NANOSTRUCTURED BULK THERMOELECTRIC MATERIALS

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Abstract

The search for bulk materials with high dimensionless thermoelectric figures of merit, ZT, has investigated novel complex structure compounds and phases that combine the electrical transport properties of heavily doped semiconductors or even semimetals with the low thermal conductivity of glassy materials. Low dimensional structures have emerged over the last decade as a promising approach to realize significant increases in thermal-to-electric energy conversion efficiency, as experimentally demonstrated in Bi_2Te_3-based superlattices and PbTe-based quantum-dots superlattices. Instead of quantum carrier confinement effects, as originally predicted, large reductions in thermal conductivity values have been experimentally found mostly responsible for the reported 100 to 200% increases in ZT.

However, a number of technical challenges remain for such materials to be of practical use, especially for medium to large-scale high temperature applications. As a result, some of the most recent research has focused on bulk materials that "naturally" display some of the attributes of the low dimensional structures, such as mixed layered compounds based on chalcogenides of silver, lead, germanium, bismuth, and antimony.

Another approach, discussed in this paper, is to engineer the low-dimensionality of bulk compounds by forming nanostructured 3-D composite materials. Nanostructuring leads to quantum confinement effects and boundary scattering at the nanoparticle interfaces. Quantum confinement enhances the density of states, and thus increases the Seebeck coefficient without reducing the electrical conductivity. Phonon scattering at the interfaces leads to significant reductions in the lattice thermal conductivity. To experimentally validate these initial theoretical predictions, various techniques were successfully developed to produce doped and undoped nanoparticles of Si, Ge, III-V compounds, skutterudite phases and their alloys in sufficient quantities to produce large samples suitable for high temperature electrical and thermal transport property measurements. Various compaction processes were used to consolidate the nanoparticles into highly dense bulk samples. Results obtained on most of the investigated nano bulk materials have shown that the lattice thermal conductivity could be reduced by as much as 90% compared to single crystalline material and that some of the most refractory materials exhibited excellent thermal stability up to 1275 K. After an overview of the most recent data, we discuss the potential of such nano engineered bulk materials for large scale power generation applications such as waste heat recovery

Introduction

The National Aeronautics and Space Administration (NASA) has more than 40 years of history of successful space flight missions that depended on radioisotope fueled power systems to provide electrical power [1]. Past technology has utilized static thermoelectric power conversion, and these Radioisotope Thermoelectric Generators (RTGs) have proven to be highly reliable, long-lived designs based on high temperature materials such as PbTe and Si-Ge alloys. However NASA has a strong need to develop power systems and technologies that will enable or improve the effectiveness of future space science missions. NASA anticipates future mission requirements that go beyond the capabilities of current heritage technology requiring systems that offer significantly better conversion efficiency, higher specific power and enhanced operational capabilities [2].

A key component of this effort is the Advanced ThermoElectric Converter (ATEC) program, a near term research and development project to mature advanced thermoelectric technology for integration into a 1st generation of advanced RTG using the most performant materials available in 2007. JPL leads the project with collaborations from the NASA Glenn Research Center, several university partners, and industry contractors .

This paper describes some of the more long term research and development activities in advanced thermoelectric materials, also supported by NASA's Science Mission Directorate, which are pursued jointly by JPL and university collaborators. The ultimate goal is to experimentally demonstrate average ZT values of 1.5 to 2.0 in a wide temperature range (1275 K to 500 K), more than three times the values obtained for state-of-the-art $Si_{0.8}Ge_{0.2}$ alloys used in past RTGs. While peak ZT values for n-type $Si_{0.8}Ge_{0.2}$ materials reach 1.0 near 1200 K, values for p-type $Si_{0.8}Ge_{0.2}$ are lower by half; in addition, taking into account the

