

New Composite Thermoelectric Materials for Energy Harvesting Applications

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The concept of using nanostructured composite materials to enhance the dimensionless thermoelectric figure of merit ZT relative to that for their counterpart homogeneous alloyed bulk crystalline materials of similar chemical composition is presented in general terms. Specific applications are made to the Si-Ge and $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ systems for use in high-temperature power generation and cooling applications. The scientific advantages of the nanocomposite approach for the simultaneous increase in the power factor and decrease in the thermal conductivity are emphasized insofar as their simultaneous occurrence is enabled by the independent control of these physical properties through the special properties of their nanostructures. Also emphasized are the practical advantages of using such bulk samples both for thermoelectric property measurements and for providing a straightforward path to scaling up the materials synthesis and integration of such nanostructured materials into practical thermoelectric power-generation and cooling modules and devices.

INTRODUCTION

Recent advances in the practical utilization of thermoelectric devices for cooling car seats, providing electrical power for both deep space probes and for data communications from remote areas,¹ together with recent research advances in the performance of bulk²⁻⁵ and low dimensional⁶⁻⁸ thermoelectric materials have set the stage for new vistas for the use of advanced thermoelectric materials for energy harvesting applications. Such applications are needed to address the challenges of a transition to renewable energy sources by the end of the 21st century. This

summary briefly reviews a role that thermoelectric materials might play in this transition process and the recent progress that has been made in the thermoelectric materials research field, thereby lending support to the implementation of this vision for providing a

viable technology to convert waste heat energy (thermal energy) to electrical energy within a useful time frame (20 years) and on a useful energy scale (GW scale) for impact on the larger energy picture.

Thermoelectric energy conversion is based on the Seebeck effect and allows for the generation of electricity directly from a supply of thermal energy. The Seebeck effect occurs when a material is subjected to a temperature gradient, where electrons diffuse from the hotter region of the material toward the colder region and consequently build up a small voltage on the order of microvolts per degree of temperature difference between the two ends of the material. If dissimilar p- and n-type materials are connected electrically in series and thermally in parallel a more substantial voltage can be developed, which can then be used to supply electrical power to a load, as shown in Figure 1. The open-circuit voltage obtained is directly proportional to the temperature difference that can be maintained ($\Delta V = S * \Delta T$). The overall performance depends on three key material properties that affect the device's ability to sustain the temperature difference and to effectively generate electrical power. Improving thermoelectric efficiency hinges on: increasing the Seebeck coefficient S so that larger voltages can be obtained for each leg of the thermoelectric device (see Figure 1); decreasing the thermal conductivity κ to minimize the heat being conducted (parasitic heat leakage) through the leg, which warms the cold side and decreases the temperature difference; and increasing the electrical conductivity σ , so that joule heating is minimized (parasitic heat generation), which also serves to warm the cold side.

How would you...

...describe the overall significance of this paper?

Thermoelectricity provides an important route for energy conservation by turning waste heat energy into useful electrical energy and for new uses of energy generation in the future from solar energy sources.

...describe this work to a materials science and engineering professional with no experience in your technical specialty?

The recent development of materials with nanostructures allows properties like electrical conductivity and thermal conductivity, which are important for thermoelectric applications, to be independently controlled through the size of the structures, whereas the same materials in bulk form follow a physical relation between these two quantities, preventing their independent control.

...describe this work to a layperson?

Close to 20 years ago the first author of this paper proposed that better thermoelectric performance could be achieved based on the use of nanostructures. Laboratory experiments were designed and carried out over a ten-year period to demonstrate that these concepts were correct in principle. The work reported here is a scaled-up version of the laboratory tests to make samples large enough for useful harnessing of waste heat energy to electricity, showing a performance 40% better than present commercial bulk modules.

