RECENT ADVANCES IN MATERIALS FOR THERMOELECTRIC ENERGY CONVERSION

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ABSTRACT

Several new developments have occured at JPL which hold promise for improved thermoelectric energy conversion efficiencies in space power applications. Significant improvements, of the order of 30%, in the figure of merit ($Z \sim 1 \times 10^{-3} \mathrm{K}^{-1}$) of SiGe alloys have been realized by double-doping n-type material. Figures of merit slightly in excess of $1 \times 10^{-3} \mathrm{K}^{-1}$ have also been achieved in the n-type ternary compound $La_{3-x}Yb_xTe_4$ ($0 \leq x \leq 1$). Property measurements on B_xC ($4 \leq x \leq 9$) have been extended to high temperatures ($T \cong 1800K$) and show that, in these p-type materials, $ZT > 1$ is possible in this temperature region. In each case, possible mechanisms will be proposed to explain these improvements in Z.

INTRODUCTION

Thermoelectric energy conversion systems have a remarkable record of performance in space applications. High specific power (Watts per kilogram) thermoelectric systems provide reliable, long term power sources for a variety of demanding space power applications. Although thermoelectric systems technology has shown steady progress, thermoelectric materials technology had advanced little, until recently, since the early 1960s. Next-generation thermoelectric materials technology is now under development in order to service the increasing demands of lighter weight, lower cost space power systems. The purpose of this note is to provide some perspective on recent theoretical and experimental advances in thermoelectric materials technology at JPL.

HISTORY

The efficiency of a thermoelectric system can be calculated from a knowledge of the dimensionless thermoelectric figure of merit (ZT) over the temperature range of interest as shown in Figure 1. ZT is related to measurable materials parameters by $ZT = S^2 \sigma T / \lambda$, where S is the Seebeck coefficient, σ is the electrical conductivity and λ is the thermal conductivity. For over 100 years it has been recognized (Boltzmann 1887) that thermodynamics places no limit on the efficiency (η) of a thermoelectric energy conversion system, other than the universal Carnot limit of $\eta_{Carnot} = (T_h - T_c)/T_h$, where T_h is the temperature of the heat source and T_c is the temperature of the heat sink (see also Littman and Davidson, 1961). In other words, there is no fundamental limit on the thermoelectric figure of merit.

Major advances in the theory and application of semiconductor physics in the 1940s and 1950s provided strong motivation, both in the U.S. and in the Soviet Union, to pursue thermoelectric energy conversion

systems. Theoretical models were developed which connected the thermoelectric figure of merit to fundamental materials properties. Reasonable estimates of possible materials properties yielded theoretical values for the figure of merit much higher than had been observed up to that time and, again, no fundamental limits on the figure of merit were found (Rittner and Neumark, 1959; Donahoe, 1960; Goldsmid, 1964; and Ure, 1972).
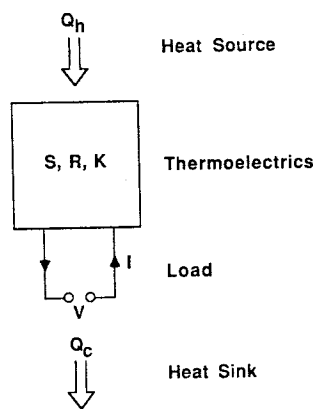
Conversion Efficiency

$$\eta = \frac{IV}{Q_h}$$

$$= \frac{I(S\Delta T - IR)}{IST_h + K\Delta T - 1/2 I^2 R}$$

Optimize Current

$$\eta_{opt} = \frac{\Delta T}{T_h} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_c/T_h}$$

Where

$$ZT \equiv \frac{S^2 T_{average}}{R K}$$

Figure 1:
The optimized efficiency of a thermoelectric device depends only on the dimensionless figure of merit, ZT, and approaches the Carnot limit for large figure of merit values.

