Log Nr. 111

ADVANCED MATERIALS FOR HIGH-TEMPERATURE THERMOELECTRIC ENERGY CONVERSION

Cronin B. Vining, Jan W. Vandersande, and Charles Wood
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109
(818) 354-9374

MANUSCRIPT prepared for:

Sixth Symposium
on Space Nuclear Power Systems
Albuquerque, New Mexico
9-12 January 1989

Author running head: C. B. Vining, J. W. Vandersande, and C. Wood
Title running head: ADVANCED THERMOELECTRIC MATERIALS

Address all correspondence to : Dr. Cronin B. Vining

ADVANCED MATERIALS FOR HIGH-TEMPERATURE THERMOELECTRIC ENERGY CONVERSION

Cronin B. Vining, Jan W. Vandersande, and Charles Wood

Jet Propulsion Laboratory

California Institute of Technology

Pasadena, CA 91109

(818) 354-9374

ABSTRACT

A number of refractory semiconductors are under study at the Jet Laboratory for application in thermal to electric energy conversio power. The main thrust of the program is to improve or develop ma high figure of merit and, therefore, high conversion efficiencies broad temperature range. Materials currently under investigation represented by silicon-germanium alloys, lanthanum telluride and h carbide. The thermoelectric properties of each of these materials prospects for their further improvement, will be discussed.

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. In order to service the increasing demands for space power systems, next-generation thermoelectric materials technology is now under development. The purpose of this note is to provide some perspective on recent theoretical and experimental advances in thermoelectric materials technology.

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. In other words, there is no fundamen limit on the thermoelectric figure of merit.

Major advances in the theory and application of semiconductor physics the 1940s and 1950s provided strong motivation, both in this country an the Soviet Union, to pursue thermoelectric energy conversion systems. Theoretical models were developed which connected the thermoelectric fi of merit to fundamental materials properties. Reasonable estimates of possible materials properties yielded theoretical values for the figur merit much higher than had been observed up to that time and, again, n fundamental limits on the figure of merit were found.

The promise for large scale applications of solid state thermoelectr energy conversion prompted an extensive research and development effor 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 curr state-of-the-art silicon germanium alloys, each of which has achieved values of about 1 as shown in Figure 2, over different temperature ra

Today, after decades of space power system technology growth to opt the mass to power ratio, practical radioisotope thermoelectric genera (RTG) systems achieve conversion efficiencies of about 7% operating b about 575 K and 1275 K. Although the overall efficiency is relativel nearly 90% of the power the thermoelectric materials produce is deliv

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 have made progress in at least thre 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 briefly discussed.

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 powe applications. Efforts to improve these materials are partly motivated by ease with which SiGe-based materials advances can be translated into syst technology advances. Recently, figure of merit values have been increase approximately 30% above standard SiGe in n-type SiGe alloys containing sm amounts of GaP, as shown in Figure 3 (Vandersande et al. 1987).

Experimental results and detailed theoretical modeling indicate the Gal coupled with proper preparation techniques, acts to increase the carrier concentration well beyond the concentration possible in standard SiGe. increased carrier concentration has three major beneficial effects. Fir the higher carrier concentration results in a higher electrical conducti Second, the lattice (phonon) component of the thermal conductivity is re

by increased scattering of phonons by electrons. 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 the Jet Propulsion Laboratory (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, based on 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.

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 is an example of recent progress on the first approach and progress on boron carbide (see below) represents the second approach.

RARE EARTH COMPOUNDS

Lanthanum telluride is a conventional n-type semiconductor. Recent studies at Thermo Electron (TECO) and JPL (Vining et al. 1988 and Danielson et al. 1988) have reliably achieved figure of merit values of ZT=1.4 at 1275 K in this system, as shown in Figure 4. Based on studies at Ames Laboratory in the lanthanum sulfur system (Nakahara, 1988) and ongoing work at JPL and TECO in the lanthanum tellurium system, doping with divalent elements such as Sm, Eu, and Yb may offer a method of improving the figure of merit even further.

These rare-earth compounds differ in many 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 0.4 to 1.1 eV. The atomic masses of La and Te are much larger than Si or Ge and this, combined with the more complex defect crystal structure of the rare earth compounds, leads to

much lower thermal conductivity values. So, while the conduction mech in the rare-earth compounds is essentially similar to that in SiGe, th material parameters are radically different and the detailed theory is significantly more complex. Already, however, these n-type materials achieved figure of merit values comparable to state of the art SiGe an because of more favorable fundamental properties, have the potential f greater gains. Although less work has been done on p-type materials, work at JPL and TECO has identified promising p-type rare earth compou which, properly optimized, may yield high figure of merit values.