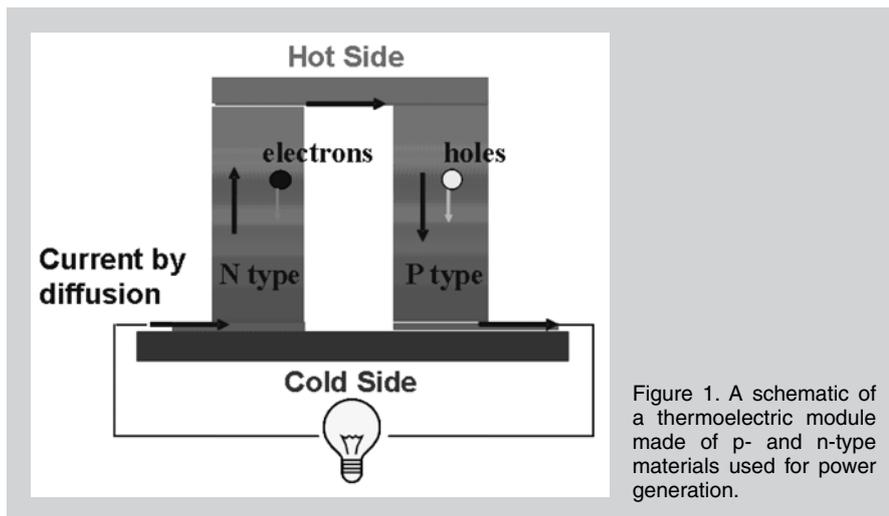


Figure 1. A schematic of a thermoelectric module made of p- and n-type materials used for power generation.

During the past 15 years, research activities in the thermoelectrics field have focused on new strategies for enhancing the dimensionless thermoelectric figure of merit ZT , which is a measure of the performance of thermoelectric energy conversion between thermal and electrical energy, where $ZT = S^2\sigma T/\kappa$ and S is the Seebeck coefficient, σ the electrical conductivity, T the absolute temperature, and κ the thermal conductivity, consisting of the contribution from phonons κ_{ph} from electrical carriers κ_e and from a bipolar contribution κ_{e-p} from electron-hole pairs that carry heat but do not transport charge or contribute to σ . During

this 15 year time frame, fundamental studies on bulk materials have focused on the study of advanced thermoelectric materials where phonon-glass and electron-crystal behavior could be established, such as in the skutterudite and clathrate families of semiconducting materials, which contain cages where phonons can rattle³ and yield very low thermal conductivities. Another approach has focused on studying model low-dimensional materials like quantum wells, quantum wires, and quantum dots where the small sample size could be used as a parameter to independently control σ , S , and κ .⁸ Laboratory studies have successfully

demonstrated that both of these approaches can enhance ZT .⁸ The concept of modifying the properties of thermoelectric materials using low-dimensional structures was introduced by L. D. Hicks and M.S. Dresselhaus in 1993⁹ as a means to increase the density of electron states near the Fermi level and thereby to increase the Seebeck coefficient without lowering the electrical conductivity. By the introduction of suitable interfaces, the thermal conductivity could also be decreased while not significantly decreasing the electrical conductivity. In the following decade these concepts were introduced at the laboratory scale to many systems. More recently, strategies have been developed for scale up of the nanostructuring process and the fabrication of bulk samples of sufficient size and heat capacity to be practical for energy-related applications. These strategies have brought the research programs on advanced bulk thermoelectrics and low-dimensional thermoelectrics together, as various forms of bulk nanocomposite materials were developed and demonstrated.^{6,8,10}

The increased activity in the field stimulated further advances. Spurred on by theoretical studies of resonant impurity states giving rise to big increases in the density of states just be-