The promise for large scale applications of solid state thermoelectric energy conversion prompted an extensive research and development effort in the 1950s and early 1960s. The remarkable achievements of this period include development of all of the material systems in common use today, including bismuth and lead telluride based systems as well as the current state-of-the-art silicon germanium alloys, each of which has achieved peak ZT values of about 1, as shown in Fig. 2, over different temperature ranges.

Today, after decades of space power system technology growth to optimize the mass to power ratio, practical radioisotope thermoelectric generator (RTG) systems achieve conversion efficiencies of about 7% operating between about 575 K and 1275 K. Although the overall efficiency is relatively low, nearly 90% of the power the thermoelectric materials produce is delivered to the load. The limiting factor is the performance of the thermoelectric materials themselves. Encouraged by the continued absence of any known fundamental limitations and the otherwise outstanding performance of thermoelectric systems, recent efforts at JPL have made progress in at least three areas of thermoelectric materials: (1) silicon germanium

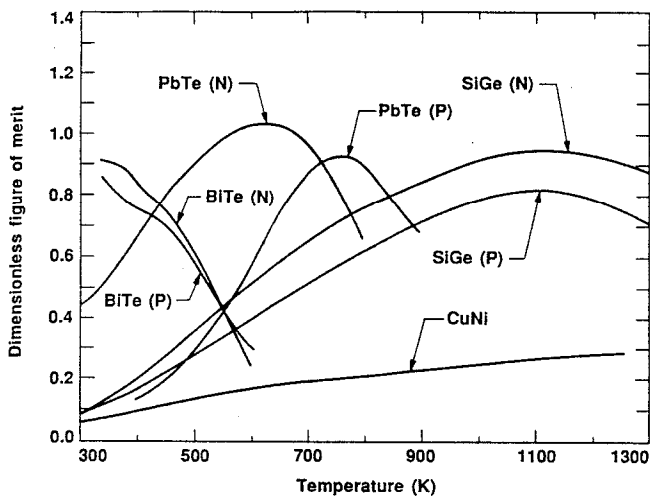alloys, (2) rare earth compounds, and (3) boron carbides. Progress in each of these three areas will be discussed.

Figure 2:
The dimensionless figure of merit for several common thermoelectric materials peak at values near ZT=1. CuNi, a metallic alloy shown for comparison, has a much lower figure of merit value.

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SILICON-GERMANIUM ALLOYS

Silicon germanium (SiGe) alloys, doped with phosphorus (for n-type materials) or boron (for p-type materials), developed at RCA in the early 1960s for the US Navy, are the current materials of choice for space power applications. Efforts to improve these materials are partly motivated by the ease with which SiGe-based materials advances can be translated into systems technology advances. Recently, figure of merit values have been increased approximately 30% above standard SiGe in n-type SiGe alloys containing small amounts of GaP, as shown in Fig. 3 (Vandersande et al. 1987).

Experimental results and detailed theoretical modeling indicate that GaP, coupled with proper preparation techniques, acts to increase the carrier concentration well beyond the concentration possible in standard doped SiGe. This increase is brought about by an increase in the solid solubility limit of P in SiGe alloys and a reduction of polytropy due to the presence of Ga. Effects of this kind have been studied over a number of years by Glazov et al, 1967, and Fistul, 1969, for a variety of Group III-V dopants in Si and Ge. Normally, at very high concentrations
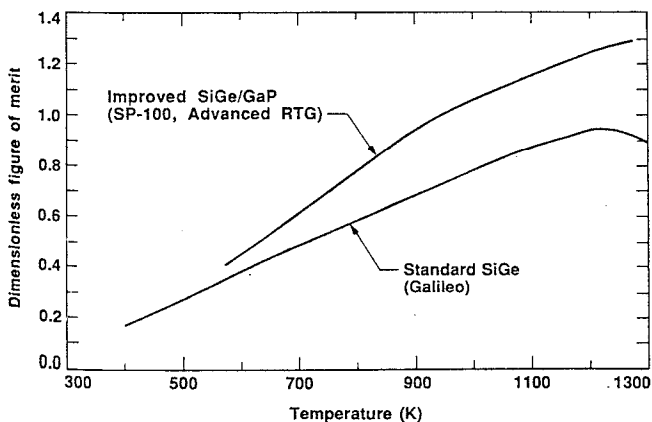

