

High-Thermoelectric Performance of Nanostructured Bismuth Antimony Telluride Bulk Alloys

Bed Poudel,^{1,2*} Qing Hao,^{3*} Yi Ma,^{1,2} Yucheng Lan,¹ Austin Minnich,³ Bo Yu,¹ Xiao Yan,¹ Dezhi Wang,¹ Andrew Muto,³ Daryoosh Vashaee,³ Xiaoyuan Chen,³ Junming Liu,⁴ Mildred S. Dresselhaus,⁵ Gang Chen,^{3†} Zhifeng Ren^{1†}

¹Department of Physics, Boston College, Chestnut Hill, MA 02467, USA. ²GMZ Energy, Inc., 12A Hawthorn Street, Newton, MA 02458, USA. ³Department of Mechanical Engineering, MIT, Cambridge, MA 02139, USA. ⁴Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, China. ⁵Department of Physics and Department of Electrical Engineering and Computer Science, MIT, Cambridge, MA 02139, USA.

*These authors contributed equally to this work.

†To whom correspondence should be addressed. E-mail: gchen2@mit.edu (G.C.); renzh@bc.edu (Z.R.)

The dimensionless thermoelectric figure-of-merit (ZT) in bulk bismuth antimony telluride alloys has remained around 1 for more than 50 years. Here we show that a peak ZT of 1.4 at 100°C can be achieved in p-type nanocrystalline bismuth antimony telluride bulk alloy. These nanocrystalline bulk materials were made by hot-pressing nanopowders ball-milled from crystalline ingots under inert conditions. Electrical transport measurements, coupled with microstructure studies and modeling, show that the ZT improvement is the result of low thermal conductivity caused by the increased phonon scattering by grain boundaries and defects. More importantly, ZT is about 1.2 at room temperature and 0.8 at 250°C, which makes these materials useful for cooling and power generation. Cooling devices that use these materials have produced high temperature differences of 86°, 106°, and 119°C with hot-side temperatures set at 50°, 100°, and 150°C, respectively. This discovery sets the stage for use of a new nanocomposite approach in developing high performance low-cost bulk thermoelectric materials.

Solid-state cooling and power generation based on thermoelectric effects have potential applications in waste heat recovery, air-conditioning, and refrigeration. The efficiency of thermoelectric devices is determined by the materials' dimensionless figure-of-merit (ZT), defined as $ZT = (S^2\sigma/k)T$, where S , σ , k , and T are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively (1–3). To make a thermoelectric device competitive, an average ZT in the application temperature range higher than 1 is required (1–3).

There have been persistent efforts to improve ZT since the 1950's, but the peak ZT of dominant commercial materials

based on Bi_2Te_3 and its alloys, such as $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ (p-type), has remained at 1. During the last decade, several groups have reported enhanced ZT in superlattices such as $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ (4) and $\text{PbSe}_{0.98}\text{Te}_{0.02}/\text{PbTe}$ (5) because of reductions in the lattice thermal conductivity, and in new bulk materials, such as silver antimony lead telluride (LAST) and its alloys (6), including skutterudites (7). Although high ZT values were reported in superlattice structures, it has proven difficult to use them in large-scale energy-conversion applications because of limitations in both heat transfer and cost. Bulk materials with improved ZT, such as LAST and skutterudites, are ideal for high temperature operations. However, near room temperature (0° to 250°C), Bi_2Te_3 -based materials still dominate.

We have pursued an approach in which the primary cause of ZT enhancement in superlattices—reduced thermal conductivity—also exists in random nanostructures (8, 9). Here, we report a significant ZT increase in bulk materials made from nanocrystalline (NC) powders of p-type $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$, reaching a peak ZT of 1.4 at 100°C. The enhanced ZT is the result of a significant reduction in thermal conductivity caused by strong phonon scattering by interfaces in the nanostructures. There have also been reports of ZT improvements at room temperature in Bi_2Te_3 -based materials caused by the addition of Bi_2Te_3 -nanotubes (10) and by melt spinning (11).

