"Phase II: The Next Generation Thermoelectric Materials for Solid State Cooling & Power Generation Applications"

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I.) Program Scope:

The demand for alternative energy technology to reduce our dependence on fossil fuels along with their environmental impacts leads to very important regimes of research, including that of high temperature energy harvesting via the direct recovery of waste heat and its conversion into useful electrical energy. Thus, the development of higher performance thermoelectric (TE) materials for power generation from waste heat recovery or solar energy conversion is becoming ever more important. As an example, solar cell and thermoelectric cooperative devices can be used in a solar energy system to transform stored heat from a thermal bath storage system into useful electrical energy. Also, a TE device can be directly coupled to a solar collector/concentrator system. An excellent overview of the state of the art TE materials, as well as an overview of recent developments is given in the following references. [1, 2]

Over the past decade there has been a heightened interest in the field of TE's driven by the need for more TE efficient materials for both electronic refrigeration and power generation. [3, 4] Some of the research efforts focus on minimizing the lattice thermal conductivity while other efforts focus on materials that exhibit large power factors. Refrigeration aspects include applications such as cooling electronics (e.g. CPU chips) and optoelectronics (IR detectors and laser diodes) for enhanced performance. [5] The modular aspects of TE cooling devices make them applicable to a wide range of uses. One of the largest current markets incorporates TE cooling devices into automotive seat coolers. Power generation applications are especially important in deep space missions (NASA) where the need for a reliable long-term power source is an absolute necessity. Other technologies such as fuel cell batteries or solar power are not feasible for many of these applications. Given the recent energy needs experienced in the United States there is even a more pressing need to investigate alternative energy conversion technologies, such as thermal to electrical energy conversion from natural heat gradients that TE technologies can provide,. The incorporation of TE power generation from recovery of the large amount of waste heat (≈ 2/3 of generated power) from an automobile's exhaust or engine and harvesting this into usable "on-board" electrical energy can provide a reduced demand for fossil fuels and reduce their detrimental impact on the environment. [6] In addition, the possibilities within the solar energy conversion technologies may even be much more important. It is not likely that any single technology can solve all the nation's energy needs of the 21st century. It is most probable that it will be a combination of many technologies, one of which we believe will be TE energy conversion.

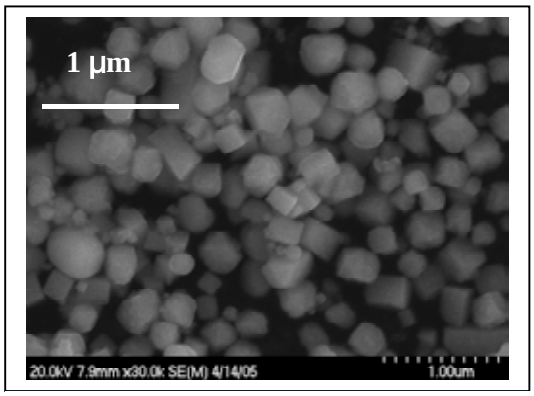
II.) Recent Progress:

The major programmatic impacts of Phase I funding was the hiring of a new faculty member and the acquisition of several major pieces of experimental equipment. Prof. Drymiotis was a new faculty hire under the Phase I part of the program. He was able to establish a state-of-the-art bulk materials synthesis laboratory. We were able to acquire several major pieces of equipment for enhancement of the research infrastructure. These include: (a) a Netzsch 457 laser flash diffusivity system, (b) a Netzsch

404 high temperature DSC (these two combined allow for high temperature thermal conductivity measurements on bulk materials) (c) a Thermal Technology hot isostatic press to provide high quality densified polycrystalline materials, (d) a Rigaku X-Ray Diffraction apparatus, (e) an Ulvac ZEM-2 high temperature resistivity and Seebeck measurement system and (f) a UV-visible spectrometer that was used to determine the position of the surface plasmon absorption peak Bi nanowires (10 nm).

One of our major scientific successes in Phase I of this DOE Implementation program has been the ability to synthesize thermoelectric nanocomposite materials. A nano-composite is a bulk material, that may weigh several grams, which is comprised of a bulk matrix of one thermoelectric material that has had a large fraction of nanomaterials incorporated into the bulk phase. This second phase of nanomaterials is typically also a good TE material, which may be the same composition as the host or may be very different. A requirement is that one must be able to synthesize large quantities of the nanomaterials that will eventually be incorporated into the nanocomposite, typically via a hot pressing technique of the nanomaterial and the bulk phase.

Using CVD or Hydrothermal Methods: We have been very successful in using both CVD (chemical vapor deposition) methods and hyrdrothermal methods to synthesize large amounts of TE nanomaterials. For example, we used a CVD method to grow large amounts (100's of mg) of the TE material, PbTe and doped PbTe as shown in Figure 2 below. [7] It is apparent from Figure 1 that the PbTe nanoparticles are about 100 nm cubic particles. We are able to grow large quantities of size selective particles ranging from about 50 nm up to 2 μm or so. The composition and phase purity is confirmed by X-Ray diffraction measurements as shown in Figure 1.