Figure 3:
Recent improvements in n-type silicon-germanium alloys doped with gallium phosphide have achieved figure of merit values 30% higher than typical of standard silicon-germanium alloys currently utlized in

of P in Si, when the solubility limit is approached, aggregates, e.g., $Si+P_4$ and vacancy + P_4, are formed, which eventually may lead to the precipitation of compounds, such as SiP. These defects reduce the number of free charge carriers to below the level of the P concentration. The presence of Ga inhibits these formations to a degree and, thereby, frees charge carriers for conduction. A theoretical and experimental study of these effects is underway at JPL and will be reported elsewhere in more detail (J.P. Fleurial and A. Borshchevsky).

The increased carrier concentration has three major beneficial effects. First, the higher carrier concentration results in a higher electrical conductivity without significantly lowering the value of the Seebeck coeffficient, i.e., it raises the value of $S^2\sigma$ in the numerator of Z to the maximum value.

Second, the lattice (phonon) component of the thermal conductivity is reduced by increased scattering of phonons by electrons (Rosi, et al, 1967). Finally, at high temperatures, a major contributor to the electronic component of the thermal conductivity of SiGe is conduction due to thermally excited minority carriers (holes in this case), called the ambipolar contribution. This contribution to λ is strongly reduced by increasing the carrier concentration.

Recent theoretical modeling of SiGe at JPL confirms the three improvement factors above and has helped motivate experimental efforts to increase the carrier concentration even further. Based upon this model, further gains in figure of merit of an additional 40 to 50% appear possible in n-type SiGe beyond what has been achieved to date, by increasing the carrier concentration alone. While substantially less work has been directed toward improving p-type SiGe materials, similar improvements in figure of merit are anticipated in this area as well.

The basic electronic conduction processes in conventional semiconductors like SiGe alloys are described as "band-type conduction," a term which implies carriers move essentially freely through the crystal lattice. Theory for this type of material is fairly extensive and can, at least in principle, connect the measured transport properties and thermoelectric performance with microscopic materials parameters such as the energy gap, effective mass, deformation potential, and dielectric constant. The values of these microscopic parameters, however, must be determined by analysis of experimental results so theory is not yet mature enough to predict a priori the performance of a material system, although an upper limit on the performance of a particular material system can be predicted.

In order to achieve really large gains, at least two paths are open: (1) examine additional conventional semiconductors with materials parameters substantially different from current materials (SiGe) or (2) examine unconventional semiconductors not well described by conventional theory. Lanthanum telluride (see below) is an example of recent progress on the first approach and progress on boron carbide (see later) represents the second approach.

