhance ZT in anomalous regions. It is assumed that the observed effects can significantly influence the properties of nanostructures in which particles of a second phase play the role of impurity atoms.

Theoretical Studies on the Thermopower of Semi-Conductors and Low Band Gap Polymers

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A computational scheme for the interpolation of electronic bands for accurate numerical differentiation is described. This scheme was implemented within the kinetic theory for the calculation of the Hall coefficient and Seebeck coefficient of crystalline materials. This method was applied to a variety of materials including semiconductors, alloys and polymers et al. In particular, we studied the mechanism for pressure-induced changes in the thermopower of AuIn2 and investigated the possibility of using low band gap polymers as potential high efficient thermoelectric materials.

Barrierless Thermoelectric Cooling and Heating on Contact of Two Conducting Mediums

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Both majority and minority charge carriers exist in the n-and p-branches of a thermoelectric module when the electric current is flowing through it. In traditional thermoelectric modules these branches are closed on the metal plates contacting with external heat reservoirs. The electron transition from the n-brunch in the metal is determined mainly by a surface electric resistance. The electrons pass into the metal freely at the perfect electric contact.

Situation for holes in a p-branch is essentially other. At any surface resistance holes do not pass in metal. At presence of an external electric field the whole concentration increases at the hot contact and decreases at the cold contact. By this reason the holes become nonequilibrium. For maintenance of stationary process bulk and surface recombination processes arise providing an electric current of majority carriers in the p-branch.

At infinity strong bulk and/or surface recombination rates the whole electric current is maximal and the contribution of minority carriers is negligible (a well-known case). In the opposite case of infinitely small recombination rates the whole current practically absent, and the charge and energy transport is carried out by minority carriers (electrons) in the p-branch. In this case the Peltier thermal flux changes its direction what leads to another work regime of the thermoelectric module. Parameters of thermoelectric module undergo changes in this case as well as in the general case of the finite values of the recombination rates.

The detail physical ideas of the specified phenomenon are presented, and criteria are formulated at which influence of nonequilibrium carriers is most essential.

The Role of Recombination Processes in Seebeck Effect – Application of Gurevich Theory [1] on $Cd_{1-x}Zn_xTe$

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The lifetime of carriers represents an important parameter of radiation detectors which is characteristic for them. Usually the current experimental technique for their measurement makes use of different experimental methods, as photoconductivity. Very often the product $\mu\tau$ of mobility μ and lifetime τ is introduced as a criterion for the semiconductor suitability of radiation detection.

In our paper we have focused on lifetime determination from common experiment performed on p-Cd0,96Zn0,04Te – temperature dependence of Hall and Seebeck effect and electrical conductivity. The evaluation of our experiments was done on the basis of the new theory of Yu. Gurevich et al [1]. The theory is formulated for a bipolar semiconductors and brings expressions for Seebeck coefficient under the assumption that bulk and surface recombination mechanisms operate.

T [K]	300 K	250 K	200 K	150 K
Seebeck coefficient	0,9 mV/K	1,2 mV/K	1,5 mV/K	3,2 mV/K
Lifetime	$8{,}4\ 10^{-4}$ s	$8{,}2\ 10^{-4}$ s	$8{,}1\ 10^{-4}$ s	$9\ 10^{-4}$ s

The concentration of holes in this sample is $1{,}6.\ 10^{16}$ cm^{-3} and activation energy is 0,26 eV. With agreement with [2] no phonon drag effect is participate.

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Advanced Thermoelectric Micro Coolers

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Many electronic and electro-optic components need cooling or temperature control to ensure their operation life and high performance. If the necessary temperature is accessible thermoelectrically, this technology proved to be the best solution providing quick cooling at relatively low cost and exceptional reliability.

The paper represents farther progress in developing cascade thermoelectric micro coolers (TECs) destined for thermal management of electro-optic components. The means to increase TECs efficiency and their correlation with cooled objects on dimensions and heat flux densities are considered. The use of cooled intermediate radiation shields in multi stage TECs is studied as a mean to considerably lower attainable cooling temperatures. Novel configurations of cascade TECs destined for low temperature cooling infrared detectors and sensors, focal plain arrays and X-ray detectors are shown and their tests results are represented.

Large Positive Thermopower of Single Bismuth Nanowires

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We have studied the magnetic-field dependence of the thermopower and resistance of glass-coated Bi wires with diameters d = 100 - 200 nm. These nanowires have anomalously large values of the zero-field thermopower (~ + 100 μV/K) and high effective resistivities (ρ ~ 100 μΩ cm) at relatively low temperatures, but their frequencies of Shubnikov-de Haas oscillations remain those of bulk Bi. The intensities of magnetic field at which the size-effect features appear on the magnetothermopower and magnetoresistance curves are essentially the same and corresponds to a value at which the diameter of hole cyclotron orbit equals d. Our analysis shows that the anomalous positive thermopower has a diffusion origin and is a consequence of the microstructure rather than the result of the surface scattering effects. The contribution of phonon-drag effect was clearly observed only in micron wires with a higher crystalline perfection (ρ < 10 μΩ cm). We found that the hole carriers play a more important role in determining the transport properties of pure Bi nanowires than generally thought. It is shown that the nanowire characterization is crucial in relating the physical models to real sample properties.

Magneto-Seebeck Coefficient Measurement of Bismuth Micro-Wire Array Under a Magnetic Field

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Magnetic field and temperature dependences of magneto-Seebeck coefficient by use of bismuth micro-wire array were measured. A poly-crystalline bismuth micro-wire array was fabricated with grass template (a hole of 25 micrometer diameter and a 1millimeter length) and formed by polishing. The grass template was dissolved by hydrogen fluoride and the both were revealed from the grass template. The both edges were bonded with the copper electrodes by using silver paste. The wire array structure has the potential to eliminate the geometry effect in a magnetic field and provide enhanced thermoelectric properties without quantum effects. The mangeto-Seebeck coefficient measurement is very important since the Seebeck coefficient is used at the second power to calculate the figure of merit. We will present experimental results of the wire array sample and how to improve the magneto-Seebeck coefficient by using from Boltzmann equation in relaxation time approximation by assuming scattering process of the carrier.

Structural Analysis of Bi_2Te_3 Thin Films and Superlattices Epitaxially Grown on BaF_2 by Transmission Electron Microscopy

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The microstructure of cross-sectional and planview Bi_2Te_3 thin films and of cross-sectional BaF_2 substrates were investigated by transmission electron microscopy (TEM). The samples consisted of 1 µm thin films of (001) oriented (a) Bi_2Te_3 and (b) $Bi_2Te_3/Bi_2(Te,Se)_3$ superlattice with a layer thickness of 12 nm epitaxially grown on a (111) oriented BaF_2 substrate. All thin films showed a dislocation density of 10^{10} cm^{-2}, more than 10 times larger as in bulk material. There are 10-80 nm small precipitates with a density of $3 \cdot 10^{14}$ cm^{-3}. The BaF_2 substrate showed a dislocation density of less then 10^8 cm^{-2}, 5 nm small agglomerates of point defects with a density of $2 \cdot 10^{16}$ cm^{-3} and precipitates 10 nm in diameter with a density of $6 \cdot 10^{15}$ cm^{-3}. The superlattice interfaces are strongly bent in the region of the dislocations and precipitates. All thin films showed a structural modulation parallel to the (1,0,10)-planes with a period of 10 nm. This domain-like defect structure has also been observed in Bi_2Te_3 bulk material and turns out to be of general character for Bi_2Te_3. The domains showed no significant bending due to the defects or the superlattice and vice versa. Multiquantum well structures of Bi_2Te_3 are predicted to have a high thermoelectric figure of merit ZT. The superimposed elastic structure might also affect significantly the thermoelectric properties yielding a one dimensional or zero dimensional behaviour resulting in anisotropic transport coefficients in the basal plane.