BORON CARBIDES

Boron carbides represent a very different class of semiconductors i the charge carriers "hop" from site to site within the crystal lattic theory of conduction in these materials is much less mature and more than for conventional semiconductors. Due to a complex crystal struc boron carbide exhibits low thermal conductivity values typical of gla amorphous materials. The electrical conductivity and Seebeck coeffic large and typically both increase with increasing temperature, which ordinarily observed in conventional semiconductors. Efforts at Gene Atomics (GA) and JPL have established the thermoelectric figure of me hot pressed, p-type boron carbide is on the order of ZT=0.5 at 1275 1988), which is about the same as standard p-type SiGe at the same temperature as shown in Figure 5, but ZT is increasing with temperat boron carbide and decreasing with increasing temperature for SiGe.

boron carbide should be useful up to 2000 K where ZT is pr
large as 3.

The hopping conduction in boron carbide is quite unique
of holes are believed to hop together in a correlated way.
different physics and chemistry of boron carbide (and othe
solids) has helped motivate an active program at Sandia Na
(SNL) and JPL to improve the basic understanding of these
concentrating on critical measurements performed on high q
characterized samples. Given the crude preparation proced
understanding available to date (compared to conventional
the achievement of figure of merit values in boron carbid
those observed in the best conventional materials is quit

CONCLUSIONS

Since the last major thermoelectric materials developme
three decades ago, the fundamental theoretical conclusion
theory still predicts much higher figure of merit values
achieved. Recent experimental and theoretical advances i
technology have generated promising new materials systems
exhibit figure of merit values comparable or superior to
art SiGe alloys, and with much greater growth potential.
have also been made in the technologically important SiG
which should see use in practice in the foreseeable futu

and SP-100 space power systems. Continued progress in thermoelectric materials technology can be expected to yield reliable space power system with double to triple the efficiency of current state of the art.

Acknowledgements

The work described in this paper was carried out by the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

References

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

Danielson, L., M. Alexander, C. Vining, A. D. Lockwood and C. Wood (198
"Thermoelectric Properties of LaTey," in
7th Inter. Conf. on Thermoelectric Energy Conv., p. 71, held in Arlin
TX, 16-18 March 1988.

Emin, D. (1987) "Icosahedral Boron-Rich Solids as Refractory Semiconduc
in Materials Research Society Symposia Proceedings, Vol. 97: 3-15.

Nakahara, J. F., T. Takeshita, M. J. Tschetter, B. J. Beaudry, and K. A
Gschneidner, Jr. (1988) "The Effect of Sm, Eu and Yb on the Thermoele
Properties of Th_3P_4-Type Lanthanum Sulfide," J. Appl. Phys., 63: 233

Vandersande, J. W., C. Wood and S. L. Draper (1987) "Effect of High
Temperature Annealing on the Thermoelectric Properties of GaP Doped
in Materials Research Society Symposia Proceedings, Vol. 97: 347-352

C. Wood, J. Parker, A. Zoltan, L. Danielson, and M. Alexander
lectrical and Thermal Transport in Lanthanum Telluride," in
. Conf. on Thermoelectric Energy Conv., p. 9, held in Arlington,
-18 March 1988.
988) "Materials for thermoelectric energy conversion," Reports o
in Physics, 51, 459-539.

FIGURE CAPTIONS

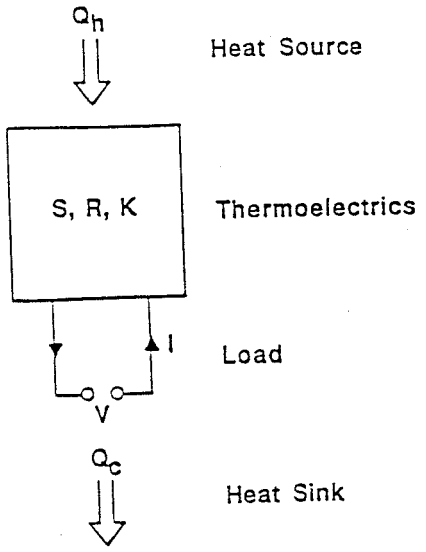
: 1 The optimized efficiency of a thermoelectric
the dimensionless figure of merit, ZT, and ap
limit for large figure of merit values.

e 2 The dimensionless figure of merit for severa
materials peak at values near ZT=1. CuNi, a
for comparison, has a much lower figure of m

'e 3 Recent improvements in n-type silicon-german
gallium phosphide have achieved figure of me
than typical of standard silicon-germanium a
in radioisotope thermoelectric generators.