RARE EARTH COMPOUNDS

Rare earth chalcogenides have long been considered for thermoelectric energy conversion applications (Cutler et. al., 1962, 1963, 1964; Ryan et. al., 1962). These materials are mostly conventional n-type semiconductors, although the carrier concentrations can be made to range from insulator to semimetallic values by changing the stoichiometry. They also differ in other important respects from current SiGe alloys. The conduction bands have extensive d-type character and exhibit energy gaps of 2.5 to 3.0 eV. SiGe alloys have much simpler sp-type conduction bands and much smaller energy gaps of 0.7 to 1.1 eV. The atomic masses of La and Te are much larger than Si or
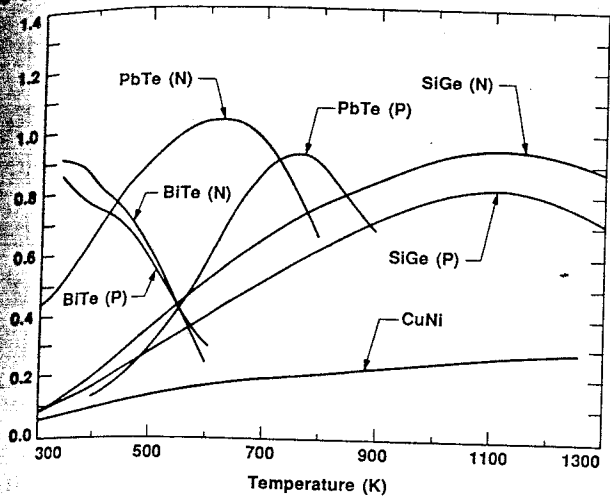
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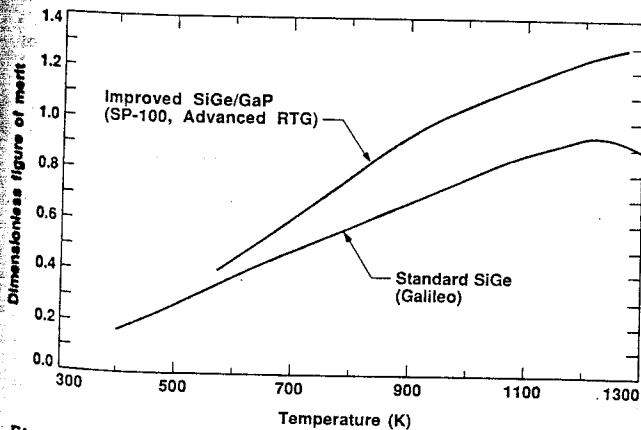

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aggregates, e.g., Si+P_4 and vacancy + P_4, are formed, which eventually may lead to the precipitation of compounds, such as SiP. These defects reduce the number of free charge carriers to below the level of the P concentration. The presence of Ga inhibits these formations to a degree and, thereby, frees charge carriers for conduction. A theoretical and experimental study of these effects is underway at JPL and will be reported elsewhere in more detail (J.P. Fleurial and A. Borshchevsky).

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earth chalcogenides, leads to much lower thermal conductivity values. So, while the conduction mechanism in these compounds is essentially similar to that in SiGe, the material parameters are radically different and the detailed theory is significantly more complex. Already, however, these n-type materials have achieved figure of merit values comparable to state of the art SiGe and, because of more favorable fundamental properties, have the potential for much greater gains.

Recent studies at Thermo Electron (TECO) and JPL (Danielson et. al. 1985, 1988 and Vining et. al. 1988) have shown that figures of merit of ZT=1.4 at 1275K can be reliably achieved in the lanthanum telluride $(La_{3-x}Te_4)$ system (see Fig. 4). Based on studies at Ames Laboratory in the lanthanum sulfur system (Nakahara, 1988) doping the lanthanum tellurium system with divalent elements such as Sm, Eu, and Yb may offer a method of improving the power factor (P) in the figure of merit even further. However, although ongoing work at JPL and TECO has shown slightly improved values for the power factors, Figs. 5 and 6 show that the Seebeck and electrical conductivity data for both doped and undoped lanthanum telluride can be fitted essentially to the same curves, suggesting that the improvements are a result of more closely approaching the optimum doping level. Nevertheless, there is a hint of a slight reduction in thermal conductivity on Yb doping (see Fig. 7) which could lead to an increase in Z.
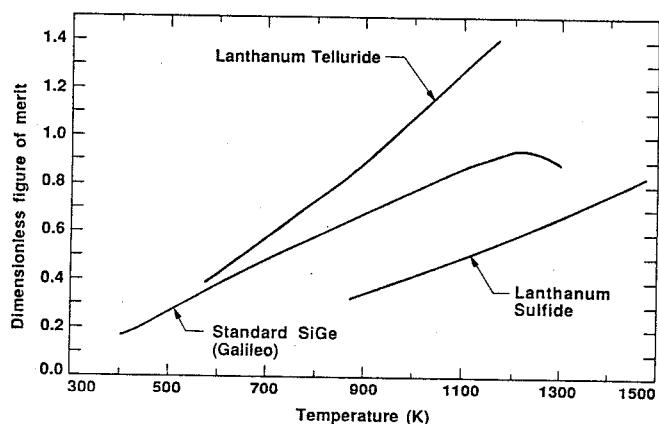