Thermoelectric Properties of Bi-Based Thin Film Structures

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The prediction of a possible significant enhancement of the thermoelectric figure of merit in Bi quantum wells with decreasing quantum well width draws attention to a detailed study of the thickness dependences of the thermoelectric properties of Bi-based thin film structures.

In the present work, thin Bi films and PbTe/Bi two-layer structures with fixed PbTe layer thicknesses and different Bi layer thicknesses grown by thermal evaporation in vacuum on mica substrates in the (111) direction were studied. The dependences of the thermoelectric properties on the Bi layer thickness and temperature (80-300 K) were obtained. The influence of the Bi layer thickness on the behavior of the temperature dependences of the thermoelectric properties was established. It was found that in the PbTe/Bi structures, as well as in the Bi thin films structures, the thickness dependences of the thermoelectric properties exhibit oscillatory behavior caused by quantum size effects.

The experimental data were analyzed within the framework, both of a model assuming an infinite barrier and the complete confinement of the wave function within the quantum well and of the model assuming non-identical and finite barrier heights and widths. It was shown that in PbTe/Bi structures one can attain higher values of the thermoelectric power factor than in thin Bi films.

A Novel cCncept of a Brick Energy Converter, Applicable to Intelligent Building Construction

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From the use of a semiconductor ceramic enamel, that gathers functional features of the anti-electrostatic materials, applied to a porcelain surface, it has been obtained a new structure performance that shows new improved electrical characteristics, and a resistance of 1K ohms. The work has been done on a thermal ceramic tile that takes advantage of all mentioned characteristics and generates heat by joule effect.

With the use of different semiconductors and ceramic materials proper for such task, it could be controlled the electrical parameters and the storage of the heat, and the generation of the thermal heat fluxes. If we applied a thermoelectric structure taking advantage of the Seebeck effect, within a multi-layer ceramic system at the reverse faces of the tile, it is possible to generate electricity, and for such decreasing the electrical expenses to feed the current to the tiles.

By the design and use of an electronic control system, it could be allowed the distribution of the obtained current, and generate controlled, voltages, currents, and ranges of power, facing dynamics, with unwanted variations.

Thermoelectric Low-Energy Generator for High Dynamic Applications

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In very many applications for fluid control process, electrical process, air process, it is required the use of electro-valves, relays, switchers, and linear control systems that requires a fast response with a high dynamics. A thermoelectric generator could supply the energy that will activate this component, as they do have a low response general speaking, that could be implemented with the power that is needed to be supply.

At this work is has been developed a structure of the thermoelectric generator that lowers down the inertia problem, adding a high changing speed between one high tension surface and other low tension area.

There is also an option to implement with a control system, the adequate regulation allowing the stabilization of the output voltage of the thermoelectric devices, as well as to supply the capacity loads with a constant current.

The working model structure of the thermoelectric generator, with an information source, and with the characteristics parameters, will report all physical properties that could be change to obtain a better global working performance, that lead us to obtain the required dynamical demand according to the application loads as state.

High-Performance Thin-Film Superlattice Technologies for Thermoelectric Cryogenic Cooling Applications

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The electronics industry has a need for solid-state cryogenic cooling techniques that can cool targets down to the range of 100K. Such applications include low noise amplifiers, infrared focal-plane arrays, and high temperature superconducting electronics. In addition to sustaining a large temperature gradient, these solid state devices need to be capable of handling large heat fluxes and, in some cases, have a very small height profile. Current bulk thermoelectric devices are limited to a cold-side temperature of about 170K, are capable of only small heat fluxes and can have heights in the range of several centimeters. Thin-film nano-structured materials offer the potential to dramatically enhance the cryogenic performance of thermoelectrics over that of state-of-the-art alloy materials. Superlattice materials are not only capable of having a significantly lower cold-side temperature but because of their thin-film nature are also capable handling much higher heat fluxes and can be made with a significantly lower profile. We will discuss the results of cryo-temperature ΔT and ZT measurements done on superlattice and state-of-the-art bulk devices, where an improvement of about 2 over bulk materials has been noted at 150K. A proposed explanation for this improvement will be presented. We will also discuss the results of COP measurements indicating that these same superlattice devices are capable of moving heat fluxes greater than 100W/cm^2 at the module level for the bottom stage of the device. Additionally, we will present results on the first multi-stage thin-film superlattice cryo-cooling devices.

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A Hybrid Photovoltaic-Thermoelectric Roof Solar Collector

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This paper presents a numerical investigation on attic heat gain reduction and air change rate by using a hybrid system between the photovoltaic (PV) and thermoelectric (TE) modules integrated into a conventional roof solar collector (RSC), namely, Hybrid Photovoltaic Thermoelectric Roof Solar Collector (PVTE-RSC). The PV and TE modules are used to generate a direct current in order to drive a ventilating fan for cooling of the cold side TE modules and, therefore, enhancing the attic ventilation as the ceiling heat transfer rate through attic ceiling is reduced. During daytime, TE modules provide a direct current for a ventilation fan whilst the PV modules generate an electricity for batteries charging. The electrical power from the batteries bank is supplied to run a ventilation fan in either during nighttime or when the power of system is not enough to run ventilation fan at a starting point. This operation is controlled by the balance of system (BOS). Consequently, the system is expected to operate continuously 24 hours a day.

Simulation modules have been developed and implemented by using the transient simulation program (TRNSYS) in order to simulate a hybrid photovoltaic-thermoelectric roof solar collector system. The simulation results i.e. the electrical output produced by the PVTE-RSC, attic heat gain reduction and air change rate are presented and discussed in this paper.

Thermoelectric Properties of Textured $Ca_3Co_4O_9$ Prepared by Large Grain Sized Powder

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The layered-structural $Ca_3Co_4O_9$ (Co-349) exhibits promising thermoelectric properties in the viewpoint of practical use as thermoelectric power generation. For that purpose, highly grain-aligned polycrystalline bulk materials are required because of its anisotropic transport properties. Powders with different grain sizes, grown in a K_2CO_3-KCl solvent, were used to synthesize hot-forged Co-349 compounds. Neutron diffraction experiments evidenced the effect of grain size on the development of the *c*-axis grain-alignment. The electrical conductivity in the direction perpendicular to the hot-forged axis was improved for higher degrees of orientation and larger grain sizes. Since the resistivity was reduced without deterioration of the Seebeck coefficient, the power factor of the Co-349 sample was improved.