temperature dependence of ZT in the temperature range of interest leads to a combined average ZT value of only about 0.55 for $Si_{0.8}Ge_{0.2}$. As illustrated in Figure 1, such a large increase in average ZT values would lead to system conversion efficiency of 14-17% and specific power values in excess of 10 W/kg.
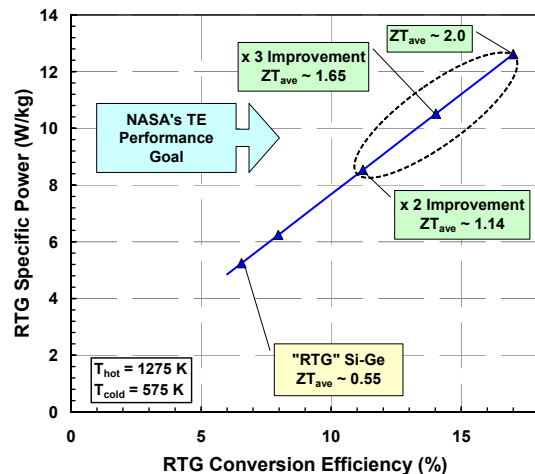

Figure 1: Preliminary calculations showing predicted RTG system specific power as a function of system conversion efficiency. Equivalence with average ZT values of the TE materials across the entire operating temperature range is also reported. For reference, the TE hot and cold junction temperatures are 1275 K and 575 K respectively.

Strategies for Achieving High ZT

For many years, the main approach to developing advanced thermoelectric materials was focused on identifying, characterizing and optimizing bulk degenerate semiconductors. After the initial discoveries of such materials as Bi_2Te_3, PbTe and Si-Ge alloys, still today's state-of-practice materials, experimental research efforts were unable to achieve peak ZT values significantly larger than 1.0 at any temperature. A significant portion of these efforts were devoted to optimizing thermal and electrical transport by controlling the type and amount of doping impurities as well as forming solid solutions. Solid solutions have been used to tune the band gap for maximizing ZT values at a given temperature, but mostly to

reduce the lattice thermal conductivity through point defect scattering of the phonons. However, introducing point defects typically also led to degradation in charge carrier mobility values, thus severely limiting overall enhancement in ZT.

It has now been understood for some time that decoupling charge carrier and phonon scattering mechanisms to enable independent optimization of the electrical and thermal transport is required to achieve much larger ZT values [3]. In the 1980's and early 1990's, a number of studies on bulk materials evaluated potential routes to lower thermal conductivity with limited impact on electrical properties, using "self-assembling" and "force-engineering" approaches to material synthesis. "Self-assembling" approaches were used to synthesize from the melt a number of layered complex chalcogenide materials that used building blocks from compounds such as Bi_2Te_3, PbTe and GeTe [4]. "Force-engineered" approaches focused in particular on Si-Ge alloys prepared through powder metallurgy processes, using techniques such as reducing grain size down to a few microns, [5], and introducing defects by neutron radiation [6], or dispersions of ultrafine inert insulating particulates [7]. While these studies advanced the state-of-the-art in materials syntheses and provided highly valuable scientific insight in understanding thermoelectric transport, improvements in ZT values were only marginal.

In the mid-1990's, building on improved control in the synsthesis of complex materials and structures, two different approaches have been investigated for developing the next generation of new thermoelectric materials: one using new families of advanced bulk thermoelectric materials, and the other using low dimensional materials systems. Several studies on low dimensional high quality thin film structures, such as superlattices based on Bi_2Te_3 and PbTe materials, have

shown that a significant increase in ZT could be achieved. While some of these structures exhibited enhancements in their electrical properties, most of the gains were attributed to scattering of phonons at interfaces leading to large reductions in lattice thermal conductivity values [8-9].

Such low dimensional thin film structures are however ill suited to the demands of high temperature power generation applications that require long term thermal and mechanical stability as well as efficient coupling with existing heat sources. In addition, it could prove to be a very significant challenge to scale-up material sysnthesis to meet the potential needs of terrestrial waste heat recovery applications.

A more recent strategy consists of replicating the nanoscale features responsible for enhanced ZT values in bulk materials using advanced synthesis techniques. Several groups have reported a significant increase in ZT in some bulk materials, such as silver antimony lead telluride (LAST) and its alloys, attributed mostly to the formation of "self-assembling" nanoclusters inside a host matrix [10-11]. To address the need for long term material stability at temperatures as high as 1275 K, we have proposed a nanostructured bulk and composite materials "force-engineered" approach focused on $Si_{1-x}Ge_x$ compositions and other electronic semiconductors [12-13]. This approach aims at generating a very large interface density, such as that formed in a superlattice, into dense bulk materials prepared from nanoparticles.