Figure 4:
The figure of merit of advanced rare-earth chalcognides based on thanthanum telluride have recently surpassed the ZT=1 values typical of prior thermoelectric materials by a significant margin.
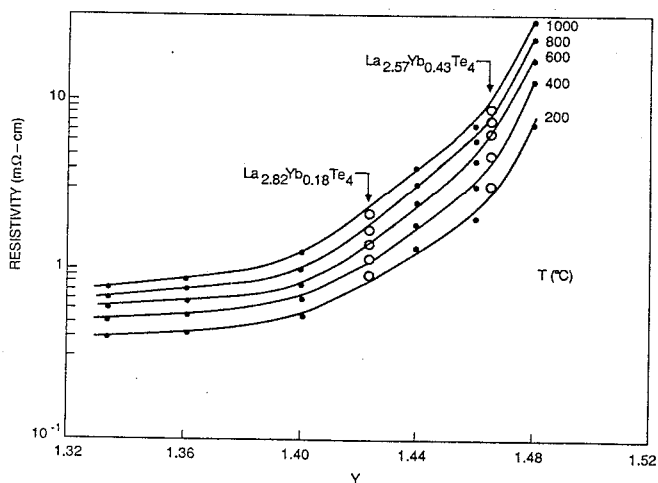

Figure 5:
Electrical resistivity of LaTey and ytterbium-alloyed lanthanum tellurides as a function of y and temperature

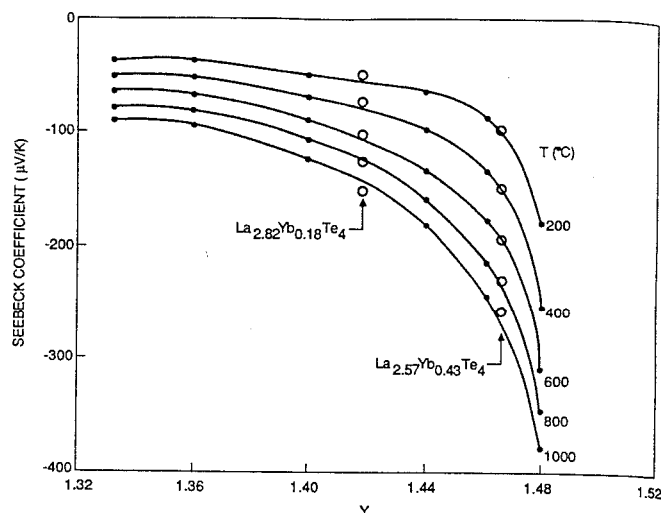

Figure 6:
Seebeck coefficient of LaTey and ytterbium-alloyed lanthanum tellurides as a function of y and temperature.
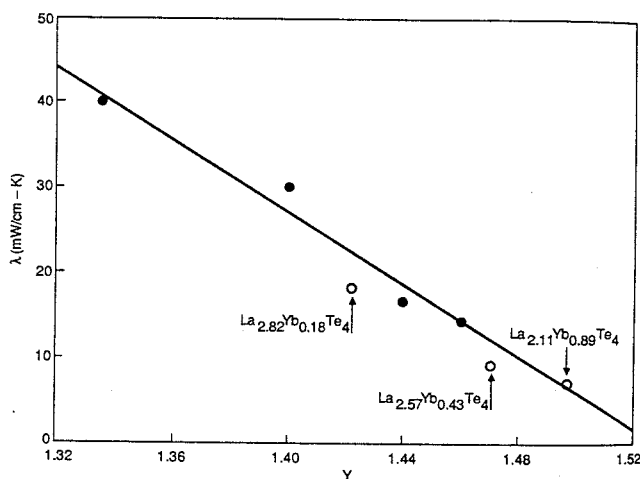

Figure 7:
Thermal conductivity of LaTe$_y$ and ytterbium-alloyed lanthanum tellurides as a function of y at 800 °C.