Reduction of Thermal Conductivity by Enhanced Phonon Scattering in Oxide Materials with Nanovoid Structure

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Reduction of the thermal conductivity by nanosized pore (nanovoid) structures was investigated for ZnO-based thermoelectric oxide, for which we have reported the largest electrical power factor of all oxide materials to date. Commercially obtained polymethylmethacrylate (PMMA) particles of 150 nm in average diameter were added as a void forming agent (VFA) into the starting powder mixture of $Zn_{0.98}Al_{0.02}O$ before sintering under inert atmosphere at 1400 °C, which composition has shown the best performance in the Al-doped ZnO system. The sintered samples showed a marked suppression in the thermal conductivity, as well as negative maxima of the Seebeck coefficient near 600 °C. It was revealed that formation of a dense ZnO matrix before burning away the VFA is a key to overcome unfavorable decrease in the electrical conductivity. The nanovoid structure of the sample thus obtained resulted in the electrical conductivity virtually unchanged over the whole temperature but the thermal conductivity reduced by 35% at room temperature and by 30% even at 760 °C.

Thermoelectric Properties of $Ba_yCo_4Sb_{12}$-based composites

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$Ba_{0.28}Co_4Sb_{12}/Si_3N_4$ and $Ba_yCo_4Sb_{12}/C_{60}$ composites have been synthesized by a solid state reaction and Spark Plasma Sintering (SPS) technique. We observed that a part of barium in filled skutterudite reacted with fullerene to form barium fullerides. Si_3N_4 and barium fullerides were dispersed mainly on the grain boundaries. The electrical conductivity and thermal conductivity decreased with increasing Si_3N_4 and fullerene contents. A significant increase in thermopower at a sufficiently high content of dispersed particles was achieved near room temperature. We attributed the enhanced thermopower to the grain-barrier scattering-dominated carrier scattering. Higher ZT values could be obtained by this composite approach with an appropriate Si_3N_4 or C_{60} content.

Structural and Thermoelectric Properties of Undoped PbSe Epitaxial Films Alloyed with Tin

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IV-VI-compounds are well known materials with favourable thermoelectric properties at elevated temperatures (~700 K). Using related mixed crystals the thermoelectric properties can be optimized due to alloy scattering which leads to a decrease of the thermal conductivity without changing the other thermoelectric properties significantly. This method is well known as Joffe concept. The Joffe concept is about 50 years old and successfully proved several times using bulk crystals. But only few data exist about semiconductor thin films. Here we report on structural (SEM-, EDX-, XRD-, FT-IR-analysis) and in particular thermoelectric properties (Seebeck coefficient and Hall-Effect measurements for carrier concentration, conductivity and mobility) of molecular beam epitaxy grown thin film based on the "Joffe-system" $Pb_{1-x}Sn_xSe$ ($0<x<8.3$). Special care was taken to evaluate the in-plane thermal conductivity of insulated free standing (Pb,Sn)Se thin films.

With increasing tin concentrations a increasing charge carrier concentration as well as increasing thermopower values were found. The bandgap decreased with increasing tin concentration – shifting the optimum operating temperatures towards room temperature – and also the lattice thermal conductivity decreased as expected due to alloy scattering. All these effects strongly increase the thermoelectric properties of PbSnSe in the room temperature region.

Thermoelectric Power in Misfit Cobaltites: Optimisation by Chemical Substitutions

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The good stability in oxidizing conditions and at high temperatures (up to 1000K) of the $Ca_3Co_4O_9$ oxide is very promising for the use of such materials as p-leg in thermogenerator to convert waste-heat into electricity. The structure of these layered materials is built up of rock-salt (RS) type layers intergrown with CoO_2 conducting layers which can be written $[Ca_2CoO_3]^{RS}[CoO_2]_{1.6}$ [1]. These two sublattices are incommensurate, i.e. the values of the b crystallographic cell parameters, b_{RS} and b_{CoO2}, differ leading to $b_{RS}/b_{CoO2} = 1.6$. According to this aperiodic character of the structure ('misfit'), the refinements from X-ray diffraction are very complex involving a 4D superspace [2]. In contrast, by using transmission electron microscopy and coupled energy dispersive analysis, it is possible to quantify the b_{RS}/b_{CoO2} ratio, reflecting the incommensurability degree, and to extract the cation contents. This technique is thus very powerful to discover new members of this class of cobaltites. In particular by studying about 10 new phases of these "misfit" cobaltites, a clear relationship between the incommensurability and the room temperature Seebeck coefficient is established: the best performances ($S_{300K} \approx +140\ \mu V.K^{-1}$) are obtained for the smallest values of the b_{RS}/b_{CoO2} ratio [3]. This can be simply understood by considering the electroneutrality between the positively and negatively charged RS and CoO_2 slabs. A very nice demonstration of this feature is realized via the isovalent substitution of Sr^{2+} for Ca^{2+}. The comparison of the $[Ca_2CoO_3]^{RS}[CoO_2]_{1.6}$ and the recently discovered $[Sr_2CoO_3]^{RS}[CoO_2]_{1.8}$ cobaltites [4] shows that the latter exhibit a lower S_{300K} value but an enhanced metallicity than the former.

This result shows that the cations size at the level of the RS layers governs the b_{RS}/b_{CoO2} ratio so that the cobalt oxidation state in the conducting layer can be varied. Furthermore, by keeping constant the b_{RS}/b_{CoO2} ratio, aliovalent substitutions in the RS layers have then been made in order to increase the shifting of the cobalt oxidation state. By doing so, the best performance $S_{300K} \approx 170\ \mu V.K^{-1}$ are obtained for tetravalent cations substituted for the cobalt of the RS layers in $[Ca_2CoO_3]^{RS}[CoO_2]_{1.6}$. These systematic structural investigations enlight also the difficulty to substitute foreign cations for cobalt at the level of the CoO_2. Interestingly, it is found that the rhodium cation is the only element entering in the structure at the level of the CoO_2 layer. The study of the electronic and magnetic properties of these new mixed Rh/Co cobaltites emphasizes the crucial role played by the low spin states of these cations to generate their remarkable electronic and thermal properties.

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The Effect of Co-substitution on the Thermoelectric Properties of $FeGa_3$

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High temperature thermoelectric property of polycrystalline $Fe_{1-x}Co_xGa_3$ (x : $0<x<1$) solid solution was reported. The bulk pelletized samples were prepared on the route of a liquid-solid reaction in an evacuated quartz ampoule and a hot pressing. The crystal structure and the stoichiometry of the sample were examined by powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectrometer (EDX) measurements to confirm the formation of $Fe_{1-x}Co_xGa_3$ solid solution. All diffraction peaks were properly identified as $FeGa_3$ phase and no impurity phase was observed. The lattice parameters of $Fe_{1-x}Co_xGa_3$ obtained from XRD measurements decreased continuously with increasing composition x. EDX examination on $Fe_{1-x}Co_xGa_3$ verified the stoichiometry of the elements. The Seebeck coefficient measurements revealed that $Fe_{1-x}Co_xGa_3$ were all *n*-type materials. The Seebeck coefficient at room temperature displayed about $120\mu VK^{-1}$ at 10% Co substitution and decreased with increasing composition x. The electrical resistivity at room temperature decreased 2 orders of magnitude at 10% Co substitution. Introducing lattice disorder by mixing Co on the Fe site was effective to reduce the lattice thermal conductivity, for example, the lattice contribution were $2.5Wm^{-1}K^{-1}$ and $1.5Wm^{-1}K^{-1}$ for $Fe_{0.9}Co_{0.1}Ga_3$ and $Fe_{0.5}Co_{0.5}Ga_3$ at room temperature, respectively. The thermoelectric dimensionless figure of merit $\boldsymbol{ZT}$ for $Fe_{0.9}Co_{0.1}Ga_3$ reached 0.21 at 680K.