Nanostructured Bulk Thermoelectrics

Even though it is possible to enhance the electrical properties of nanostructured materials through several mechanisms such as energy filtering at grain boundaries, our main focus was on drastically reducing the lattice thermal conductivity of good electronic semiconductors that already possess high power factor values. For bulk systems, the dominant phonon scattering

mechanisms are phonon-phonon scattering, charge carrier-phonon scattering, and point defect-phonon scattering. In addition to phonon-phonon scattering, point defect scattering is most important for reducing the thermal conductivity in the $Si_{1-x}Ge_x$ system for the short wavelength phonons, while electron-phonon scattering is effective for long wavelength phonons (see Fig.2). Nanostructures not only introduce a high density of interfaces (grain boundaries), but also extended point defects generated during nanoparticle synthesis and bulk compaction. As a result, phonon scattering due to nanostructuring is effective at both long and short wavelengths through the presence of nanoparticles with a wide distribution of sizes.
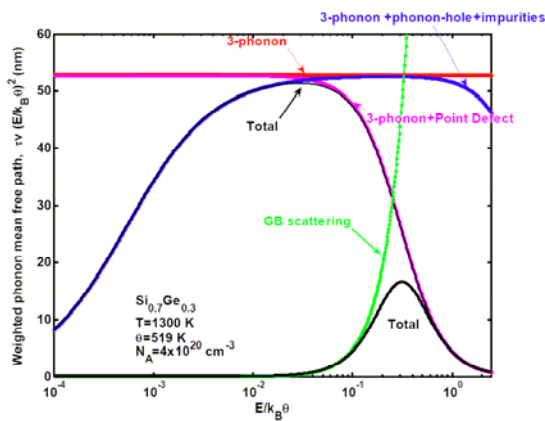

Figure 2: Effect of various phonon scattering mechanisms on the thermal conductivity of $Si_{0.7}Ge_{0.3}$. Scattering due to nanostructuring (GB) could effectively scatter long wavelength phonons.

A detailed analysis of the relative contribution of phonons to the lattice thermal conductivity according to their mean free path or to their wavelength was conducted for pure silicon [14]. Calculation results, summarized in Figure 3 for two temperatures of 300 K and 1000 K, show that these contributions cover many orders of magnitude of their mean free path. In order to achieve reductions at high temperatures (~ 1000 K) of the order of 90% over that of single crystal Si, the calculations suggest that the mean free path

of phonons must be limited to less than 10 nm, as highlighted in Figure 3. These feature sizes are smaller by two orders of magnitude than those studied for "fine grained $Si_{0.8}Ge_{0.2}$" materials. But they are comparable however to the nanostructure of $Si_{0.8}Ge_{0.2}$ materials that were produced in the early 1990's by an innovative spark erosion technique [15]. Unfortunately, decreases in thermal conductivity values as large as 40% were typically accompanied by reductions in carrier mobility values of a similar magnitude, resulting in no or only limited net improvement in ZT. However, experiments did demonstrate that the nanoscale nanostructuress were thermally stable at temperatures as high as 1300 K for several weeks.
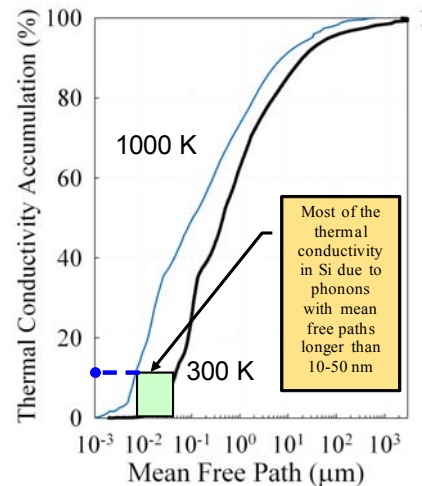

Figure 3: Calculated thermal conductivity accumulation for Si as a function of the phonon mean free path . Most of the heat conduction is carried by phonons with a mean free path greater than 10 nm.