Our method, on the other hand, is based on the ball milling and hot-pressing of nanoparticles into bulk ingots. This approach is simple, cost effective, and can be used on other materials. Our materials have a ZT of about 1.2 at room temperature and 0.8 at 250°C with a peak of 1.4 at 100°C. In comparison, conventional Bi_2Te_3 -based materials have a peak ZT of about 1 at room temperature and about 0.25 at 250°C.

The high ZT in the temperature ranges of 25° to 250°C makes the NC bulk materials attractive for cooling and low-grade waste-heat recovery applications. The materials can also be integrated into segmented thermoelectric devices for thermoelectric power generation that operate at high temperatures. In addition to the high ZT values, the NC bulk materials are also isotropic. They do not suffer from the cleavage problem that is common in traditional zone-melting-made ingots, which leads to easier device fabrication and system integration, and a potentially longer device lifetime.

Sample preparation. Nanopowders were made by ball milling bulk p-type BiSbTe alloy ingots (12). Bulk disk samples of 1¼ to 2½ cm in diameter and 2 to 15 mm thick were made by hot-pressing the nanopowders loaded in 1¼ to 2½ cm (inner diameter) graphite dies (12). Disks of 1¼ cm (diameter) and 2 mm thick, and bars of about 2 mm by 2 mm by 12 mm, were cut from both the axial and disk plane directions. The disks and bars were also polished for electrical and thermal conductivity (k) and for Seebeck coefficient (S) measurements.

To achieve high ZT, control of the size and quality of the starting nanoparticles are essential. For good electrical conductivity, it is especially important to prevent oxidation. Figure 1 shows the x-ray diffraction (XRD) pattern of the nanopowders after ball milling (Fig. 1A), the scanning electron microscope (SEM) image (Fig. 1B), and low- and high-magnification transmission electron microscope (TEM) images (Fig. 1, C and D). The XRD patterns verify that the powder is in a single phase and is well matched with $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$. The broadened diffraction peaks indicate that the particles are small, which is also confirmed in the SEM image (Fig. 1B) and the low-magnification TEM image (Fig. 1C). The TEM image (Fig. 1C) also shows that the nanoparticles have sizes ranging from up to 50 nm, with an average size of about 20 nm. The high-resolution TEM image (Fig. 1D) confirms the excellent crystallinity of the nanoparticles and the clean surfaces. The inset in Fig. 1D also shows that some of the nanoparticles are even smaller than 5 nm.

Transport properties. The temperature dependences of several key properties of a typical NC bulk sample are compared in Fig. 2 with the state-of-the-art (SOA) p-type BiSbTe alloy ingot. All of the properties were measured in the same direction and reproduced on about 100 samples. The electrical conductivity of the NC bulk sample is slightly higher than the SOA ingot (Fig. 2A), but the Seebeck coefficient is either slightly lower or higher than the ingot depending on its temperature (Fig. 2B). Ultimately, the power factor ($S^2\sigma$) values are comparable to that of an ingot below 50°C and higher above 75°C (Fig. 2C).

We also found that the thermal conductivity of the NC bulk samples is significantly lower than that of the ingot and,

more importantly, the difference increases with increasing temperature (Fig. 2D) leads to significantly enhanced ZT values (Fig. 2E) in the temperature range of 20° to 250°C. It also shows that the peak ZT value shifts to a higher temperature (100°C). The peak ZT of the NC bulk samples is about 1.4 at 100°C, which is significantly greater than that of the SOA Bi_2Te_3 -based alloys. The ZT value of the SOA ingot starts to drop above 75°C and is below 0.25 at 250°C, whereas the ZT values for the NC bulk samples are still above 0.8 at 250°C. Such ZT characteristics are suitable for power generation applications because of a lack of available materials with high ZT in this temperature range.