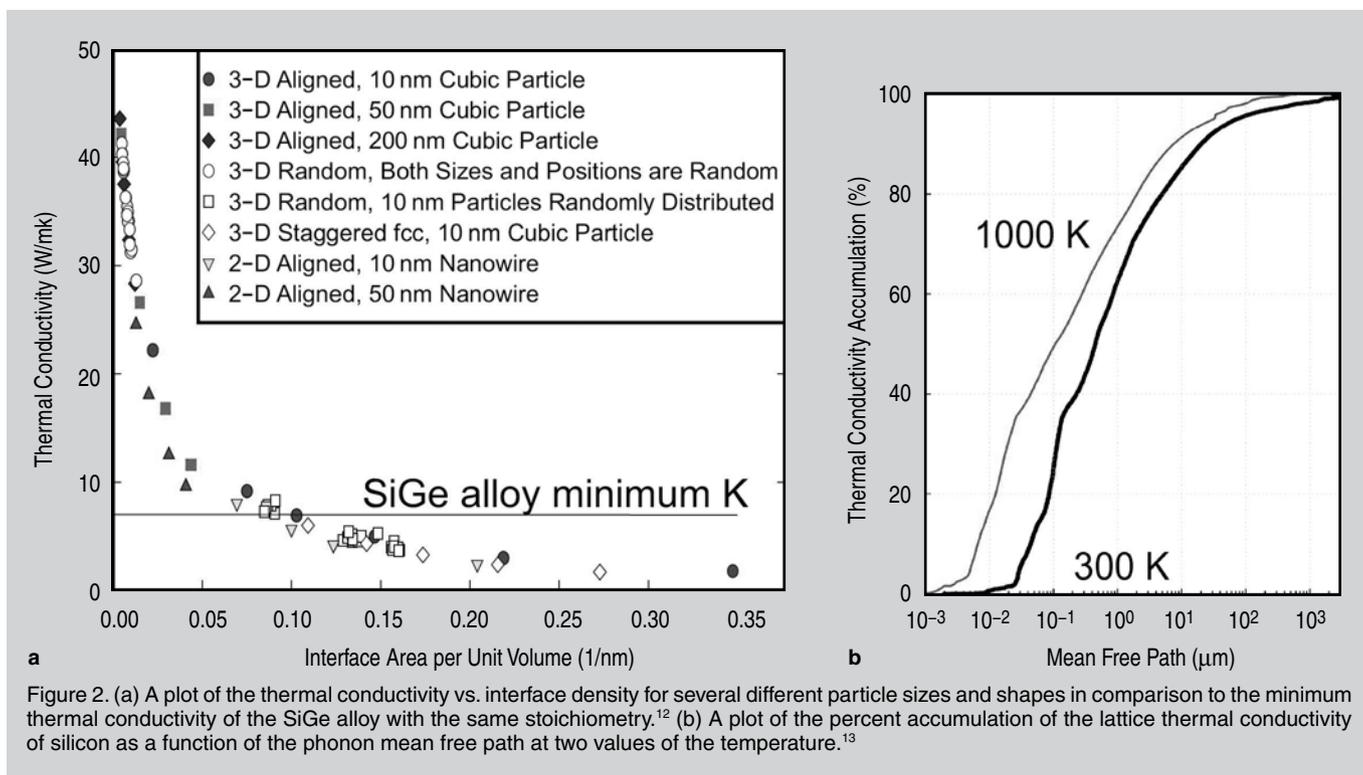


Figure 2. (a) A plot of the thermal conductivity vs. interface density for several different particle sizes and shapes in comparison to the minimum thermal conductivity of the SiGe alloy with the same stoichiometry.¹² (b) A plot of the percent accumulation of the lattice thermal conductivity of silicon as a function of the phonon mean free path at two values of the temperature.¹³