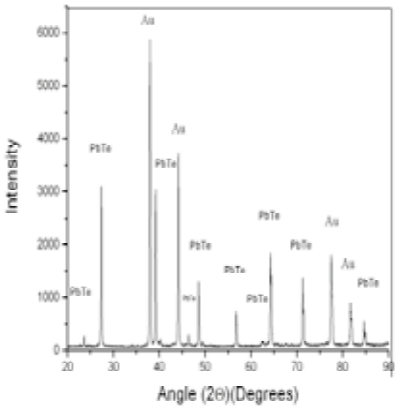


Figure 2. PbTe nanoparticles (100 nm) grown by CVD are shown above. The PbTe structure is confirmed by X-Ray (right).

We have used CVD methods in order to obtain large yield growth of nanostructures of several TE materials including Bi_2Te_3. In addition, we have also used solvothermal and hydrothermal methods in order to yield large quantities (grams per growth) of other TE materials such as: PbTe, Bi_2Te_3, Bi_2S_3 and $CoSb_3$. Skutterudite nanomaterials were also grown via this technique, such as $CoSb_3$. The techniques are described in more detail elsewhere. [24, 8] The nanomaterials can vary in size from several nanometers to submicron and subsequently even several micron size materials, depending on the material and the conditions. These materials are then incorporated into a bulk structure using our hot pressing capabilities and investigated as a bulk composite made up of the parent material and the incorporated nanostructured material. In addition, we have synthesized large amounts of nanoscaled $CoSb_3$ and mixed with other non-reactive nanomaterials though hot pressing. Incorporating these nano-particles into a composite should lower the lattice thermal conductivity. Results on each system will be presented. It has been known since the 1980s that the ZT for highly disordered PbTe alloys with a

mean grain size of 1 μm could be ~10% higher than the equivalent single-crystal value. In addition, we believe that investigations of the interface of these nanostructures and its role after hot pressing could be very interesting scientifically. We have recently developed a technique with which the hydrothermal techniques are used to grow the nanostructures directly onto seed particles. [9] The seed particles can be either nanoparticles or small particle size-grains. This has been performed successfully in the PbTe system and these results will be discussed.

III.) Future Plans:

An exciting possibility for increasing the efficiency is based on preparing thermoelectric materials that includes an inherent nanophase component. This research direction has been motivated by several recent theoretical and experimental investigations. It was proposed by Hicks *et al*. that an increase in ZT can be expected due to an increase in the electronic DOS per unit volume in quantum-well structures. [10] The results from an experimental measurement of a 2-D PbTe/$Pb_{1-x}Eu_xTe$ quantum well system found such a large increase in the figure of merit confirming this prediction. [11] Thus, by shrinking conventional thermoelectric materials to the nanoscale it may be possible to convert these materials into higher efficiency materials. [12, 13] Certainly low dimensional structures of TE materials have shown to possess higher ZT values than their bulk counterparts such as the PbTe quantum dot structures [14] and the Bi_2Te_3/Sb_2Te_3 superlattice materials have already been shown to be quite feasible. [15] Therefore we plan to:

- Develop methods of synthesis and investigate thermally stable phases of TE materials embedded with nanoparticles of a semiconducting phase (e.g. rare-earth oxides).
- Utilize current method of hydrothermal and solvothermal synthesis of nanostructures in order to incorporate these nanostructures into a matrix of a high ZT filled TE materials, thus forming a TE nanocomposite. Hopefully, point defect, strain field and two-phase effects will yield significant reductions in the lattice thermal conductivity. Investigate effect of nanoparticle size and density of nanoparticles on phonon scattering; and investigate κ_L reduction by employing distributed particle sizes to scatter phonons over a broad spectrum.
- Utilize spark plasma sintering techniques to form highly densified TE nano-composite materials. Investigate role of overall density on the specific thermoelelctric properties of the nano-composites.
- Develop the TE phenomenology of composites through investigation of effects of microstructure and bandgap on thermopower and electrical conductivity in order to provide the basis for identifying and evaluating the relevant transport mechanisms that can contribute to the enhancement in the power factor, α^2T/ρ.
- Characterize the structural, electrical and thermal properties; and subsequently analyze and model the TE properties. This will occur over a broad range of temperature from 10 K up to temperatures as high 1400 K.

Summarizing, the proposed composites and nano-composites will contain selective second TE phases or nano-inclusions, and that the microstructure and local composition must not change at high temperatures (e.g, 600-800°C). The role of the specific nanoparticles, size and/or density of nanoparticles and the interface effects and interface materials will be a major focus of our Phase II investigations. The composites to be designed are to have the following material characteristics:

IV. References:

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Solution-chemical synthesis of nano-structured Bi_2Te_3 and PbTe thermoelectric materials
X. Ji, J. He, B. Zhang and Terry M. Tritt Jour Elec. Materials, (2007) in press

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Jason Reppert Rahul Rao; Malcolm Skove; Jian He; Matthew Craps; Terry Tritt;
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