High Power Density Thermoelectric Systems

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Broad usage of thermoelectric systems for high-wattage applications such as air conditioning and vehicle waste power recovery require much lower cost per unit of output than is presently achieved. Higher ZT materials and advanced thermodynamic cycles offer the promise of acceptable efficiency, but the cost and volume of such systems have remained unresolved limitations.

An approach is presented to reconfigure thermoelectric systems which reduces bulk material usage and system size. The governing equations are presented and their application to advanced cycles that employ thermal isolation are discussed. Requirements and limitations to high power density operation are analyzed in terms of material and system properties. High power density configurations that maintain high thermodynamic efficiency are presented for operation with air, liquid, and solid working media. It is concluded that a factor of 10 to 25 reduction in thermoelectric material usage is possible for many important high-wattage applications.

Design of a 126 litre Refrigerator/Freezer Commercial

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Designing a thermoelectric refrigerator/freezer to cost and performance targets set by refrigerator manufacturers is a difficult task which requires innovation and creative design, coupled with sound engineering practices.

A 126 litre refrigerator, incorporating a 36 litre freezer compartment, was designed, built and performance tested to strict cost, efficiency and performance targets set by Matsushita Refrigeration Company. The design of this refrigerator will be explained with a detailed description of the materials and components utilized. A key component to meeting efficiency targets was the liquid coolant used with Hydrocool's high performance thermoelectric heat exchangers. The choice of insulation levels and materials is another key factor as well as high efficiency power supplies.

Modelling High-Power Density Thermoelectric Assemblies which use Thermal Isolation

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A numerical model made up of a series of simultaneously solved, non-linear, energy balance equations has been created to simulate high-power density thermoelectric assemblies which utilize thermal isolation in heating and cooling applications. In the devices modeled, the thermoelectric elements are incorporated into liquid-liquid heat exchangers that eliminate many of the loss mechanisms for a typical thermoelectric assembly, including the ceramic electrical isolation layer. The model can accurately predict data for experiments using advanced thermodynamic cycles in various configurations to within 3-5% for coefficient of performance (COP), input power, and mass flow rates for a broad current range.

The ability to accurately and precisely model such devices further confirms the concept of improving device COP through the use of thermal isolation, since the devices being modelled shows about a factor of 2 improvement in COP over a typical thermoelectric configuration for the same conditions. Such an accurate and precise model also allows the device to be more extensively studied without additional experimentation. In addition, using advanced multi-parameter optimization techniques, the devices can be optimized for a particular set of temperature and flow conditions.

A Miniaturized Thermoelectrically Driven Adsorption Chiller for Micro-Electronics Cooling and Air Conditioning Applications

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The design and the current status of development of an electro-adsorption chiller will be presented. The electro-adsorption chiller is envisioned to be a miniaturized chiller that could provide active and high-density cooling effect at an efficiency that is twice as good as that of thermoelectric chillers. The electro-adsorption chiller design regeneratively combines the operation of thermoelectric devices with that of an adsorption chiller. Powered by a DC-power source, those thermoelectric devices absorb heat from the adsorber of the adsorption chiller and regeneratively pump the heat to the desorber of the adsorption chiller. This regenerative pumping action of those thermoelectric devices sustains the adsorption-induced evaporation of the working fluid from the evaporator and the desorption of the working fluid from the desorber of the electro-adsorption chiller. Switching the polarity of the DC-power source serves to switch the cold and hot junctions of those thermoelectric devices and thereby the role of the adsorber and desorber in the electro-adsorption chiller. The research team is currently prototyping a bench-top prototype and is at the phase of detailed design and component testing. The final target is to fabricate a palm-size prototype.

Development of Small Footprint and Low-Current TE Modules for Optoelectronics Thermal Management

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Thermal management of optoelectronic packages for both long-haul and short-haul fiber-optic communications in the near-term as well as for integrating lasers within high-density electronic systems require extremely small foot-print thermoelectric coolers. In addition to high efficiencies, these coolers need to pump large heat-flux levels in excess of 100 W/cm2 at the module level. We will discuss the fabrication of small footprint thermoelectric modules fabricated using the Thin Film Superlattice Materials that we reported two years ago. The thermoelectric elements employed in this device are P-Type Bi2Te3/Sb2Te3 and N-Type Bi2Te3/Bi2Te2.85Se0.15 superlattices. The key objectives for this prototype effort were module size and module performance. The smallest module physical dimensions are 1mm (L) x 2mm (W) x 1mm (H). In 2mm x 2mm x 1mm size modules, heat pumping capacities of up to 1.8 Watts (Qmax) were measured, translating to a cooling power density of 45 W/cm2 at the module-level and 125 W/cm2 at the couple-level. The initial modules operated at currents of 10 to 12 Amps. We will discuss our progress on higher cooling power density modules. This work will enable us to match the foot-print of the cooling devices to that of spot heat loads. In addition to improving the COP and power densities, we have been developing high aspect ratio devices to lower the operating currents significantly. To date, we have p-n couples and modules with Imax in the range of 1.5 Amps and DT in excess of 50C at Thot~75C. These results will be discussed.

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First Principles Study of Effects of Ca and Sr addition on Thermoelectric Properties of Mg_2Si

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The effects of Ca and Sr addition on thermoelectric properties of Mg_2Si were studied by using the full-potential linearized augmented-plane-wave method with the supercell method within the local density approximation. We have calculated the electronic structure of $(Mg_{0.875}Ca_{0.125})_2Si$ and $(Mg_{0.875}Sr_{0.125})_2Si$. The concentration of added atom in the matrix is approximately 8.3 %. The band structure of the conduction band is not quite affected by addition of Ca or Sr, whereas that of the valence band is greatly affected. The top of the valence band is changed to more dispersionless character, and this results in a steep rise in the density of states of the topmost valence band. This is originated from strong hybridization between the valence band of Mg_2Si matrix, which is mainly consists of Si 3p band, and d-band of Ca or Sr. We also calculated the electronic structure of $(Mg_{0.75}Be_{0.125}Ca_{0.125})_2Si$ and $(Mg_{0.75}Be_{0.125}Sr_{0.125})_2Si$. Addition of Be atom can cancel out the volume expansion due to Ca or Sr addition. Seebeck coefficient and power factor were based on Boltzmann transport equation and relaxation time approximation. An improved thermoelectric performance is predicted for p-type Mg_2Si by addition of Ca or Sr with adequate concentration.

First-Principle Investigations on the Electronic Structure of Mg_2B_{IV} (B_{IV} = Si, Sn, Ge) and their Solid Solutions

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Compounds of the Mg_2B_{IV} type, where B_{IV} is one of the group IV elements Si, Sn or Ge, are perspective materials for thermoelectric applications at moderate temperature up to 800 K. Particularly interesting for this application is that solid solution of almost any ratio can be derived from these compounds to reduce the lattice thermal conductivity. However, the lack of reliable theoretical and experimental data makes it difficult to identify optimal compositions and therefore first-principle investigations were performed following the density functional theory (DFT). We used the program package WIEN2k, which is based on the full-potential (linearized) augmented plane-wave ((L)APW) + local orbitals (lo) method, one among the most accurate schemes for band structure calculations.