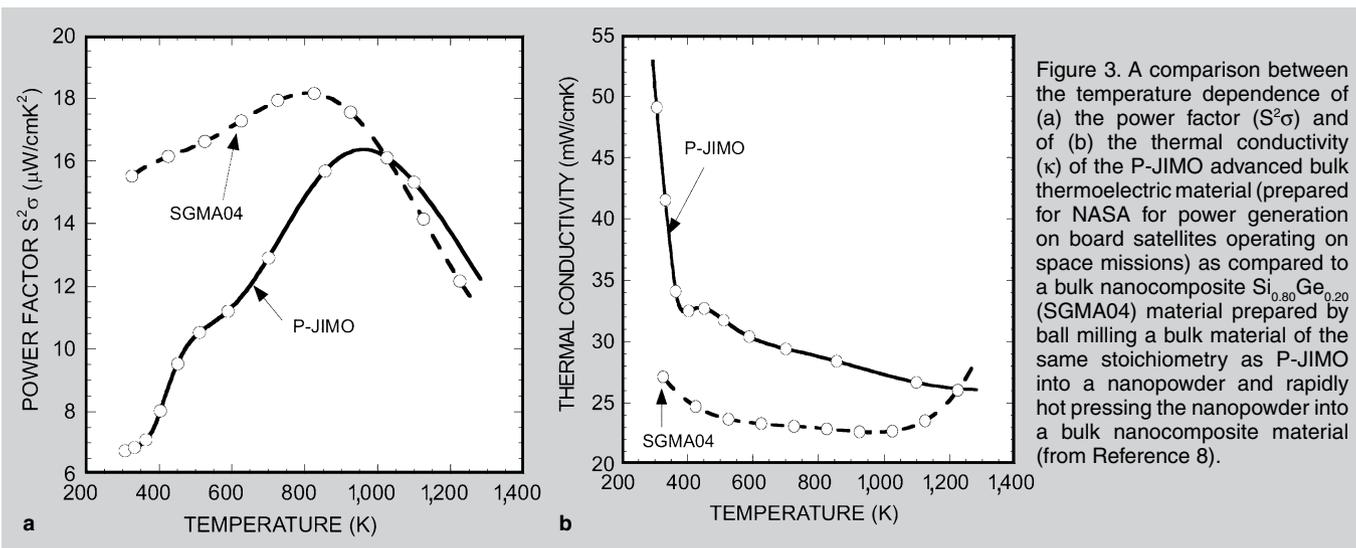


Figure 3. A comparison between the temperature dependence of (a) the power factor ($S^2\sigma$) and of (b) the thermal conductivity (κ) of the P-JIMO advanced bulk thermoelectric material (prepared for NASA for power generation on board satellites operating on space missions) as compared to a bulk nanocomposite $\text{Si}_{0.80}\text{Ge}_{0.20}$ (SGMA04) material prepared by ball milling a bulk material of the same stoichiometry as P-JIMO into a nanopowder and rapidly hot pressing the nanopowder into a bulk nanocomposite material (from Reference 8).

low the Fermi level in p-type PbTe, this phenomenon has now been observed experimentally giving rise to a large increase in ZT to a value of 1.5 for this bulk thermoelectric system.⁵ Another promising approach to enhancing the performance of thermoelectric materials has been the development of thermoelectric materials with very complex crystal structures as a means to reduce the thermal conductivity of bulk materials.¹¹

Modeling studies have been highly influential in guiding the development of nanostructured thermoelectric materials. One important breakthrough was the demonstration that the reduction in the thermal conductivity was mainly controlled by the interface density (the surface area to volume ratio), as shown in Figure 2a,¹² indicating that long-range crystalline order is not necessary for producing a material with a high ZT, and the introduction of crystalline disorder through the generation of a high interface density was in fact desirable for enhancing ZT. A second breakthrough was the modeling studies to identify the contribution of each phonon branch to the thermal conductivity of a material used for thermoelectric applications such as silicon.¹³ Some of the early modeling approaches approximated phonon transport with an average phonon mean free path. By conducting a more detailed analysis of the different phonon contributions to thermal conductivity, the necessity for considering the frequency dependence of phonon mean free paths became clearer. This then stimulated the strat-

egy of targeting the most efficient heat carriers, which are the low frequency modes with long mean free paths. For silicon, these modeling studies indicated that a mean free path of less than 10 nm was needed to reduce the thermal conductivity by a factor of 10 (see Figure 2b), thereby setting a scale for the grain size that is necessary for good thermoelectric performance in nanostructured nanocomposite materials.

These concepts were exploited in the fabrication of the earliest bulk nanocomposite material based on the $\text{Si}_{0.80}\text{Ge}_{0.20}$ alloy, which had been used by NASA in its bulk form for thermoelectric power generation for various space missions. Figure 3 presents results from this early nanocomposite thermoelectrics work, showing that for a nanostructured material it is possible to produce a reduction in the thermal conductivity and at the same time to enhance the power factor, thereby demonstrating an enhancement in ZT in this nanostructured bulk thermoelectric material. Such an approach is shown here to simultaneously increase the power factor $S^2\sigma$ and decrease the thermal conductivity κ , a phenomenon that does not occur in three-dimensional (3-D) bulk materials.⁸

The nanocomposite material is prepared by simply ball milling macro-size pieces taken from ingots of the desired chemical composition into a nano-scale powder as pioneered by the Thermoelectric Group at the NASA Jet Propulsion Laboratory. The powder is then pressure sintered at elevated temperatures into a bulk mate-

rial to achieve a mass density close to (within 1%) the theoretical bulk density of the stoichiometric composition of the powdered material. Tests of the thermal stability of the nanostructured material (over a one month period at 1,000°C) were also carried out to confirm the viability of such a nanocomposite material for practical in-service applications by examining the grain size distribution using high-resolution transmission-electron microscopy (TEM) imaging. Such structural characterization revealed the presence of smaller grains within a grain of ~10 nm size. Such convoluted complex structures were found to inhibit grain growth even at elevated temperatures, thereby contributing to the stability of the nanocomposite materials under service conditions, which is critical for possible application to power systems for long life deep space and planetary science missions.

One example of materials for which a more complete development of such bulk nanocomposite samples has been successfully demonstrated is the nanocomposite $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ system. Results are shown in Figure 4a–e.⁶ In bulk form, this material is the most common thermoelectric material used today for fabricating commercial thermoelectric modules. The main result of Figure 4 is the demonstration of a 40% increase in ZT in the bulk nanocomposite material relative to its 3-D bulk counterpart, as seen in Figure 4e.

