

Large Improvement in Thermoelectric Properties in Pressure-Tuned p-Type $\text{Sb}_{1.5}\text{Bi}_{0.5}\text{Te}_3$

D. A. Polvani,[†] J. F. Meng,[†] N. V. Chandra Shekar,^{†,§} J. Sharp,[‡] and J. V. Badding^{*,†}

Department of Chemistry, Pennsylvania State University,
University Park, Pennsylvania 16802, and Marlow Industries, 10451 Vista Park Road,
Dallas, Texas 75238

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There is widespread interest in the search for materials that would allow the fabrication of more efficient thermoelectric devices for cooling and power generation applications. Here, we report a large increase in the thermoelectric power of p-doped antimony bismuth telluride alloys upon pressure tuning under nonhydrostatic compression conditions. Together with measurements of the electrical conductivity and an upper bound estimated for the thermal conductivity under pressure, these results indicate that values of the dimensionless thermoelectric figure of merit, ZT , in excess of 2 have been achieved, substantially larger than the best observed values in bulk materials to date. We suggest an explanation for the observed behavior and strategies for attempting to reproduce it at ambient pressure.

Introduction

Solid state thermoelectric devices can be used both as generators that convert heat into electricity and as refrigerators that utilize electricity for cooling. The full technological potential of these devices could be realized if materials that improve their efficiency could be found.¹ There is an especially critical need for thermoelectric materials that can cool to low temperatures for electronic device applications. Doped Bi_2Te_3 – Sb_2Te_3 alloys are the most efficient thermoelectric materials at ambient temperature discovered thus far. Recently, a new material, CsBi_4Te_6 ,² has been discovered that exhibits better properties than Bi_2Te_3 – Sb_2Te_3 alloys at temperatures below 270 K. Doped Bi_2Te_3 – Sb_2Te_3 alloys can be used to fabricate thermoelectric coolers that function with approximately 10% of the theoretical maximum Carnot efficiency.¹ The efficiency of thermoelectric devices is dependent on several materials properties. It can be quantified by the dimensionless thermoelectric figure of merit, ZT , where T is the temperature and $Z = S^2\sigma/\kappa$ (S is the thermoelectric power, σ is the electrical conductivity, and κ is the thermal conductivity). Suitably doped Bi_2Te_3 – Sb_2Te_3 alloys can exhibit a ZT of ≈ 1 near room temperature and CsBi_4Te_6 exhibits a value of 0.82 at 225 K. A ZT value of 3 or 4 is likely necessary for thermoelectric refrigerators to be widely adopted, although more modest increases in ZT would still have a substantial impact on applications.¹

Several approaches have been adopted in the search for improved thermoelectric materials, ranging from the synthesis of new bulk materials^{2,3} and quantum-well structures that may exhibit improved ZT ⁴ to combinatorial synthesis techniques that rapidly screen materials for desirable thermoelectric properties.⁵ Pressure tuning may offer a means to guide the search for higher ZT thermoelectric materials.^{6,7} The goal is to demonstrate improved properties in suitably compressed materials. Observation of improved properties under pressure can provide targets for synthesis at ambient pressure. Pressure can be changed more rapidly than new materials can be synthesized (at least by conventional methods), allowing the phase space of interaction parameters that determine materials properties such as thermoelectric power to be explored more rapidly.⁶ Several fold increases in ZT have recently been reported upon pressure tuning $\text{Nd}_x\text{Ce}_{3-x}\text{Pt}_3\text{Sb}_4$.⁷

Here, we report a large increase in the thermoelectric power of heavily doped $\text{Sb}_{1.5}\text{Bi}_{0.5}\text{Te}_3$ compressed nonhydrostatically to ≈ 2 GPa. These thermoelectric power measurements, together with measurements of the electrical conductivity and an estimate of the upper bound on the thermal conductivity, indicate that ZT values in excess of 2 have been achieved under pressure. These results demonstrate that significantly enhanced values of ZT are possible and may provide insight into how to reproduce the improved behavior at ambient pressure in $\text{Sb}_{1.5}\text{Bi}_{0.5}\text{Te}_3$ or other classes of materials.

* To whom correspondence should be addressed. E-mail: jadding@chem.psu.edu.

[†] Pennsylvania State University.

[‡] Marlow Industries.