:e 4 The figure of merit of advanced rare-earth c
lanthanum telluride have recently surpassed
of prior thermoelectric materials by a sign

re 5 Boron carbides have been shown to have figu
comparable to state of the art p-type silic
1300 K and have the potential for much high
values.



Conversion Efficiency

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

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

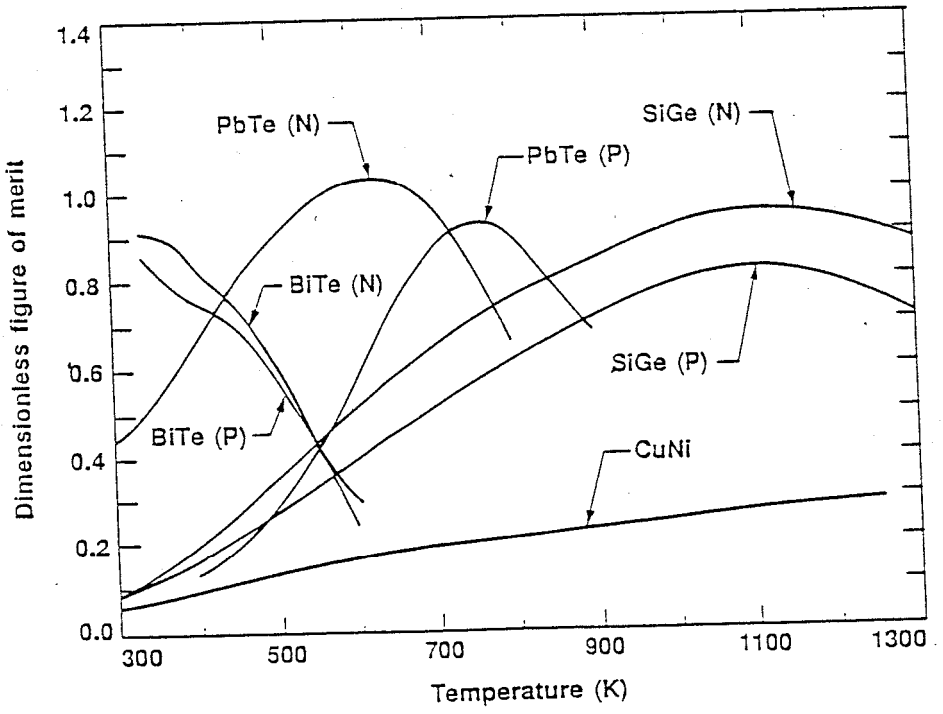
Optimize Current

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

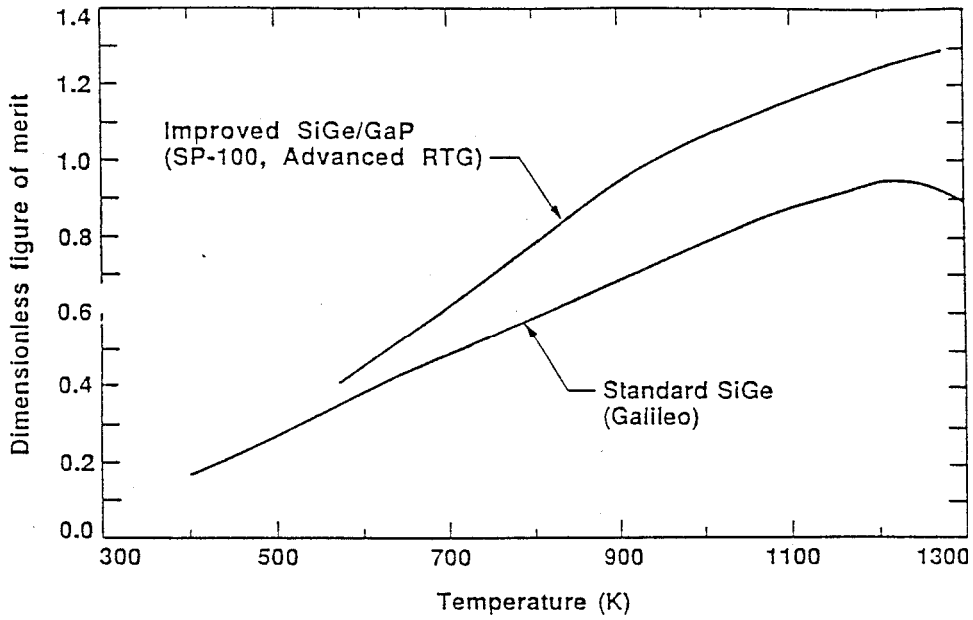
Where

$$Z\bar{T} \equiv \frac{S^2 T_{average}}{R\,K}$$

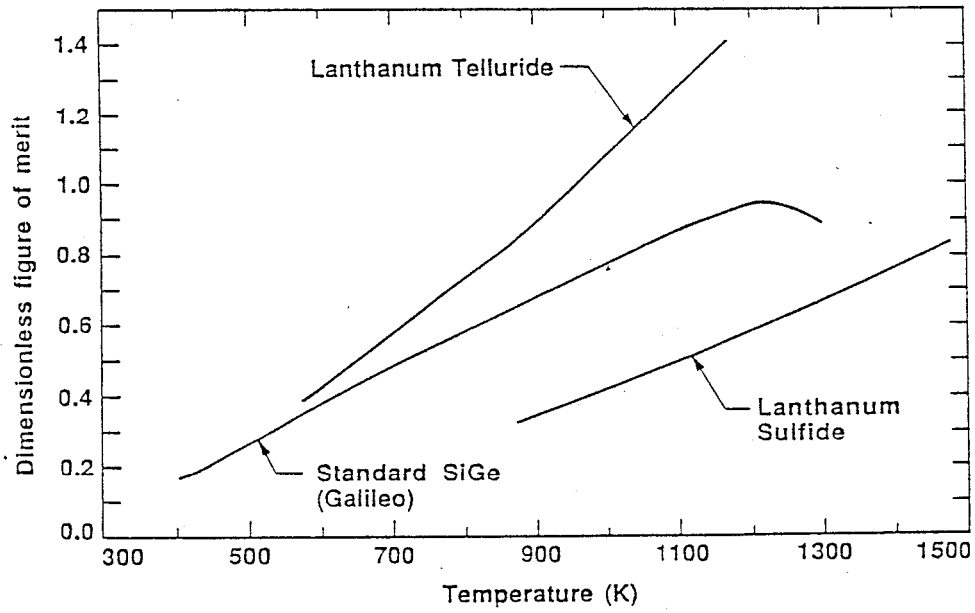
1 The optimized efficiency of a thermoelectric device depends o the dimensionless figure of merit, ZT, and approaches the Car limit for large figure of merit values.