This increase in ZT mainly arises from the reduction in the thermal conductivity shown in Figure 4d. The

main reason for the decrease in κ is the increased phonon scattering at the many grain boundaries and by the lattice defects introduced into the nanostructured material. The increase in κ occurring at temperatures above 150°C is due to an increase in the electronic contribution to the thermal conductivity associated with the increase in the concentration of thermally excited carriers. This increase in $\kappa(T)$ is not as pronounced in the nanostructured material as it is in its bulk counterpart because of the larger amount of phonon-electron scattering which decreases the thermal conductivity. It is furthermore of interest to note that it is possible for this system to realize at the same time an enhanced electrical conductivity and an enhanced Seebeck coefficient, a phenomenon that only occurs for nanostructured systems and does not occur in their 3-D counterparts. As a result, this nanostructured composite material shows an enhanced power factor at the same time that the thermal conductivity is reduced, which only occurs for nanostructured systems. At the heart of these findings are the small-grained nanostructures of less than 5 nm contained within larger nanostructures of ~50 nm size.

A detailed high-resolution HRTEM structural study of the nanostructure of this $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ nanocomposite material¹⁰ shows four types of nano-precipitates, including type-1 which is a region which is antimony-rich and tellurium-poor and has diffuse boundaries; type-2 which has the same composition as the surrounding material but shows a twisted boundary with respect to it; type-3 which also has a twisted boundary but is antimony-rich; and type-4 which is a pure tellurium nanodot with sharp boundaries to its surroundings. About 50% of the grains are surrounded by an interface region that is on the order of 4 nm thick as observed by high-resolution TEM images. Energy dispersive x-ray spectra (EDS) show that the stoichiometric composition of these interface regions are often different from their surroundings, thereby generating charged carriers which in fact contribute significantly to increasing the electrical conductivity, and the power factor. Even though the volume of the nano-precipitates and the interface regions are, respectively, only 5% and 1.3% of the total volume of the nanocomposite, they result in a 25% increase in the electrical conductivity, largely due to

carriers generated by the differences in the stoichiometry of the interface regions relative to their surroundings. Structural analysis of the nanostructures of these nanocomposite materials is important for formulating theoretical models for gaining a detailed understanding of the role of each of these defect types and of the interface regions in controlling the temperature dependence of the physical transport properties affecting ZT. Such modeling studies can then be used in an optimization procedure to provide feedback for the preparation of the nanostructured powders and for the processing parameters to be used in the hot press processing to form bulk nanocomposite materials with yet higher ZT values.

As mentioned above, one advantage of working with bulk nanostructured composite samples is the fact that thermoelectric property measurements can be made on bulk size samples, which improves the reliability and repeatability of the measurements using well-established measurement techniques and measurement instrumentation. Nevertheless, the practice of making an actual device out of the nanocomposite material to test its performance in cool-