Nanoparticle Synthesis and Bulk Consolidation

At the onset of this research, only very small amounts of nanoparticles could be produced. Developing synthesis techniques that could scale up production from milligrams to grams to hundreds of grams enabled a throrough evaluation of the potential of nanostructured bulk ("nano bulk") and nanostructure composites ("nanocomposites") for high temperature thermoelectric power generation

applications. Doped nanoparticles of Si, Ge and $Si_{1-x}Ge_x$ solid solutions can be produced by several techniques, but we have focused our efforts mostly on high energy ball milling from the pure elements and chemical metathesis processes. Building upon previous work on the powder metallurgy of Si-Ge materials, the high energy ball milling has been successfully used for processing 5 to 15 g batches of materials with nanoparticles as small as 10 nm, and then scaled up to the 100 g batch quantity which is currently used by the ATEC program.
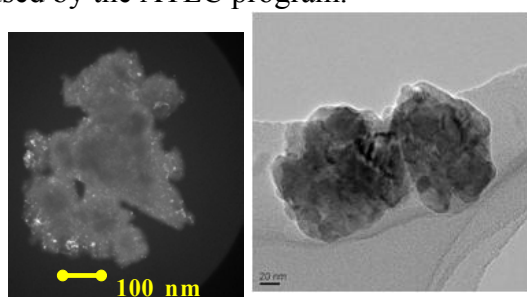

Figure 4: (a) Large agglomerate of $Si_{0.8}Ge_{0.2}$ nanoparticles as seen by TEM analysis and (b) close up showing that most particles are smaller than 10 nm in size.

Because the nanoparticles easily aggregate, it is challenging to precisely determine their size distribution and chemical purity. A combination of techniques is often useful to precisely characterize the batches of nanoparticles, including x-ray-diffraction, SEM, TEM, DLS and BET. These are used to evaluate the average particle and crystallite size, and to evaluate crystal phases, sample purity, and the presence of lattice strain. TEM pictures of dry agglomerates of Si-Ge nanoparticles are shown in Figure 4.

A number of compaction techniques (hot-pressing, spark plasma sintering, and high pressure low temperature sintering) have been evaluated. The higher temperature processes typically result in compacted samples whose mass density is 96% to 100% of the theoretical density. Similar processes have also been developed for III-V compounds, such as GaAs and InSb, with synthesis and compaction

conditions appropriately adjusted. For these materials, only limited grain growth has been observed after compaction.

Thermoelectric Properties

To better understand the change in the thermal and electrical transport properties of nano bulk samples prepared from nanoparticles, Si was used a a model system. It eliminated point defect scattering effects due to Ge as well as potential issues such as inhomogeneity in compositions and allowed for an in-depth study of the synthesis, compaction and doping conditions. Experimental results were compared with predictions made by theoretical models and used interactively to both refine the models and improve synthesis and compaction techniques.

Transport property measurements have been conducted at several of the participating institutions as a function of temperature using both commercial and custom-made setups that have been described elsewhere. The properties measured included electrical resistivity (ρ), Hall coefficient (R_H) and Seebeck coefficient (S) as well as thermal conductivity (λ). The Hall carrier mobility (μ_H) and Hall carrier concentration (n) are calculated from the combined electrical resistivity and Hall coefficient values.

The lattice thermal conductivity, λ_L, is calculated by subtracting the electronic portion of thermal conductivity from the total thermal conductivity using the Wiedemann-Franz law.

Table 1: Comparison of room temperature properties of heavily doped n-type single crystal, polycrystalline and nano bulk Si

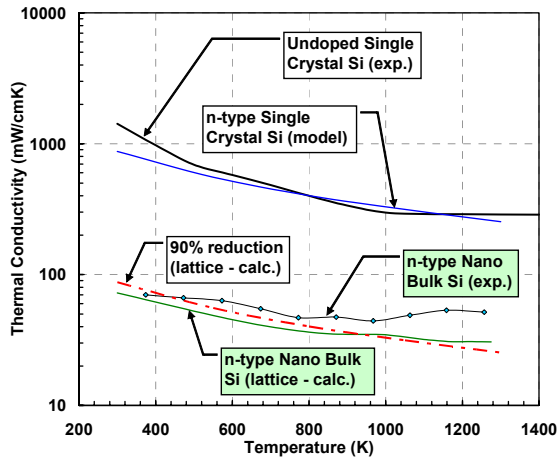|	Single Crystal Si	Poly-crystal Si	Nano Bulk Si
n (x10^{20} cm^{-3})	4.5	9.5	4.6
S (μV/K)	-86	-73	-70
ρ (mΩ.cm)	0.33	0.45	0.91
μ_H (cm^2/Vs)	42.8	14.7	15.1
λ_L (mW/cmK)	873.1	385.1	62.6
μ_H/λ_L	0.05	0.04	0.24

| ZT | 0.08 | 0.09 | 0.023 |

Figure 5: Thermal conductivity as a function of temperature for single crystal and nano bulk Si. The large reduction in lattice thermal conductivity observed experimentally in n-type nano bulk Si is in good agreement with theoretical models.

