

## Recent Advances in Thermoelectric Materials

Matthew Thorum

Literature Seminar

November 16, 2006

The ability of thermoelectric materials to accomplish direct conversion between thermal and electrical energy in compact, durable, solid-state devices without moving parts makes them an attractive technology for refrigeration and waste heat recovery applications. However, current thermoelectric materials perform at levels much lower than is theoretically possible, which limits the efficiency of thermoelectric devices, and has restricted their use to small scale applications where efficiency is not a major concern.<sup>1</sup>

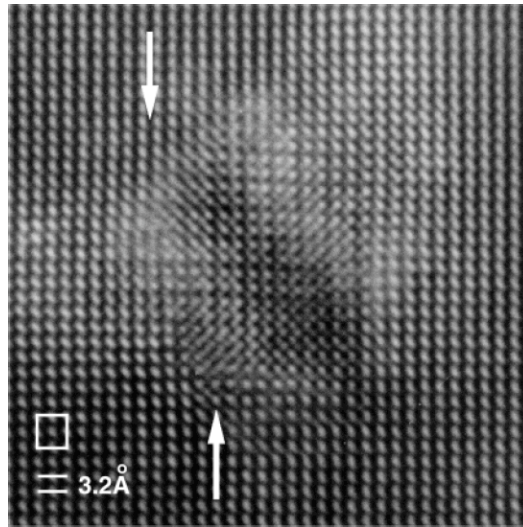
The performance of thermoelectric materials is described by the dimensionless figure-of-merit:  $ZT = S^2\sigma/\kappa$ , where  $S$  is the Seebeck coefficient (the size of the voltage produced by a thermal gradient in a material, defined by  $S = \Delta V/\Delta T$ ),  $\sigma$  is the electrical conductivity and  $\kappa$  is the thermal conductivity. There is no thermodynamic upper limit to  $ZT$ , although all commercially available thermoelectrics have  $ZT < 1$ . To be competitive, thermoelectrics with  $ZT > 3$  are needed.<sup>1, 2</sup> A more efficient thermoelectric will have a large  $S$  and high electrical conductivity, but must also have a small thermal conductivity. The thermal conductivity can be separated into electrical and lattice parts ( $\kappa = \kappa_{el} + \kappa_{latt}$ ). The value of  $\kappa_{el}$  is directly proportional to  $\sigma$ , and so there is no way to reduce it while preserving a high electrical conductivity; however,  $\kappa_{latt}$  may be minimized. The reduction of  $\kappa_{latt}$  by designing materials that minimize the propagation phonons has proven to be the most successful strategy for the production of more efficient thermoelectric materials.

The materials with the highest  $ZT$  reported to date are thin-film superlattices and quantum-dot superlattices. Venkatasubramanian and others<sup>3, 4</sup> deposited alternating epitaxial layers of 10 Å thick BiTe<sub>2</sub> and 50 Å thick Sb<sub>2</sub>Te<sub>3</sub> by metal-organic chemical vapor deposition (MOCVD). Because the crystal structures are matched between the layers, charge carriers retain a high mobility and pass between layers relatively unimpeded and the value of  $S$  remained the same as for the bulk material ( $\sim 243$  mV K<sup>-1</sup>). However, phonons are strongly scattered by the interfaces leading to a small  $\kappa_{latt}$  of 0.22 W m<sup>-1</sup> K<sup>-1</sup> (vs. about 0.49 W m<sup>-1</sup> K<sup>-1</sup> in the bulk material). This results in an increase of  $ZT$  to about 2.5. Harman et al. have reported the preparation of thin-film quantum dot superlattices based on PbSe and PbTe using molecular beam epitaxy.<sup>2</sup> The net result is a large number of phonon scattering interfaces are formed between PbSe dots and a PbTe matrix. A  $ZT$  of 1.6 is achieved at 300 K, but it increases to 3 at 550 K.<sup>5</sup> This represents the largest value of  $ZT$  reported to date. The Harman group has managed to construct devices to demonstrate the favorable cooling and power generating capabilities of this material.<sup>2, 6</sup>

The success realized in enhancing  $ZT$  in thin-film materials has complemented a search for more practical bulk materials with improved  $ZT$ . The most successful work has been produced by the Kanatzidis group. Chung et al.<sup>7-9</sup> reported the properties of CsBi<sub>4</sub>Te<sub>6</sub> and demonstrated that it is the most efficient bulk material available below

room temperature. It consists of laths of  $[\text{Bi}_4\text{Te}_6]^-$  that are bound together into layers by a series of unusual Bi-Bi bonds, the  $\text{Cs}^+$  ions separate the layers. While ZT reaches a maximum value of only 0.8, it does so at  $\sim 200$  K making it particularly well suited for cooling applications. The enhanced ZT at low temperatures is due to the affect of the Bi-Bi bonds on the electronic band structure. The value of ZT falls off above this temperature because the narrow bandgap ( $\sim 0.1$  eV) of the p-type material allows the thermal excitation of electrons into the conduction band creating an opposite n-type thermoelectric effect that attenuates ZT.

