Concept Paper* on

# Energy Conversion Using Second Generation Thermoelectric Materials

Submitted by:

**Jerry Suitor (818) 354-4917 and**
**Cronin Vining (818) 354-9374**

**Thermal Power Conversion Group,**
**The Jet Propulsion Laboratory/**
**California Institute of Technology**
**Pasadena, California 91109**

Prepared for:

**Office of Basic Energy Sciences,**
**The United States Department of Energy**

## Summary

Energy conversion technologies have a major impact on natural resource utilization and the environment. National concerns such as global warming, ozone depletion and energy costs are directly affected by the technologies available for converting one form of energy to another. This concept paper highlights a conversion technology with great potential to be both environmentally benign and enable better utilization of available resources: thermoelectricity. Existing thermoelectric technology is extremely reliable and can provide either power generation or refrigeration with no moving parts or emissions, other than heat. Unfortunately, the efficiency is currently limited due to reliance on technology nearly unchanged since the early 1960's.

Efforts focused on the basic science of thermoelectricity can improve the efficiency several fold, resulting in a second generation of thermoelectric energy conversion technology with a greatly increased range of applications. Potential benefits to society range from environmentally benign refrigerators for homes and automobiles to topping cycles for more efficient and reliable industrial power generation. This concept paper will provide a brief overview of current thermoelectric technology and describe how modern materials science methods can be applied to this area.

* Concept papers, statements of interest, presolicitation qualification synopses, and the like from the Jet Propulsion Laboratory are intended to stimulate discussion of the topic described. They are not commitments to work but are precursors to formal proposals if they generate sufficient mutual interest.

## Basic Thermoelectricity

The basic thermoelectric device is illustrated in Figure 1. The two materials labeled 'N' and 'P' in the figure represent n-type and p-type semiconductors, respectively. In the current context, these materials are called 'thermoelectric materials' and the electrical connection at the heat source is called the thermocouple junction. The charge carriers in each semiconductor tend to migrate from the heat source to the heat sink. By completing the circuit, electrical current can be delivered to a load, represented by the resistor in the figure. In the absence of a load Figure 1 represents an ordinary thermocouple, where the open circuit voltage is a measure of the temperature difference between the heat source and heat sink. If the resistor is replaced by a power supply, current may be forced through the circuit which has the effect of cooling the thermocouple junction, an effect called *Peltier cooling*.

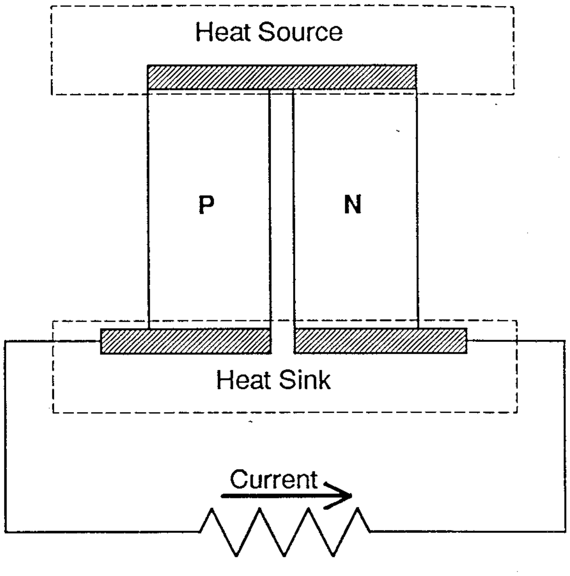

Fig. 1: A thermoelectric device.

The efficiency of a thermoelectric device, whether for power generation or for refrigeration, depends on a property of the materials used as the 'N' and 'P' elements. This property, called the thermoelectric figure of merit, is given by $Z = \alpha^2\sigma/\lambda$, where $\alpha$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity and $\lambda$ is the thermal conductivity. The Seebeck coefficient represents the electric potential generated in a thermal gradient. The electrical (or thermal) conductivity is a measure of the amount of electricity (or heat) which flows in response to an electrical (or thermal) gradient. Z has units of inverse temperature ($K^{-1}$), so it is often more convenient to deal with the dimensionless quantity ZT. Semiconducting alloys are selected because they provide greatest efficiency. Thermoelectric devices are cheap, compact, rugged and reliable. Modern thermoelectric manufacturing techniques routinely package tens or hundreds of such couples per cubic centimeter.