All of these measurements were confirmed by two independent techniques on more than 100 samples. The electrical conductivity was measured by a four-point current-switching technique. The Seebeck coefficient was measured by a static DC method based on the slope of a voltage versus temperature-difference curve, using commercial equipment (ZEM-3, Ulvac, Inc.) on the same bar-type sample with a dimension of 2 mm by 2 mm in cross-section and 12 mm in length. The properties in the same sample were also measured by a homemade system and the two sets of measurements are within 5% of each other.

The thermal diffusivity α was first measured by a laser-flash method on a disk using a commercial system (Netzsch Instruments, Inc.). After the measurement, bars were diced from the disks and α values were measured using the Ångström method in the same home-built system. The α values from the bar and the disk are in an agreement within a range of 5%.

The thermal conductivity was calculated using the equation $k = \alpha \rho c_p$, where ρ is the density and c_p is the specific heat of the material which was measured using a differential scanning calorimeter (Netzsch Instruments, Inc.). To further check the property isotropy of the NC bulk samples, disks and bars were cut along and perpendicular to the press direction and then measured. Although individual properties may differ by 5% within the two directions, the final ZT values are isotropic. Such nearly isotropic characteristics are the result of the random orientation of the nanograins, showing that our NC bulk materials are superior to zone-melting-made SOA Bi_2Te_3 -based alloys which have layered structures and, consequently, anisotropic thermoelectric properties. The highest ZT of the zone-melting-made materials is along the basal plane of the crystal, but unfortunately this direction is vulnerable to cleavage, resulting in a difficult and low yield module fabrication process.

For cooling applications, the stability of the nanostructures should not be a serious concern. High temperature stability testing on the current NC bulk materials by repeated measurements up to 250°C did not show any sign of

degradation, suggesting potential power generation applications for waste heat recovery in the reported temperature range.

Microstructure of NC Bulk Ingots. Detailed microstructure studies by TEM were carried out on NC bulk samples. The TEM specimens were prepared by dicing, polishing, and ion milling the bulk samples (13). Figure 3 shows the main structural features we observed. In general, most of the grains are nanosized (Fig. 3, A and B). Furthermore, these nanograins are highly crystalline, completely random (large angles between adjacent lattice planes) and have very clean boundaries between grains. They are also closely packed (Fig. 3B), which is consistent with our full density measurements. We also observed some larger grains as shown in Fig. 3C. However, under high-resolution TEM observation, these grains consist of nanodots about 2 to 10 nm in size and having fuzzy boundaries (Fig. 3D). Usually, these nanodots are Sb-rich with a typical composition close to Bi: Sb: Te = 8: 44: 48 with Sb substituted for Te.

Although some of the nanodots are without boundaries (Fig. 3D), we found other nanodots that make small angle boundaries with the matrix (Fig. 3E). In addition, we also observed pure Te precipitates of 5 to 30 nm in size (Fig. 3F). The SAED pattern (inset of Fig. 3F) confirms the presence of this Te phase. Generally speaking, nanodots can be found within a 50 nm diameter area.

We speculate that these nanodots could be formed during the hot-press heating and cooling processes. Similar types of nanodots have been observed in LAST alloys and were allegedly responsible for the ZT enhancement in those alloys (6). However, because there are so many interfaces from nanograins in our material, nanodots may not be the only reason for the strong phonon scattering. The larger sized grains containing nanodots (Fig. 3C) are likely to be the result of the non-uniform ball milling of the ingot, and may have experienced some grain growth during the hot-press compaction via Oswald ripening. More uniform nanograins produced during ball milling may retain their nanosize during the hot-press processing.