The Kanatzidis group has also developed a series of quaternary semiconductor thermoelectric materials, the most successful of these materials are the n-type  $\text{AgPb}_{18}\text{SbTe}_{20}$  (or LAST) and the p-type  $\text{Na}_{0.95}\text{Pb}_{20}\text{SbTe}_{22}$  (or SALT).<sup>10-12</sup> Both of these materials exhibit low thermal conductivities of  $\sim 1 \text{ W m}^{-1} \text{ K}^{-1}$  and  $\text{ZT} \sim 2$  around 700 K. Again, the increase in ZT is due to the decrease in the thermal conductivity. The  $\text{M}^+$  and  $\text{Sb}^{3+}$  ions aggregate into nanocrystals within the PbTe structure. Because the nanocrystals maintain the crystal lattice they have been described as “endotaxial”. In a manner analogous to epitaxial thin-films, the lattice matching allows the carriers to pass freely, but phonons are scattered by the interfaces. Aggregation is favored over dispersion because dispersion causes a larger local charge imbalance in the PbTe lattice.



**Figure 1:** HRTEM image of LAST with an endotaxial nanocrystal. The box indicates a unit cell, and arrows indicate dislocations in the nanocrystal/matrix interface.<sup>10</sup>

In order to see widespread use, thermoelectric materials with  $\text{ZT} > 3$  are required. Recent research has demonstrated that it is possible to achieve this level of performance using thin-films. The enhancement is due to the design of nanoscale features that lower the thermal conductivity by scattering phonons, but do not adversely affect the thermopower or electrical conductivity. Progress has also been made with bulk materials that contain nanoscale features and  $\text{ZT} \sim 2$  has been achieved.

## References

1. Tritt, T. M.; Subramanian, M. A., Thermoelectric Materials, Phenomena, and Applications: A Bird's Eye View. *MRS Bulletin* **2006**, 31, (3), 188-194.
2. Harman, T. C.; Taylor, P. J.; Walsh, M. P.; LaForge, B. E., Quantum dot superlattice thermoelectric materials and devices. *Science* **2002**, 297, (5590), 2229-2232.
3. Venkatasubramanian, R.; Colpitts, T.; O'Quinn, B.; Liu, S.; El-Masry, N.; Lamvik, M., Low-temperature organometallic epitaxy and its application to superlattice structures in thermoelectrics. *Appl. Phys. Lett.* **1999**, 75, (8), 1104-1106.
4. Venkatasubramanian, R.; Siivola, E.; Colpitts, T.; O'Quinn, B., Thin-film thermoelectric devices with high room-temperature figures of merit. *Nature* **2001**, 413, (6856), 597-602.
5. Harman, T. C.; Walsh, M. P.; Laforge, B. E.; Turner, G. W., Nanostructured thermoelectric materials. *J. Electron. Mater.* **2005**, 34, (5), L19-L22.
6. Harman, T. C.; Reeder, R. E.; Walsh, M. P.; LaForge, B. E.; Hoyt, C. D.; Turner, G. W., High electrical power density from PbTe-based quantum-dot superlattice unicomple thermoelectric devices. *Appl. Phys. Lett.* **2006**, 88, (24).
7. Chung, D. Y.; Hogan, T.; Brazis, P.; Rocci-Lane, M.; Kannewurf, C.; Bastea, M.; Uher, C.; Kanatzidis, M. G., CsBi<sub>4</sub>Te<sub>6</sub>: A high-performance thermoelectric material for low-temperature applications. *Science* **2000**, 287, (5455), 1024-1027.
8. Chung, D. Y.; Hogan, T. P.; Rocci-Lane, M.; Brazis, P.; Ireland, J. R.; Kannewurf, C. R.; Bastea, M.; Uher, C.; Kanatzidis, M. G., A new thermoelectric material: CsBi<sub>4</sub>Te<sub>6</sub>. *J. Am. Chem. Soc.* **2004**, 126, (20), 6414-6428.
9. Larson, P.; Mahanti, S. D.; Chung, D. Y.; Kanatzidis, M. G., Electronic structure of CsBi<sub>4</sub>Te<sub>6</sub>: A high-performance thermoelectric at low temperatures. *Phys. Rev. B: Condens. Matter* **2002**, 65, (4).
10. Quarez, E.; Hsu, K. F.; Pcionek, R.; Frangis, N.; Polychroniadis, E. K.; Kanatzidis, M. G., Nanostructuring, compositional fluctuations, and atomic ordering in the thermoelectric materials AgPb<sub>m</sub>SbTe<sub>2+m</sub>. The myth of solid solutions. *J. Am. Chem. Soc.* **2005**, 127, (25), 9177-9190.
11. Poudeu, P. F. P.; D'Angelo, J.; Downey, A. D.; Short, J. L.; Hogan, T. P.; Kanatzidis, M. G., High thermoelectric figure of merit and nanostructuring in bulk p-type Na<sub>1-x</sub>Pb<sub>m</sub>Sb<sub>y</sub>Te<sub>m+2</sub>. *Angew. Chem., Int. Ed. Engl.* **2006**, 45, (23), 3835-3839.
12. Hsu Kuei, F.; Loo, S.; Guo, F.; Chen, W.; Dyck Jeffrey, S.; Uher, C.; Hogan, T.; Polychroniadis, E. K.; Kanatzidis, M. G., Cubic AgPb<sub>m</sub>SbTe<sub>(2+m)</sub>: Bulk thermoelectric materials with high figure of merit. *Science* **2004**, 303, (5659), 818-21.