To investigate the solid solutions a super cell containing 8 primitive unit cells was derived from the original crystals with varying composition. It was possible to reveal the band structure and band characteristics, the density of states, and spatial electron-density distribution for the pure crystals as well as for the intermediate compounds. Finally the effective mass of the carriers m^* was derived from the calculated band structure. Special interest was paid to this property as the conversion efficiency of thermoelectric materials Z is directly proportional to this property $Z \propto m^{*3/2}$. Under the reasonable assumption of a relatively week dependence of the carrier-phonon interaction in the intermediate composition region of the alloys, this property can be excellently used for optimizing the material.

Crucible Dependent Thermoelectric Properties of Bulk Mg_2Si Crystals Growth by the Vertical Bridgman Method

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Mg_2Si, an ecologically friendly semiconductor, is a promising thermoelectric material at temperatures ranging from 500 to 800 K. Mg_2Si crystals were grown by the vertical Bridgman method in various crucibles made of quartz, alumina, SiN_x-coated quartz, CVD pyrolytic graphite, CVD SiC-coated graphite in order to minimize the reaction and sticking of molten Mg-Si during growth. Congruent crystallization was derived from a stoichiometric melt of Mg_2Si and incongruent crystallization was derived from nonstoichiometric melts having Mg:Si ratios of 85:15, 70:30, and 60:40. Grown samples were characterized by x-ray diffraction and electron-probe microanalysis, and their power factors were calculated from the Seebeck coefficients and electrical conductivities measured from room temperature to 773 K. The grown crystals were single crystal and showed n-type conductivity in undoped condition. A sample derived from a stoichiometric melt had a Seebeck coefficient of -470 □V/K, while the highest power factor, 1.1 x 10^{-5} W/cmK^2 at 373 K, was obtained for the sample derived from an incongruent melt with an Mg:Si ratio of 70:30. The use of the graphite based crucibles such as pyrolytic and SiC–coated graphites caused the carbon incorporation in the grown crystals, resulting in an increase in the Seebeck coefficient and the electrical conductivity.

Thermoelectric Properties of Sintered $Mg_2Si_{(1-x)}Sn_x$

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$Mg_2Si_{(1-x)}Sn_x$ with the composition range 0.0x1.0 sintered compacts was prepared by a hot-pressing technique. The powders of Mg_2Si and Mg_2Sn were mixed for the composition range 0.0x1.0 as the $Mg_2Si_{(1-x)}Sn_x$. And the mixture powders were synthesized by hot-pressing. The relative density of the sintered compacts $Mg_2Si_{(1-x)}Sn_x$ were measured about 99% as compared with the theoretical value. The phases of the samples were analyzed with X-ray powder diffraction (XRD). As for the composition range 0.4□x□0.6, single phase was not obtained until now. However, single phase was able to be obtained. The effect of sintering-time on phase of the $Mg_2Si_{(1-x)}Sn_x$ is investigated. The samples, short on sintering-time for the hot-press, were two-phases. But the samples with 20 hours of sintering-time were became single phase. The thermoelectric properties on sintered samples of single phase were measured at room temperature. The thermal conductivity of $Mg_2Si_{0.5}Sn_{0.5}$ was decreased to 1/4 at room temperature compared with Mg_2Si or Mg_2Sn. And Seebeck coefficient was -500μV/K, resistivity was 2.2mΩm. The effect of composition x on the thermoelectric properties of the $Mg_2Si_{(1-x)}Sn_x$ compacts is reported.

Temperature Gradient Solution Growth and Seebeck Coefficient of -$FeSi_2$ Bulk Single Crystal

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We have examined the effects of addition elements, strain and defect of crystal on thermoelectric properties of -$FeSi_2$. However, drastic improvement in the thermoelectric property was not achieved yet. We therefore pay attention to the crystal structure of -$FeSi_2$ for improving the thermoelectric properties. Anisotropy in the thermoelectric properties of -$FeSi_2$ is expected because of complicated and highly anisotropic crystal structure. However, experimental results have not been reported yet. The -$FeSi_2$ single crystals were grown by temperature gradient solution growth (TGSG) method using Ga solvent. The crystals were polyhedral with mirror-like growth facets. They were a few mm in size. X-ray diffraction measurements indicated that all specimens obtained in the experiments are single phase -$FeSi_2$. Furthermore, Laue back reflection photographs taken from the specimens showed clear diffraction patterns, indicating high quality -$FeSi_2$ single crystals without twins. The crystal orientation of the single crystals was determined by the Laue pattern. For measurements of the Seebeck coefficient, we developed an apparatus that is capable of measuring the Seebeck coefficient of a small specimen down to a few mm in size. We have tried to examine the anisotropy of Seebeck coefficient of -$FeSi_2$ using the bulk single crystals we prepared.

Effect of Crystallinity on Thermoelectric Properties in rf-Sputtered Beta-Fe1-xCoxSiy Films

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The thermoelectric properties were studied on Co-doped beta-FeSi2 films prepared by RF magnetron sputtering. The investigations were focused on the crystallinity dependences of Seebeck coefficient (S) and electrical resistivity (rho) in the temperature region 470K-970K, for samples with $0 \leq x \leq 0.1$ and $2.0 \leq y \leq 2.5$ in Fe1-xCoxSiy. The crystallinity was varied by changing the substrate temperature, 650K (Type I) and 350K (Type II), during the sputtering, and was evaluated by SEM and XRD after the annealing at 1020K for 3 hours in Ar atmosphere.

The Type I samples crystallized to beta-phase in the as-sputtered state and showed a larger crystal grain and stronger XRD signals showing single beta-phase after the annealing. Whereas the Type II samples (same thickness with Type I) were amorphous in the as-sputtered state and showed a smaller grain size and weaker XRD signals after the annealing though it was single beta-phase.

For Co substitution of x=Co/(Fe+Co)=0.05 with y=Si/(Fe+Co)=2.3, S showed a similar value for Type I and Type II over the measured temperature range, whereas rho in Type II showed a lower value than that of Type I. For Type II sample, the maximum value in the thermoelectric power factor (PF) of 6.6 microV/(K2-cm) was obtained at 830K with S=-209 microV/K and rho=6.6 mohm-cm.

The x and y dependences of PF will be discussed.

Improvement of Thermoelectricity of Fesi2 by Addition of Rare Earth Oxide

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FeSi2 has been investigated in the last several years for environmentally -friend of these elements with low cost as the substances , but the figure of merit has not yet been improved drastically. A few investigators studied this materials to enhance the performance. As well known, the material is peculiar in a low electrical resistivity of an order of 10E-5. Seebeck coefficient was 150 to 200 micro volts/K which were not so large at the temperature ranges of 400 to 970K. One of purpose for adding oxide is to reduce thermal conductivity such as 5W/mK around 800 to 900K while the non-additive FeSi2 showed 7W/mK. Furthermore, the power factor of 3% Gd2O3 addition to FeSi2 was 1.1×10E-3 at 873K. The non-addition specimen presented the power factor of 0.7×10E-3 at the same temperature. The existence of oxide was also studied in the morphology of the specimen. We are going to investigate another oxides for addition to FeSi2.