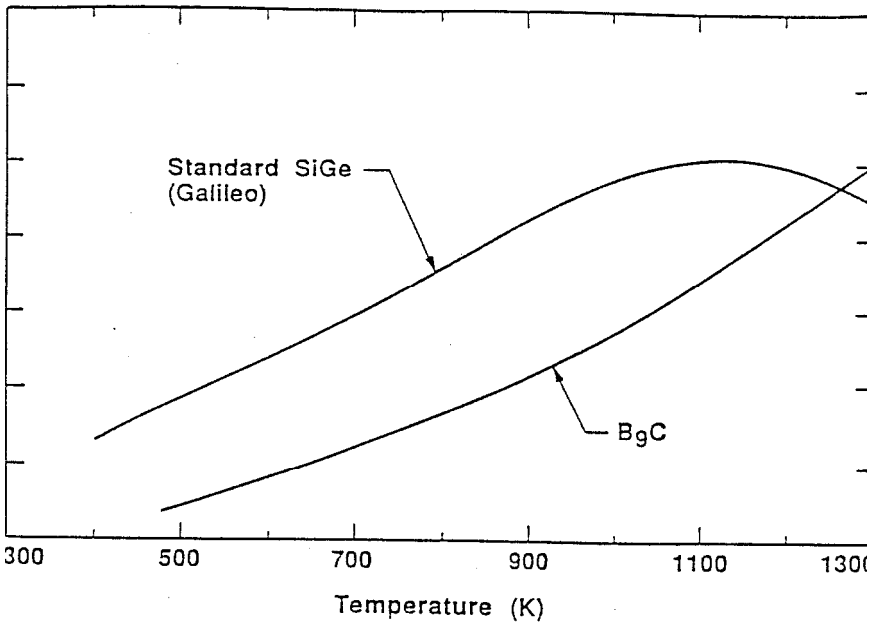
re 2 The dimensionless figure of merit for several common thermoe materials peak at values near ZT=1. CuNi, a metallic alloy for comparison, has a much lower figure of merit value.



Recent improvements in n-type silicon-germanium alloys doped w gallium phosphide have achieved figure of merit values 30% hig than typical of standard silicon-germanium alloys currently ut in radioisotope thermoelectric generators.



The figure of merit of advanced rare-earth chalcogenides base lanthanum telluride have recently surpassed the ZT=1 values t of prior thermoelectric materials by a significant margin.



:arbides have been shown to have figure of merit value:
ıble to state of the art p-type silicon germanium allo
and have the potential for much higher figure of meri