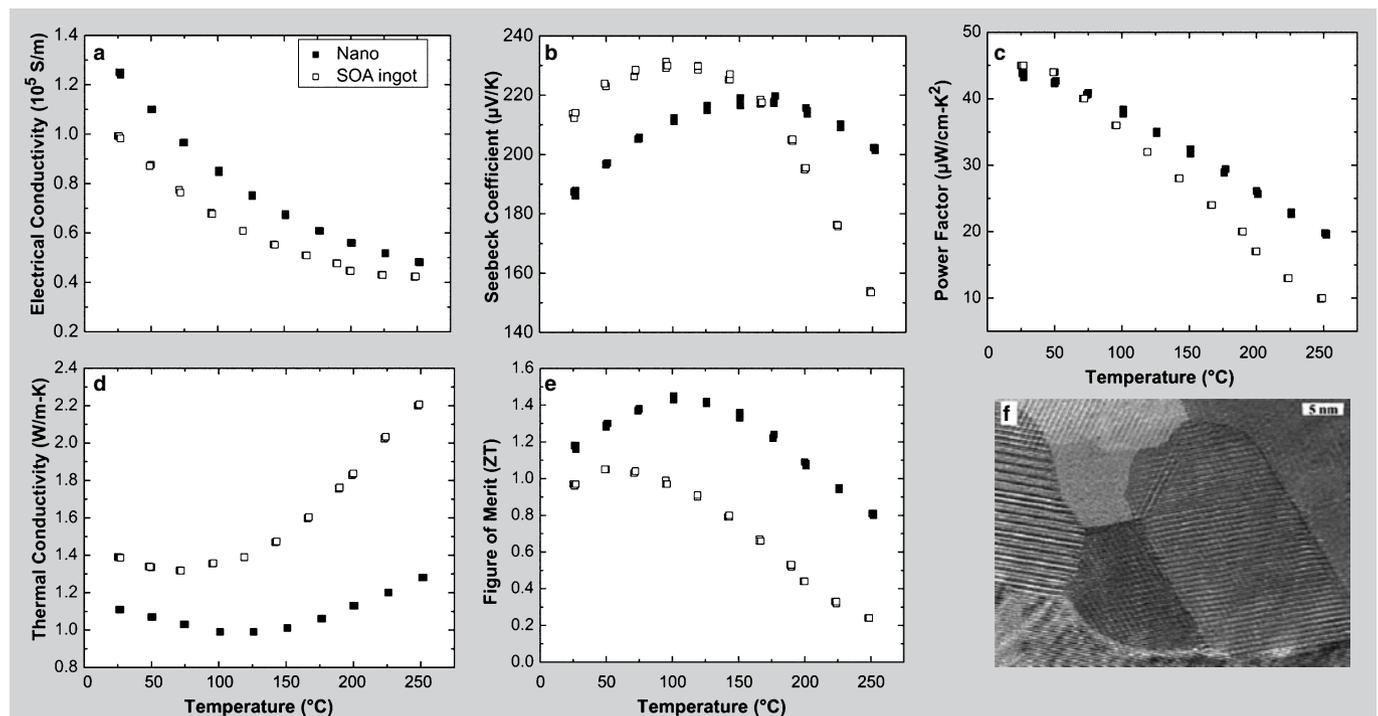


Figure 4. Results for the temperature dependence of the parameters describing the thermoelectric properties of the nanostructured bulk nanocomposite $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$, including the: (a) electrical conductivity (σ), (b) Seebeck coefficient (S), (c) power factor ($S^2\sigma$), (d) thermal conductivity (κ), and (e) the dimensionless thermoelectric figure of merit ($ZT = S^2\sigma/T$).⁶ (f) A TEM image of nanometer-sized grains with crystalline structure that comprise the nanocomposite material (from Reference 6).

ing or in power generation is highly recommended. Such a cooling test was in fact reported for a device based on the $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ nanocomposite material shown in Figure 4, operating between a hot side and cold side at 100°C and 0°C , respectively, showing good agreement between the measured curve for the cooling temperature achieved over a thermal load as the current through the device was varied.⁶

The approach of using nanostructured nanocomposite thermoelectric materials has also been demonstrated by using the ball milling/hot pressing approach discussed above to both p-type SiGe ¹⁴ and n-type SiGe ¹⁵ systems. Here again the goal is to exploit the length-scale differential between electrons and phonons. With nanometer-sized grains of different materials, silicon and germanium, the thermal conductivity is reduced because of enhanced boundary scattering of phonons, which have long mean free paths on the order of hundreds of nanometers (see Figure 2b). For electrons, which have shorter mean free paths on the order of several nanometers, boundary scattering is not significantly enhanced and therefore the electrical conductivity is largely preserved. Furthermore, the choice of two semiconductors from the same column of the periodic table allows conduction electrons to cross a grain boundary into a similar electronic environment, which helps reduce the probability of electron scattering at the interfaces. In the case of the p-type SiGe nanocomposite material an enhancement in ZT by a factor of about 2 was achieved for operation at about 800°C , while the enhancement in ZT for the n-type SiGe nanocomposite was about 30% for similar high-temperature operation. Tests at long-term (1 month) high-temperature operation conditions were carried out on both these materials systems, verifying the thermal stability of these materials for high temperature operation.

The advances in the development of thermoelectric materials with ZT approaching a value of 1.5 is expected to enable the increased use of thermoelectric materials as a cost-effective route for increasing the energy efficiency of large-scale systems, such as automobiles, buildings, and various high-

temperature commercial processes through energy harvesting applications by the conversion of waste heat energy, now released into the atmosphere, into electrical energy for increased system efficiency. These prospects are having a significant impact on stimulating the development of start-up companies and on the education of a new cadre of engineering and applied science students working on materials research, chemistry, nanomaterials, nano-heat transfer, and related fields. On a longer time scale are visions of using thermoelectric materials for photovoltaic and thermo-photovoltaic applications to expand the future possibilities of renewable energy availability and efficient utilization.

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