Electron Channelling X-ray Microanalysis for Site Occupation of the Third Element in ß-$FeSi_2$

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A semiconductor of the ß-$FeSi_2$ structure is considered to be a prospective material for thermoelectric conversion. The thermoelectric properties are improved and controlled by doping with the third element. The material has characteristics of an N-type semiconductor if doped with Co and Ni atoms, or a P-type semiconductor if doped with Cr or Mn atoms. To explain such a doping effect, it is important to clarify the site occupation state of the third element in the ß-$FeSi_2$ structure.

The method for atomic location by channeling enhanced microanalysis (ALCHEMI) in a transmission electron microscope is an effective technique to find the site occupation state of various atoms. In the present work, the ALCHEMI technique was applied to ß-$FeSi_2$. In the technique, the characteristic X-ray intensities were measured at various electron incidence directions, and were calculated till the calculated intensities agree with the measured intensities. The occupation probabilities of the third element on Fe?, Fe?and Si sites, and also sample thickness were determined by using the Lerenberg-Marquardt least squares method.

Microstructure and Thermoelectric Property of Iron-Silicide Doped with Co or Mn and Sb

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Co or Mn and Sb-doped iron-silicide ribbons were prepared by spin-casting and subsequent annealing at 1073K. The microstructure and thermoelectric property of the ribbons were investigated by X-ray diffraction, transmission electron microscopic observation, EDX analysis, and the measurement of Seebeck coefficient and electrical resistivity. The spin-cast ribbons consisted of □-$FeSi_2$, □-FeSi and Sb phases. The semiconducting □-$FeSi_2$ phase appeared in the annealed ribbons and contained Co or Mn atoms. Sb atoms precipitated to form Sb phase in the boundaries of □-$FeSi_2$ grains. The Co-doped or Mn doped ribbons were characteristic of N type or P type semiconductor. The Seebeck coefficient and electrical resistivity decreased with increasing Sb content, and as a result, the power factor was improved for both ribbons of N type and P type semiconductors.

Solid State Power Synthesis and Thermoelectric Properties of Zn_4Sb_3

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Single phase ε-Zn_4Sb_3 powders were successfully produced by a solid state powder synthesis. Subsequent vacuum hot pressing produced single phase bulk specimens without microcracks. Phase transformations in this alloy system during synthesis were investigated using DSC, XRD and SEM. Thermoelectric properties as a function of temperature were investigated from room temperature to 600 K. Thermoelectric properties of single phase Zn_4Sb_3 materials produced by the solid state powder synthesis and hot pressing are comparable to the published data. Solid state powder synthesis offers a potential processing route to produce a bulk Zn_4Sb_3.

Preparation and Thermoelectric Properties of Oxygen-Deficient Misfit Layer Cobaltite $[Ca_2CoO_{3-\delta}]_pCoO_2$

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We have prepared a series of oxygen-deficient misfit layer cobaltite $[Ca_2CoO_{3-\delta}]_p CoO_2$. Under different annealing conditions, we have successfully prepared such samples with δ = 0 - 0.10. The *c*-axis length increases with increasing δ, indicating that a part of the oxygen atoms of the CoO layer in the rocksalt-type Ca_2CoO_3 subsystem are preferentially removed. By appropriately annalizing the magnetic susceptibility data, we evaluated the spin state of each Co ion, and therefore the average valence state of the Co ions (Co^{n+}). With the increase in δ, the *n*-value decreases from 3.2 to 3.05. This decrease in the valence state of Co is also supported by the experimental data. Both the Seebeck coefficient and electric resistivity of the samples gradually increase with δ, lowering the power factor from S^2/ρ = 1.1 x 10^{-4} W/mK^2 to 0.4 x 10^{-4} W/mK^2.

Thermoelectric Properties of Polycrystalline Transition-Metal Dichalcogenides TiS_2 Synthesized by Chemical Vapor Transport Technique

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Low-dimensional conductor titanium disulfide TiS_2 is formed by S-Ti-S basic triangular layers stacked by van der Waals forces. It is known that single crystals of TiS_2 whose shape are small thin flake indicate large values of power factors $\alpha^2\sigma$ and dimensionless figure of merit ZT~0.15 at room temperature. The high thermoelectric performance of this material, however, was suppressed of the order of 1/10~1/50 by sintering at 623 K. [1]

In this paper, we present that the thermoelectric performance of polycrystalline layered TiS_2 (poly-TiS_2) is developed by tuning of synthesis conditions for chemical vapor transport technique; we have obtained random-oriented poly-TiS_2 samples which size were about ϕ8 mm x 10 mm. The poly-TiS_2 shows metallic behavior and high value of negative thermopower same to the single crystals. This result suggests that conduction carrier scattering by grain boundaries and/or pores in the poly-TiS_2 affected much electrical resistivity and thermal conductivity. The thermoelectric performance of poly-TiS_2 comes up to 1/3 of single crystal's values by using this synthesize technique. The technique will apply to synthesize of other new low-dimensional thermoelectric materials with layered or needle shape.

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Crystal Structure and Electrotransport Properties of Solid Solutions Based on $R_3Cu_3Sb_4$ Compounds (R- Rare Earths)

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In previous works [1,2] the crystal structure and physical properties of the compounds with $Y_3Au_3Sb_4$ type structure were described. They are characterized by satisfactory values of thermopower (S), resistivity (ρ), power factor (S^2/ρ) and seem to be applicable as thermoelectrical materials.

We had prepared by arc melting the alloys of the $R_3Cu_3Sb_{4-x}Sn_x$ solid solutions (R = La, Ce, Pr, Nd, and Sm). The crystal structure of the phases was refined and electrotransport properties were measured at temperature between 80 and 380 K. The solubility range of tin in $R_3Cu_3Sb_{4-x}Sn_x$ solid solutions was found to be quite low ($x \leq 0.1$). The positive thermopower values and smaller resistivity in compare with initial compounds were found.

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Numerical Analysis of Thermoelectric Properties of Bismuth Under Magnetic Field

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Thermoelectric and thermomagnetic properties for bismuth were numerically calculated by solving the Boltzmann equation with relaxation time approximation. Taking into account the thermoelectric properties as a function of magnetic field, the phenomenological Ohm's law and heat flux equations were solved by using finite element method.

The effective thermoelectric properties for wire elements with electrodes were calculated with various lengths and diameters of wires. The effective thermoelectric power has the optimum strength of magnetic field. The increase of magnetoresistivity is suppressed when the ratio of length and diameter exceeds 10. Experimentally, the thermoelectric power of micro wire array element under magnetic field was improved to be 1.2 times. Thus the figure of merit is expected to be improved for the sample with high aspect ratio and the optimum magnetic field. Moreover, effective thermoelectric powers of the bismuth wire arrays with bismuth electrode were calculated and the influence of bismuth electrode was estimated.