Experimental results for heavily doped n-type nano bulk Si are summarized in Table 1 and Figure 5, and compared to values typical of single crystal Si. At equivalent doping levels, room temperature results (Table 1) show significant decreases in both electron mobility and lattice thermal conductivity. However when comparing the magnitude of the ratio of these two properties (μ_H/λ_L), much higher values are obtained for nano bulk Si. The larger decrease in λ_L over μ_H due to nanostructuring effects translates in three fold higher ZT values. The nearly 90% reduction in λ_L is maintained over the full temperature range (Figure 5), and was found to be in reasonable agreement with first principle thermal conductivity calculations based on 10 nm nanocrystallite sizes. Detailed analysis of the nano bulk samples has shown however that a wide distribution of grain sizes is present, from less than 10 nm up to microns.

Preliminary experimental data on nano bulk III-V compounds also highlighted the very large reductions (70 to 90%) in lattice thermal conductivity values over those of high quality single crystals. These results emphasize the potential of "nano grained" semiconductors which possess excellent electrical properties to achieve thermal conductivity values typical of good thermoelectric materials.

Table 2: Comparison of room temperature thermal conductivity (in mW/cmK) of lightly doped single crystal and nano bulk III-V compounds

compound	Single Crystal	Nano bulk
GaAs	500	40
GaSb	320	67
InP	600	93
InAs	269	41
InSb	201	42

The variations of ZT at elevated temperatures for some nano bulk Si and nano bulk $Si_{0.8}Ge_{0.2}$ samples are plotted in figures 6 and 7 respectively. Comparisons are made with values for n-type single crystal Si, and n-type and p-type $Si_{0.8}Ge_{0.2}$ used in current RTGs. Figure 6 demonstrates that the best nanobulk n-type Si samples have a peak ZT value of 0.7 at 1200 K, more than 3 times that of single crystal Si at an equivalent carrier concentration, but only about 25% lower than that of state-of-the art $Si_{0.8}Ge_{0.2}$.
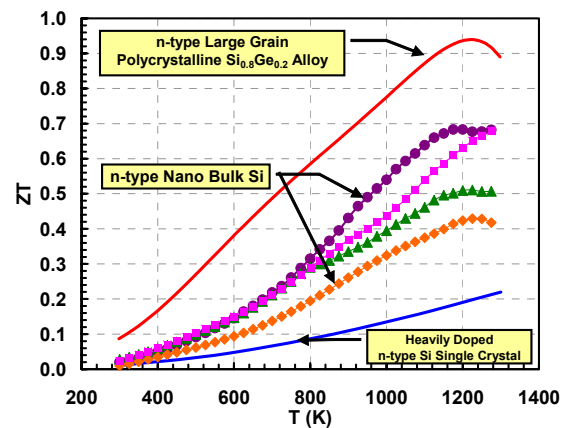

Figure 6: ZT as a function of temperature for single crystal (blue line) and nano bulk

Si. Data are also shown for state-of-the-art $Si_{0.8}Ge_{0.2}$ (red line).