Obviously, from an applications viewpoint, it would be most desirable to select the n- and p-legs from the same materials system. Although less work has been done on p-type materials, recent work at JPL and TECO has identified promising p-type rare earth compounds which, properly optimized, may yield high figure of merit values. Of particular interest is the fact that doping lanthanum telluride with high concentrations of Yb (>15%) leads to p-type material. Efforts to exploit this finding and optimize the figure of merit are now underway.

BORON CARBIDES

Boron carbides represent a very different class of semiconductors in which the charge carriers "hop" from site to site within the crystal lattice (Wood and Emin, 1984). The theory of conduction in these materials is more complex than for conventional semiconductors. The hopping conduction in boron carbide is quite unique (Emin 1987). Pairs of holes are believed to hop together in a correlated way. The radically different physics and chemistry of boron carbide (and other boron-rich solids) has helped motivate an active program at Sandia National Laboratories (SNL) and JPL to improve the basic understanding of these materials by concentrating on critical measurements performed on high quality, well
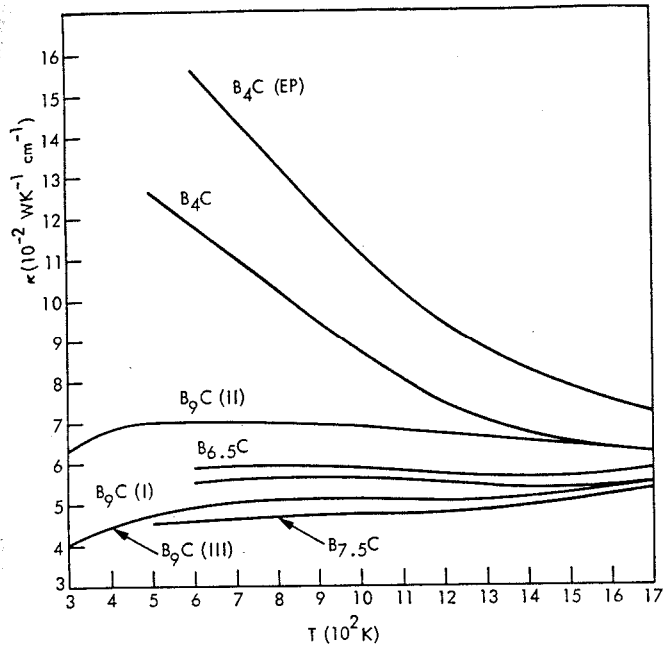
Figure 8:
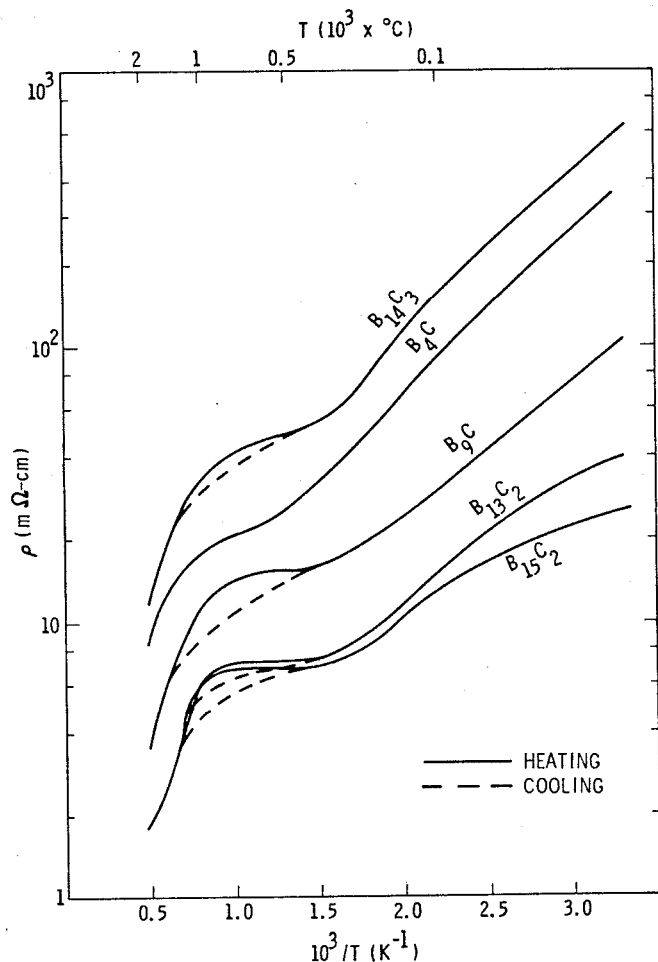Thermal conductivity of boron carbides as a function of composition and temperature.