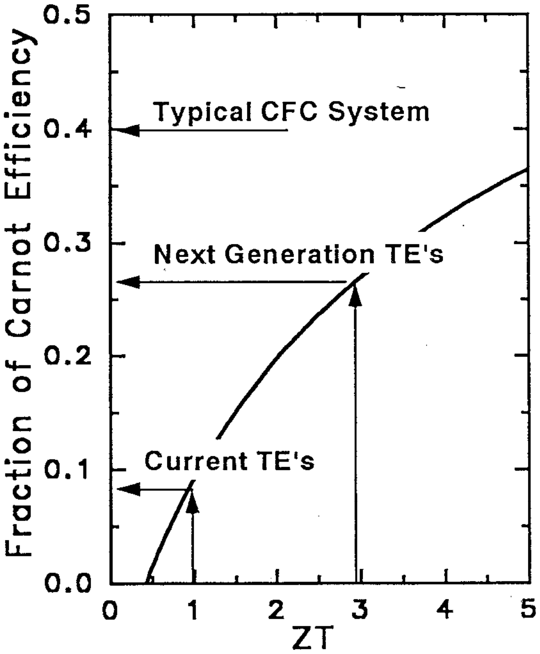

Fig. 2: Efficiency as a function of the material figure of merit, ZT

The principle drawback of current thermoelectric technology is that the best available materials achieve less than 10% of

Carnot efficiency, much less than typical compressor-based refrigeration systems. Figure 2, however, demonstrates that with higher ZT values, the efficiency of thermoelectric devices becomes competitive with existing mechanical compressor-based technologies. Figure 2 has been calculated for thermoelectric refrigeration systems, but the results are similar for thermoelectric power generation systems as well.

For many applications, the reliability of thermoelectric devices compensates for the relatively low efficiency. While thermoelectric generators have seen only limited application on earth (such as remote gas and oil pipelines), such generators remain the only practical alternative for deep-space applications[1]. There is a modest commercial market for thermoelectric refrigerators (often called *Peltier coolers*) and a few small companies service this market, both here and abroad. In addition, there are important aerospace and military applications for thermoelectric coolers in order to cool various sensors and detectors to their optimum operating conditions.

These specialized applications will certainly continue, and may expand to some extent. A recent feasibility study in France, for example, on small household refrigerators has concluded[2] that even the current generation of thermoelectric technology is economically competitive (within 20%) with CFC-based technology. A second study, performed under a DOE-sponsored Energy-Related Inventions Program grant, concluded that current thermoelectric generator technology is economically feasible as the electrical power source for certain diesel truck applications.[3]

**Prospects for Improved Efficiency through Higher Z Values.**

Given the inherent simplicity and reliability of thermoelectric technology, even modest improvements in the fundamental materials should significantly expand the range of practical thermoelectric applications. Moreover, recent advances in the understanding of existing thermoelectric materials[4] have reopened the possibility that much higher efficiencies should be possible with this technology. A factor of 3 improvement (as suggested in Fig. 2 for next generation materials), is well within the range predicted by current theory. While no detailed studies have been performed on this point, it seems clear that as thermoelectric technology approaches the efficiency of existing compressor based technology, the inherent advantages of solid state conversion should lead to major economic and environmental advantages.

---

[1] C. Wood, "Materials for Thermoelectric Energy Conversion," Reports on Progress in Physics, **51**(4), pp. 459-530 (1988).

[2] P. M. Schlicklin, "Thermoelectricity, A Possible Substitute for the CFC's," *IX International Conference on Thermoelectrics (USA)*, March 19-21, 1990, Pasadena, California, pp. 381-395 (1990).

[3] J. C. Bass, R. J. Campana, and N. B. Elsner, Hi-Z Technology, Inc., San Diego, California, "Evaluation of Novel Waste Heat Recovery," Energy-Related Inventions Program Grant Final Report Number HZ-021191-1 under Martin-Marietta/Oak Ridge Contract Number DOE 86X-SF170C, May 22, 1991.

[4] C. B. Vining, "A Model for the High-Temperature Transport Properties of Heavily Doped n-type Silicon-Germanium Alloys," J. Appl. Phys., **69**(1), pp. 331-341 (1991).

The key, as with so many technologies, is to develop new materials. New materials work in the thermoelectric field essentially halted by the mid-1960's. By then, most of the normal semiconductors known at that time, such as III-V and II-VI compounds, had been rather thoroughly examined. All the thermoelectric materials in use today are based on these 'classical' semiconductors and were invented in this early period of basic semiconductor research.

Today, materials science is a much more rich and rapidly expanding field. Thousands of electronic materials available today were unknown in the 1960's: superlattices, ceramics, organic and polymer conductors, and of course the copper oxides so important to high temperature superconductivity. Modern preparation techniques allow preparation of materials with modulated compositions and/or doping levels almost at will. But virtually none of these materials have been seriously or systematically examined for thermoelectric applications.

### Recent Progress

The Thermal Power Conversion Group at the Jet Propulsion Laboratory/California Institute of Technology has been at the forefront of recent thermoelectric development programs. Due to NASA's need for reliable power sources for outer planetary exploration missions such as Voyager and Galileo, a major effort has been directed toward improving the efficiency of high temperature silicon-germanium (SiGe) alloys, in use for space power applications since 1965. Today, substantial improvements of up to 25% in Z have been achieved in the laboratory and this technology is being transferred to industry for implementation in future, lower cost space power systems.