In comparing the transport properties of the NC bulk samples with the SOA ingot, it is important to note the relative slow increase in k as a function of temperature for the NC bulk samples (Fig. 2D). This increase indicates a smaller bipolar contribution (2) to the conductivity by thermally generated electrons and holes in the NC bulk materials. We explain this reduced bipolar effect by assuming the existence of an interfacial potential that scatters more electrons than holes. Past studies in Bi_2Te_3 -related materials suggested that structural defects, such as antisites, i.e., Bi atoms go to Te sites, and serve as an important doping mechanism (14, 15). We anticipate that such antisites are more likely to occur at

interfaces. Uncompensated recombination centers at interfaces associated with defect states and antisites are responsible for charge buildup at grain-boundaries and thus increase the hole density in the grains. This explanation is consistent with the observed increase in the electrical conductivity as well as the reduction in the Seebeck coefficient of the NC bulk samples, compared to those of the SOA ingot parent material (Fig. 2, A and B). We modeled the transport properties based on the Boltzmann equation within the relaxation time approximation, including the interfacial potential, and we thus obtained the lattice contributions to the thermal conductivity shown in Fig. 4. The modeled results show that phonon contributions to the lattice thermal conductivity are reduced by a factor of 2.

Cooling Devices. To further confirm the ZT values, we constructed two uncouple cooling devices to measure their maximum temperature difference. One uncouple uses a nanostructured p-type material as one leg and a commercially available n-type material as the other leg (Fig. 5A). The performance of this uncouple was compared to that of a uncouple made of commercially available n and p-type materials from the same vendor. Testing was performed in a cryostat chamber with a typical pressure of 10^{-3} Torr so that the hot-side temperature could be controlled by a combination of a heater and continuous flow of liquid nitrogen. Figure 5B shows the temperature difference created at different current injection levels when the hot side is maintained at 100°C . The inset displays the temperature differences created by the two devices at different hot-side temperatures. The temperature differences created with commercial legs are consistent with values given in the vendor catalog, while the performance of the uncouple made of nanostructured p-type material is significantly better. Device modeling using the measured properties is consistent with our experimental results.

Conclusion. We have developed a nanostructuring approach and we have demonstrated significant improvement in ZT in p-type bismuth antimony telluride NC bulk alloys. The value of ZT starts at 1.2 at room temperature, peaks to 1.4 at 100°C , and decreases to 0.8 at 250°C . Such ZT characteristics are attractive for both cooling and low-temperature waste heat recovery applications. These materials are synthesized using ball milling, followed by direct-current hot pressing. The ZT enhancement comes mainly from a large reduction in the phonon thermal conductivity, but also benefits from a reduction of bi-polar contributions to the electronic thermal conduction at high temperatures. In the past, ZT enhancements have been reported in superlattice structures because of phonon thermal conductivity reduction. Our study suggests that similar mechanism can be reproduced in random nanostructured bulk materials. Unlike superlattices and bulk crystals, nanostructured bismuth antimony telluride displays nearly isotropic ZT values. We further confirmed ZT

enhancements by measuring the temperature difference created by unicouple devices constructed out of the materials for hot side temperature maintained between 50° to 150°C. The nanostructure synthesis method we developed is low cost and can be readily scaled for mass production. These results open a cost-effective way to improve the performance of thermoelectric materials.