Figure 9:
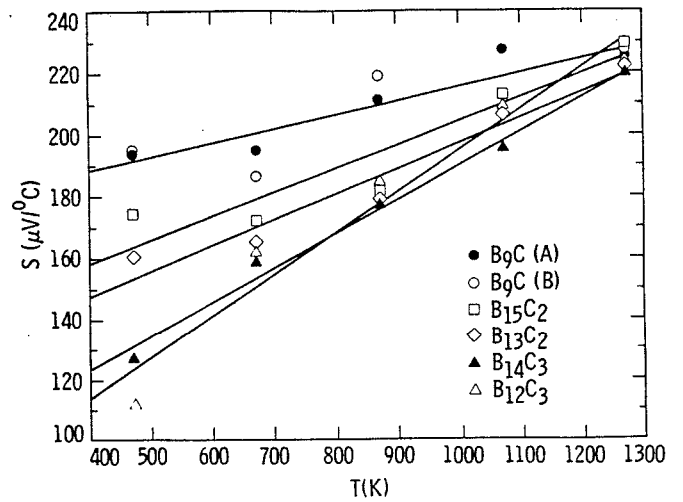Electrical resistivity of boron carbides as a function of composition and temperature.

Figure 10:
Seebeck coefficient of boron carbides as a function of composition and temperature.

Due to a complex crystal structure, involving boron icosohedra, boron carbide exhibits low, temperature-invariant thermal conductivity values typical of glassy or amorphous materials (Fig. 8). The electrical conductivity and Seebeck coefficient are large and typically both increase with increasing temperature, which is not ordinarily observed in conventional semiconductors (Figs. 9 and 10). Efforts at General Atomics (GA) and JPL have established the thermoelectric figure of merit of hot pressed, p-type boron carbide is on the order of ZT=0.6 at 1275 K, as shown in Figure 11 (Wood 1988), which is about the same as standard p-type SiGe at the same temperature, but ZT is increasing with temperature for boron carbide and decreasing with increasing temperature for SiGe. Further, boron carbide should be useful up to 2000 K where, assuming a steady increase of Seebeck coefficient with increasing temperature, ZT is projected to be as large as 3. Given the crude preparation procedures and level of understanding available to date (compared to conventional semiconductors), the achievement of figure of merit values in boron carbide comparable to those observed in the best conventional materials is quite remarkable.
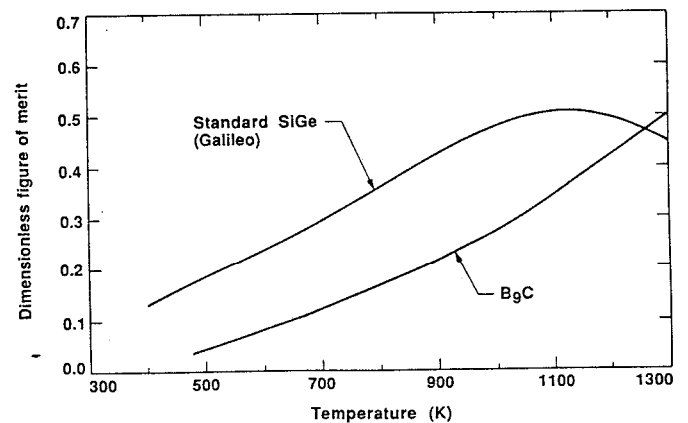