Exploratory Study of Semiconducting Chimney-Ladder Phase Compounds on the Basis of the Calculated Electronic Densities of States

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Compounds known as Nowotny Chimney-Ladder (CL) phases are expected as thermoelectric (TE) materials since they would have low lattice thermal conductivities due to their complex structures. Since semiconductive nature is favorable for good performance as TE materials, exploratory study of semiconducting CL compounds are desirable. There is an empirical rule that the CL compounds with a valence electron concentration (VEC) of 14 is a semiconductor. So, we have made first-principle band calculations of several CL compounds so as to ascertain this rule. Ru_2Si_3 and Ru_2Ge_3 with VEC=14 are predicted to be direct-gap semiconductor but the band gap decrease in the heavier elements results in the closure of the gap of Ru_2Sn_3. Ir_3Ga_5 and Ir_4Ge_5 are found to be metallic or semimetallic though their VEC value are 14. The Fermi level of $Mn_{11}Si_{19}$, whose VEC is a bit smaller than 14, is located just before the gap and seems not to be inconsistent with *p*-type semiconducting behavior. The Fermi levels of $Rh_{10}Ga_{17}$ and $Rh_{17}Ge_{22}$ whose VECs exceed 14 are located past the gap. $Cr_{11}Si_{19}$ and $Mo_{13}Ge_{23}$, whose VECs are smaller than 14, are predicted to be metallic.

Thermoelectric Properties of $Zn_{4+x}Sb_{3-x}$ Compounds

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We have investigated metallurgical, structural and thermoelectric properties of $Zn_{4+x}Sb_{3-x}$ compounds prepared by the gradient freeze method. The single phase is obtained in the sample prepared from Zn-rich starting composition of 58:42. It is also revealed from the EPMA measurement and Rietveld analysis for powder XRD profiles that the real composition of the Zn_4Sb_3 phase is found to be 58:42. The samples with the stoichiometric and Sb-rich starting compositions consist of Zn_4Sb_3 and impurity ZnSb phases. On the other hand, in the Zn-rich samples, Zn metal is segregated as an impurity phase. The amount of these impurity phases becomes larger for larger deviation from the starting ratio 58:42. No significant difference in the composition is found in the samples prepared by different methods. However, the thermoelectric properties are strongly dependent on the starting composition. Especially the electrical resistivity of Zn-rich samples shows a large increase at the □ to □ structural phase transition temperature. The Seebeck coefficient also exhibits a strong enhancement at the transition temperature. As a result, the dimensionless figure of merit takes a maximum in the sample with the starting composition of 58:42. These facts suggest that the control of the composition and impurity phases is important to optimize the thermoelectric performance of the Zn_4Sb_3 system.

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Analysis of Carrier Density and Mobility of Polycrystalline Bi Dominated by Impurity Scattering of Carrier

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Seebeck coefficient and resistivity by using polycrystalline Bi, which is rectangular solid (4.00mm length and 2.00×1.85mm^2 cross section) were measured from 20 to 300K. The Seebeck coefficient was about –60μV/K at 300K and turned over from n-type to p-type around 200K. The resistivity at 300K was about twice larger than that of single-crystal Bi. Hall coefficient measured by using Van der Pauw method turned over around 200K as well as temperature dependence of the Seebeck coefficient and suggested that cause of changing sign is influence of contamination such as Sn. From the results, intrinsic condition was not applied to the sample for the analysis of carrier density and mobility even if pure Bi is a kind of semi-metal. Absolute value of the Seebeck coefficient always decreased in the magnetic field, therefore it guessed that dominant scattering process of the carrier in the sample was impurity scattering. In addition, their Fermi energy in the sample was varied because of contamination of Sn. In this paper, the carrier density and the mobility for the electron and the hole (n, p, μ_n, and μ_p) were analyzed by using relations of Hall coefficient, resistivity, magnetoresistance, and Seebeck coefficient, which were obtained from Boltzmann equation in relaxation time approximation by assuming scattering process of the carrier.

Numerical Calculation of Magneto-Seebeck Coefficient of Bismuth under a Magnetic Field

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Seebeck and Nernst coefficients were numerically calculated by solving the Boltzmann equation with relaxation time approximation for bismuth under a magnetic field as functions of the products of cyclotron frequency (ω_c) and relaxation time (τ_0), taking into consideration the scattering process of carriers as a function of energy. The relationship between $\omega_c\tau_0$ and magnitude of the magnetic field was derived from the definition of mobility, and each coefficient was estimated as a function of the magnetic field. The magneto-Seebeck coefficient was estimated by the addition of the Seebeck coefficient to the Nernst coefficient, and the contribution of thermoelectric effect in the presence of the magnetic field was dominant, being derived from the Seebeck effect. The magnetic field and temperature dependences of the magneto-Seebeck coefficient were evaluated by the use of a two-carrier model and mobility of single-crystal bismuth. The results show that the magneto-Seebeck coefficient can be improved by a factor of 1.3 to 1.4 in the presence of a magnetic field to control the scattering process of the carriers.

Transport Properties of Bi-Sb Sintered Alloys Prepared by Spark Plasma Sintering

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The transport properties of Bi-Sb sintered alloys have been studied. The Bi-Sb sintered alloys were prepared by spark plasma sintering process using Bi and Sb fine powder. We performed the measurements of the electrical conductivity, Seebeck coefficient, thermal conductivity and Hall coefficient in 10 to 300K. The electrical conductivity and Seebeck coefficient of the obtained sample increased with increasing sintering temperature in the whole temperature range. We will focus on the thermal transport properties of Bi-Sb sintered alloys in reaction process Bi and Sb.

The Effect of Side Chain Size on Thermoelectric Properties of Polythiophenes

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Polymers, which are characterized by light element system, abundant resources, low fabrication and production energy, and possible recovery, are superior to inorganic materials concerning to environmental burden. We have investigated the effect of side chain size on the thermoelectric properties of polythiophenes that are comparatively stable conductive polymer in the air. The polythiophenes with side chains of -H, n-hexyl, n-octyl and n-dodecyl were synthesized. Conductivity was changed in the range of 10^{-4}～10^{1}S/cm. The results were as follows:

1. Seebeck coefficient decreased with an increasing conductivity independently of side chain size.
2. In the range below 10^{-1}S/cm, Seebeck coefficient increased with a decreasing side chain size.
3. In the range above 10^{-1}S/cm, thermoelectric properties were almost independent of side chain size.

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Thermoelectric Properties of Half-Heusler $Zr_{1-x-y}Y_xNb_yNiSn$

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We have synthesized the half-Heusler ZrNiSn alloys where the Zr site is partially substituted by Y and/or Nb. Such substitution much affects the thermoelectric properties of ZrNiSn by changing the valence electron count (VEC) of the material. The behaviors in the Seebeck coefficient and electrical resistivity for $Zr_{1-x}Y_xNiSn$ or $Zr_{1-y}Nb_yNiSn$ system can be understood as the result of the increase in the hole or electron carrier with an increase of x or y, respectively. $Zr_{0.98}Nb_{0.02}NiSn$, whose VEC is 18.02, showed a maximum power factor. With an increase of x or y, the thermal conductivity for $Zr_{1-x}Y_xNiSn$ decreases, while that for $Zr_{1-y}Nb_yNiSn$ increases. In order to more reduce the thermal conductivity, we have also synthesized the samples whose Zr site is substituted by both Y and Nb atoms, $Zr_{1-x-y}Y_xNb_yNiSn$. The value of y-x is fixed at 0.02, by which the optimum VEC for power factor is maintained. The thermal conductivity is almost constant independent of x and y. The substitution for Zr by both Y and Nb is not so effective for the reduction of thermal conductivity, and as a result $Zr_{0.98}Nb_{0.02}NiSn$ shows a maximum *ZT* of 0.34 at 573K.