References and Notes

1. D. M. Rowe, Ed. *CRC Handbook of Thermoelectrics* (CRC Press, Boca Raton, FL, 1995).
2. H. J. Goldsmid, *Thermoelectric Refrigeration* (Plenum Press, New York, 1964).
3. T. M. Tritt, Ed. *Semiconductors and Semimetals* (Academic Press, San Diego, CA, 2001).
4. R. Venkatasubramanian, E. Siivola, T. Colpitts, B. O'Quinn, *Nature* **413**, 597 (2001).
5. T. C. Harman, P. J. Taylor, M. P. Walsh, B. E. LaForge, *Science* **297**, 2229 (2002).
6. K. F. Hsu, S. Loo, F. Guo, W. Chen, J. S. Dyck, C. Uher, T. Hogan, E. K. Polychroniadis, M. G. Kanatzidis, *Science* **303**, 818 (2004).
7. J. P. Fleurial, T. Caillat, A. Borshchevsky, in *Proceedings of the 13th International Conference on Thermoelectrics*, 40 (1994).
8. G. Chen, *Phys. Rev. B: Condens. Matter Mater. Sci.* **57**, 14958 (1998).
9. M. Dresselhaus, G. Chen, M. Tang, R. Yang, H. Lee, D. Z. Wang, Z. F. Ren, J. P. Fleurial, P. Gong, *Adv. Mater.* **19**, 1 (2007).
10. X. B. Zhao, X. H. Ji, Y. H. Zhang, T. J. Zhu, J. P. Tu, X. B. Zhang, *Appl. Phys. Lett.* **86**, 062111 (2005).
11. X. F. Tang, W. J. Xie, H. Li, W. Y. Zhao, Q. J. Zhang, *Appl. Phys. Lett.* **90**, 012102 (2007).
12. Bulk p-type BiSbTe alloy ingots were loaded into a jar with balls inside the argon filled glove box to avoid oxidation of the nanopowder. The jar was loaded into a ball mill and processed for a number of hours. When the nanopowder was ready, it was loaded into dies of 1¼ to 2½ cm inner diameter and compacted into a 100% dense solid NC bulk sample by a hot-press. Samples are available for testing upon request.
13. Hot-pressed NC bulk pellets were cut into blocks of 2 mm by 3 mm by 1 mm and ground down to 2 mm by 3 mm by 0.002 mm using a mechanical Tripod Polisher. The sample was glued to a copper grid and milled using a precision ion polishing system (Gatan Inc.) for 30 minutes with incident energy of 3.2 kV and beam current of 15 µA at an incident angle of 3.5°.
14. T. C. Harman, S. E. Miller, H. L. Goering, *Bull. Amer. Phys. Soc.* **30**, 35 (1955).
15. T. Thonhauser, G. S. Jeon, G. D. Mahan, J. O. Sofo, *Phys. Rev. B* **68**, 205207 (2003).
16. The work is supported by DOE DE-FG02-00ER45805 (ZFR), DOE DE-FG02-02ER45977 (GC), and NSF NIRT 0506830 (GC, ZFR, and MD). GC and ZFR are cofounders of GMZ Energy, Inc.

13 February 2008; accepted 11 March 2008
Published online 20 March 2008; 10.1126/science.1156446
Include this information when citing this paper.

Fig. 1. XRD (A), SEM (B), low- (C) and high- (D) magnification TEM images of an as-ball-milled nanopowder.

Fig. 2. Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), power factor (C), thermal conductivity (D), and ZT (E) of a hot-pressed NC bulk sample in comparison with an SOA ingot.

Fig. 3. TEM images showing the microstructures of a hot-pressed NC bulk sample. (A) low-magnification image showing the nanograins, (B) high-magnification image showing the nanosize, high crystallinity, random orientation, and clean grain boundaries, (C) low-magnification image showing larger grains, (D) high-magnification image showing the nanodots in the matrix without boundaries, (E) high-magnification image showing the nanodots in the matrix with small angle grain boundaries, (F) high-magnification image showing Te precipitate in the matrix. SAED pattern (inset) shows the Te phase of the precipitated nanodot in the matrix.

Fig. 4. Thermal conductivity of Bi_xSb_{2-x}Te₃ NC bulk alloy. Solid- and hollow-squares represent the experimental results for an SOA ingot and our NC bulk alloys, respectively. Solid lines represent the corresponding calculations of the total and lattice contribution to the thermal conductivity, respectively.

Fig. 5. (A) Experimental setup of the device cooling test. Two thermoelectric legs were mounted onto 6.5 mm thick copper blocks and then bridged by a top copper plate. Two cold side thermocouples were soldered into small holes drilled on both ends of the top copper plate. Hot side thermocouples were soldered on the edge of each copper block. (B) Cooling test results with hot side fixed at 100°C. The inset compares the maximum temperature difference of two unicouples with hot side temperatures set at 50°, 100° and 150°C.