In figure 7, recent results for n-type and p-type nano bulk $Si_{0.8}Ge_{0.2}$ samples show that significant increases in ZT over state-of-the-art materials have been achieved. This is particularly true of heavily doped p-type compositions which approach our goal of nearly doubling ZT values.
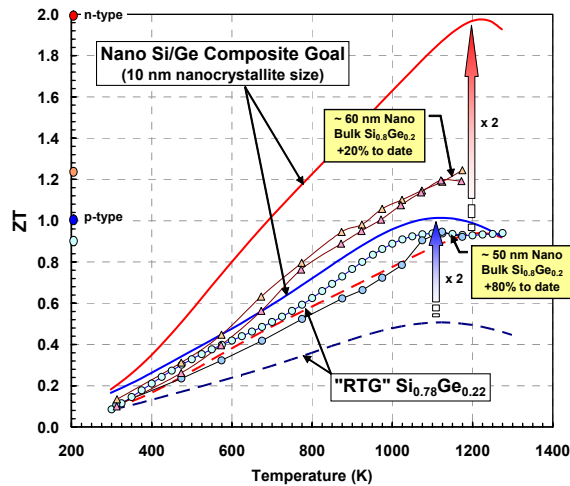

Figure 7: ZT as a function of temperature for p-type and n-type nano bulk $Si_{0.8}Ge_{0.2}$ samples. Data are also shown for state-of-the-art $Si_{0.8}Ge_{0.2}$ as well as extrapolated curves corresponding to a factor of 2 improvement over state-of-the-art.

Thermal Stability

While the "force-engineering" approach to nanostructuring bulk materials has yielded very encouraging results, of particular concern to high temperature power generation applications is the thermal stability of such nanostructures. While there is ample experimental evidence that for some material systems long term thermal stability (i.e. grain growth and interdiffusion) may be a very difficult challenge, preliminary short term studies conducted by the ATEC program have shown nano bulk $Si_{1-x}Ge_x$ to be highly stable. This is best illustrated by Figure 8, which shows thermal conductivity measurements on p-type nanobulk $Si_{0.8}Ge_{0.2}$ samples produced by the large 100 g batch method. After ageing the samples for more

than three months at 1275 K, results show that the thermal conductivity remained much lower than that of state-of-the-art $Si_{0.8}Ge_{0.2}$ material, with any variation within the experimental error limits.
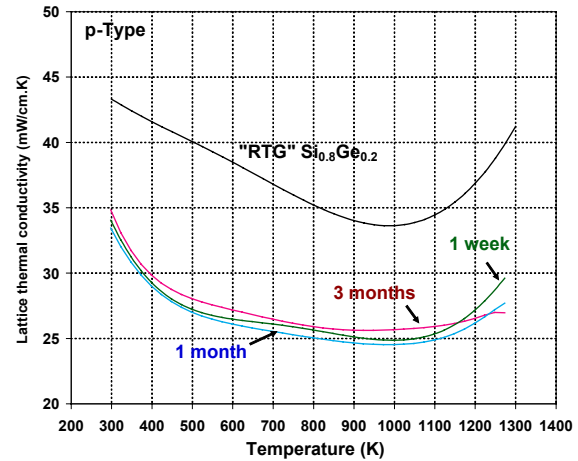

Figure 8: Thermal conductivity as a function of temperature and time for p-type nano bulk $Si_{0.8}Ge_{0.2}$ samples. Data are also shown for state-of-the-art $Si_{0.8}Ge_{0.2}$.

The ability to scale material synthesis in similar fashion to state-of-the-art materials produced through more traditional powder metallurgy techniques, combined with likely long term thermal stability are critical enabling requirements. While results will undoubtedly vary from one material class to another, it is clear that nano bulk $Si_{1-x}Ge_x$ materials are suitable candidates for high temperature thermoelectric applications. This work has now expanded to III-V compounds and skutterudite materials.

Conclusions

This brief overview presents a "force-engineered" approach to nanostructuring bulk thermoelectric materials and replicate enhancements in ZT values observed in some low dimesional material systems.. The approach is applicable to both n and p type samples for a wide variety of materials, though the details for each materials system are different. It is especially attractive for good electronic semiconductors, such as III-V compounds, who exhibit high power factor values but also large lattice thermal conductivity

values. Although enhancement in ZT has already been demonstrated in n-type and p-type nano bulk $Si_{1-x}Ge_x$ systems, further enhancement in ZT is expected with better understanding of theoretical issues, better control of materials processing parameters, doping levels, nanoparticle sizes and size distribution. Moreover, the preparation of unique composite nanostructures will likely offer additional tuning of the transport properties. Nano bulk $Si_{1-x}Ge_x$ has also demonstrated its suitability for extended operation at temperatures of interest to NASA applications as well as terrestrial systems using high grade heat.

Acknowledgments

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