Thermoelectric Properties of Titanium-, Zirconium-, Hafnium-, and Alkali-Metal-Doped Lanthanum Sesquisulfide with Th_3P_4 Type Structure

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It is well known that lanthanum sesquisulfide (La_2S_3) has three polymorphic forms: alpha, beta and gamma. The alpha-phase is in orthorhombic phase. The beta-phase is in tetragonal phase. It is well known that this phase is actually an oxysulfide, which has a limiting composition of $La_{10}S_{14}O$. The high temperature gamma-phase forms a cubic defect Th_3P_4 type structure. While the beta-La_2S_3 transforms to the gamma-La_2S_3 at around 1573 K, $La_{10}S_{14}O$ is stabilized in the beta-phase at the high temperature above 1573 K. Over the past few decades the gamma-La_2S_3 has attracted interest as high temperature thermoelectric materials. In this paper, we report the low temperature formation of the gamma-La_2S_3 with titanium, zirconium, hafnium, and alkali metal additives. The phase transformation from $La_{10}S_{14}O$ to the gamma-La_2S_3 is accelerated by titanium, zirconium, and hafnium at 1573 K. The alkali-metal-doped gamma-phase is obtained by the sulfurization of powder mixture of lanthanum oxide (La_2O_3) and an alkali metal sulfide using carbon disulfide gas at 873 K. We measured the electric resistivity and thermoelectric power of doped gamma-La_2S_3 in the temperature range from 300 K to 900 K. While the Ti-, Zr-, and Hf-doped gamma-La_2S_3 have a large thermoelectric power factor like the non-doped gannma-La_2S_3, the alkali-metal-doped gamma-La_2S_3 is insulator.

Structural Refinement for (Zn, Cd)Sb Compounds Grown by Vacuum Casting Method

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ZnSb compounds have a powerful potential as a p-type thermoelectric material for the intermediate temperature range (300 to 700 K) as well as beta-Zn_4Sb_3 compounds. The thermal conductivity of ZnSb is higher than that of Zn_4Sb_3, whereas both compounds have the same level of power factor (3 - 6 x10^{-4} W/m/K^2 at 300 K). Substitution of Cd for the Zn site was therefore carried out as the most promising way to reduce the lattice thermal conductivity of ZnSb. However, the crystal structures over the whole compositional range of (Zn, Cd)Sb compounds have not been refined yet. In this study, 11 bulk crystals of $Zn_{1-x}Cd_xSb$ (x=0 to 1) were obtained using vacuum casting method. The powder X-ray diffraction experiments were carried out at room temperature on a JOEL JDX-3500K, and the diffraction patterns were refined by the Rietveld profile fitting program RIETAN2000. The major peaks of all samples were indexed for an orthorhombic structure with a space group *Pbca.* The quantities of impurity phases ((Zn, Cd)$_4Sb_3$, Zn, Cd, and Sb) in the 11 samples were analytically determined. The refined structure parameters for the whole range of the (Zn, Cd)Sb compounds will be systematically summarized, and the structural information thus obtained will lead to an improvement of the performance of (Zn, Cd)Sb as a new thermoelectric material.

The Role of Dislocation Scattering in Diffusion Thermopower of GaN Hetrostructures

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Recently, GaN/AlGaN heterostructures (HS) have attracted attention as potential systems for use in high-temperature, high-power opto-electronic devices [1], the performance of which is, to a large extent, determined by the transport properties of the two-dimensional electron gas (2DEG) confined at the interface. However, dislocations (DS) formed in the GaN layer due to lattice and thermal mismatch are known to strongly influence the carrier mobilities [1-3].

Thermopower (TP), which is sensitive to the scattering mechanisms operative in a system, is an important property for study in GaN HS. At very low temperatures, the diffusion contribution, S_d, to TP dominates over the phonon drag contribution, S_g [4].

Numerical results of the temperature and electron concentration dependence of the very-low-temperature S_d of a 2DEG at a GaN/AlGaN heterojunction are presented. The electrons, in EQL, are assumed to be scattered by DS, background and remote impurities, surface roughness (SR) and bulk acoustic phonons via deformation potential and piezoelectric couplings. For $T<10$ K, S_d is found to be controlled by scattering from DS and SR. Scattering by DS (SR) becomes important at lower (higher) values of n_s. Experimental results are awaited to test the prediction.

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Technologies Competing with Thermoelectrics

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Thermoelectric devices have been put to use in a variety of applications ranging from cooling electronic components in every day devices to powering spacecraft. Their main advantages are seen to be in their small size, light weight and reliability. Yet, there are other alternatives with similar features. This paper reviews existing and emerging technologies with potential for competing with thermoelectric devices in the areas of electricity generation, heating and cooling. Both terrestrial and space applications are considered in appraising the viability of these various different technologies. Relative merits and disadvantages are discussed.

Japanese National Project/Development for Advanced Thermoelectric Conversion Systems

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The development for advanced thermoelectric conversion systems is positioned as one of the main innovative projects in many projects to prevent global warming in Japanese energy systems and this project has been supported by the Ministry of Economy, Trade and Industry(METI) and the New Energy and Industrial Technology Development Organization (NEDO)since FY2002 for 5 years. The goal is to contribute to the reduction of greenhouse gas emissions after 2010 through developing and commercializing the advanced thermoelectric modules and systems that recover waste heat from industrial and private sectors into electricity.

The final R&D goal of the thermoelectric modules is to establish 15% efficiency (with ΔT of 550K), while the goal for the interim evaluation scheduled in 2004 is 12% efficiency(with ΔT of 550K).

Moreover, thermoelectric conversion systems for high temperature waste heat to be applied to electric heating furnaces and diesel engines, as well as those for lower temperature one to be applied to projector lamps and so on are being realized.

Composition and Nanostructure, Processing and Performance: Narrowing and Expanding the Dimensions of Thermoelectrics for Power Generation

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The application of "interface engineering" at the nanoscale has generated intriguing increases in thermoelectric performance in thin films and, possibly, bulk materials. This "engineering" includes seemingly divergent techniques such as high vacuum thin film superlattice growth, melt-grown bulk materials containing compositional segregation, and post-growth processing, among others. How far will interface engineering take us? What role will quantum confinement play? How can these effects be leveraged to maximum effect in bulk materials? What insights have been gained for future materials development from the multiplicity of compositions and phases prepared to date? Where does theory and modeling stand in moving the field forward? How much improvement can be realized from post-growth processing? Can the thermoelectrics field benefit from standard reference materials and protocols for characterization for different temperature regimes?

The U.S. Office of Naval Research program on Thermal-to-Electrical Energy Conversion is focused on these and other critical science and engineering question, with the goal of developing a prototype 1MW energy conversion plant. The performance metrics for this grand challenge are > 20% conversion efficiency ($ZT = 4$) with 1 W/cm^2 at $T_{hot} < 1000$ºC. An overview of the ONR programs and objectives will be presented, with time for discussion of the issues outlined above and others that the community feels are important.

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