Figure 11:
Boron carbides have been shown to have figure of merit values comparable to state of the art p-type silicon germanium alloys at 1300K and have the potential for much higher figure of merit values.

CONCLUSIONS

Since the last major thermoelectric materials development efforts nearly three decades ago, the fundamental theoretical conclusions have not changed: theory still predicts much higher figure of merit values than have yet been achieved. Recent experimental and theoretical advances in materials technology have generated promising new materials systems which already exhibit figure of merit values comparable or superior to current state of the art SiGe alloys, and with much greater growth potential. Important advances have also been made in the technologically important SiGe-based materials, which should see use in practice in the near future in advanced RTG and SP-100 space power systems. Continued progress in thermoelectric materials technology can be expected to yield reliable space power systems with double to triple the efficiency of current state of the art.

References

Boltzmann, L. (1887) Wien. Ber., 96: 1258.

Cutler, M., Appel, J.C., Guthrie, G.L. and Kurnick, S.W. (1962) Final Report, Contract #:bs-77144 ARPA, Order #8159

Cutler, M., Fitzpatrick, R.L. and Leavy, J.F. (1963), J. Phys. Chem. Solids 24: 319

Cutler, M. (1964), Phys. Rev. 133: A1143

Danielson, L., M. Alexander, C. Vining, A. D. Lockwood and C. Wood (1988), 7th Inter. Conf. on Thermoelectric Energy Conv., p. 71, Arlington, TX, 16-18 March 1988.

Donahoe, F.J., (1960), Electr. Eng. 79: 488

Emin, D. (1987) Materials Research Society Symposia Proceedings, Vol. 97: 3-15.

Fistul, V.I. (1969), Heavily Doped Semiconductors, New York, Plenum Press

Goldsmid, H.J., (1964), Thermoelectric Refrigeration, New York, Plenum Press

Littman, H. and Davidson, B, (1961), J. of Appl. Phys., 32: 217.

Nakahara, J. F., T. Takeshita, M. J. Tschetter, B. J. Beaudry, and K. A. Gschneidner, Jr. (1988) J. Appl. Phys., 63: 2331.

Rittner, E.S. and Neumark, G.F., (1959) J. of Appl. Phys. 34: 2071

Rosi, F.D., (1968) Solid State Electron. 11: 833

Ryan, F.M., Greenberg, I.N., Carter, F.L. and Miller, R.C. (1962) J. of Appl. Phys. 33: 864

Ure, R.W., (1972), Energy Conv. 12: 45

Vandersande, J. W., C. Wood and S. L. Draper (1987) Materials Research Society Symposia Proceedings, Vol. 97: 347-352.

Vining, C., C. Wood, J. Parker, A. Zoltan, L. Danielson, and M. Alexander (1988) 7th Inter. Conf. on Thermoelectric Energy Conv., p. 9, Arlington, Texas, 16-18 March 1988.

Wood, C. (1988) Reports on Progress in Physics, 51: 459-539.

Wood, C. and Emin, D., (1984), Phys. Rev. B 29: 4582

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