Materials preparation capabilities at JPL (including zone leveling, Bridgman growth, traveling solvent method, and liquid phase epitaxy) have enabled execution of critical experiments to verify the improved SiGe results. Theoretical models, also developed at JPL, have provided guidance key to reliably reproducing the results. Preliminary high Z values[5], for example, had appeared anomalous and difficult to reproduce, but were later shown to be completely consistent with conventional solid state physics.[4] Moreover, the carrier concentration enhancement effect utilized in the JPL program to improve SiGe was predicted to have an optimum, which has since been observed experimentally.

Development of quantitative models for existing thermoelectric materials has also stimulated a re-examination of possible new materials with much better performance, well beyond the 25% gains achieved by optimizing existing materials. Figure 3 shows a prediction made possible by models of this type.[6] In this case, the thermoelectric figure of merit has been calculated as a function of the deformation potential, a microscopic parameter characterizing the interaction between electrons and phonons in a solid. The other parameters have been chosen to reflect the actual properties of SiGe and the

---

[5] Vandersande, J.W., Wood, C., and Draper, S.L., *Mat. Res. Soc. Symp. Proc.*, **97**, pp. 347-352 (1987).

[6] Vining, C., *25th Intersociety Energy Conversion Engineering Conference*, pp. 387-391 (1990).

vertical line labeled 'A' (for 'actual') comes very close to the observed ZT values for SiGe. The vertical line labeled 'L' (for 'low') represents the low end of the range of deformation potential values actually observed in compounds similar to SiGe. The point of Figure 3 is to demonstrate that ZT values of 3 or even higher are well within the range of current theory.

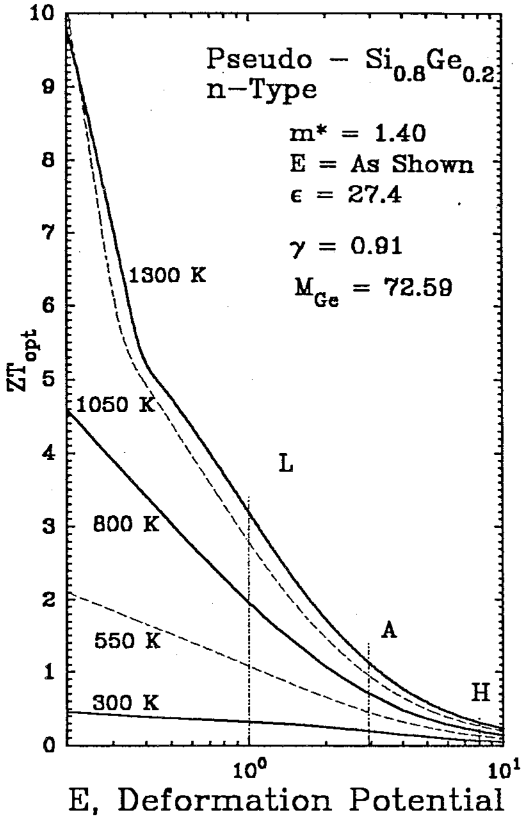

Fig. 3: Prediction of High ZT values.

## Suggested Effort

The temperatures required for terrestrial thermoelectric applications such as refrigeration and power co-generation are much lower than typical of space power conversion systems, which operate at temperatures up to 1300 K. This suggests that rather different materials should be considered for terrestrial applications. Virtually all recent effort on thermoelectric materials, however, has been narrowly focused on existing high temperature materials suitable for space applications. Therefore, a great many distinct approaches for materials suitable for terrestrial applications have simply not been examined. Moreover, the chances of developing an improved, lower temperature thermoelectric material is much better, since so many more materials are stable at lower temperatures.

A particularly promising approach is based on composition-modulated materials, which are known to exhibit effects beneficial to thermoelectricity such as thermal conductivity reduction and mobility enhancement. Initially, we propose to examine such effects in 'proof of principle' experiments utilizing simple materials such as alternating layers of bismuth and antimony, or possibly alternating layers of GaAs and InAs. Such materials systems have the advantages of being very tractable experimentally, and amenable to theoretical analysis.

Samples will be prepared with compositional changes on the order of every few hundred Angstroms. This length scale is typical of the most important heat carrying phonons and the modulations can be expected to inhibit the phonon transport, which will enhance the figure of merit. Other possible effects such as mobility enhancement could also contribute to significantly higher Z values. Models describing these effects are available, but key input parameters must be determined experimentally on high quality, prototypical systems. A few systematic studies on composition-modulated semiconductor alloys, combined with theoretical analysis, should be sufficient to determine the viability of this particular approach.