[§] On leave from Indira Gandhi Centre for Atomic Research, Materials Science Division, Kalpakkam 60312, Tamil Nadu, India.

(1) DiSalvo, F. J. *Science* **1999**, *285*, 703.

(2) Chung, D. Y.; Hogan, T.; Brazis, P.; Rocci-Lane, M.; Kannewurf, C.; Bastea, M.; Uher, C.; Kanatzidis, M. G. *Science* **2000**, *287*, 1024.

(3) Sales, B. C.; Mandrus, D.; Williams, R. K. *Science* **1996**, *272*, 1325.

(4) Hicks, L. D.; Dresselhaus, M. S. *Phys. Rev. B* **1993**, *47*, 12727.

(5) Xiang, X. D.; Sun, X. D.; Briceno, G.; Lou, Y. L.; Wang, K. A.; Chang, H. Y.; Wallacefreedman, W. G.; Chen, S. W.; Schultz, P. G. *Science* **1995**, *268*, 1738.

(6) Badding, J. V.; Meng, J. F.; Polvani, D. A. *Chem. Mater.* **1998**, *10*, 2889.

(7) Meng, J. F.; Polvani, D. A.; Jones, C. D. W.; DiSalvo, F. J.; Fei, Y.; Badding, J. V. *Chem. Mater.* **2000**, *12*, 197.

The observed behavior is suggestive of a change under compression in the topology of the Fermi surface $Sb_{1.5}Bi_{0.5}Te_3$, known as an electronic topological transition (ETT) or Lifshitz transition.⁸ An ETT can be induced by any means that allows continuous tuning of electronic structure, such as compression or alloying.

Experimental Section

Thermoelectric power measurements as a function of pressure were made in Mao-Bell-type diamond anvil cells at ambient temperature. The details of the technique (e.g., experimental configuration, thermal insulation of the thermocouples, pressure measurement, etc.) have been described previously.⁹ Its accuracy has been verified by means of measurements on several standard materials. The polycrystalline $Sb_{1.5}Bi_{0.5}Te_3$ alloy samples, which have a layered rhombohedral crystal structure identical to that of the antimony and bismuth telluride end members, were doped for optimal thermoelectric properties ($ZT \sim 0.9$) at ambient pressure and temperature. The samples were cut to dimensions of $\approx 50 \times 50 \times 600 \mu\text{m}$. A monoclinic ZrO_2 medium was used, which induces a substantial uniaxial stress component in the direction perpendicular to the diamond culets and the long axis of the sample. Pressure was measured by means of ruby fluorescence. Type K thermocouple junctions with $12.5\text{-}\mu\text{m}$ leads were embedded in the sample for the thermoelectric power measurements. A temperature gradient was induced by means of an infrared laser focused to a narrow line. To assess the contact resistance, two-probe four-lead resistance measurements were performed by passing a current through two of the thermocouple leads while measuring the voltage between the other two leads. In this geometry, the resistance measured is the sum of the two contact resistances between the thermocouples and the sample and the sample resistance. Because the total resistance measured was a few tenths of an ohm or less, the contact resistances must be less than this value. We assume that if the contact resistance is small, there is good thermal contact between the thermocouples and the sample. Sample resistance measurements were made by means of a conventional four-probe technique. At ambient pressure the thermoelectric power measured in the diamond cell is $212 \mu\text{V/K}$, in good agreement with the value of $222 \mu\text{V/K}$ measured on bulk samples by standard techniques.

Results and Discussion

Upon compression, the thermoelectric power increases to $305 \mu\text{V/K}$ at 1.5 GPa. If the pressure is not increased above 1.5 GPa, there is no hysteresis upon release of pressure and the thermoelectric power returns to the previously measured ambient pressure value (Figure 1). The reversibility of this measurement indicates that errors that could be caused by motion of the thermocouples or changes in the thermal or the electrical contact between the thermocouples and the sample are not significant. If the pressure is further increased, the thermoelectric power (Figure 1) peaks at about 1.7 GPa. This peak was reproduced in several experiments on different $Sb_{1.5}Bi_{0.5}Te_3$ samples. It was not observed in experiments on many other metallic and semiconducting samples. We have found that a few other semiconductors exhibit large peaks in the thermoelectric power, but of different magnitude and at different pressures.⁷ Upon release of pressure, the peak in the thermoelectric power recurs, but there is considerable hysteresis and the

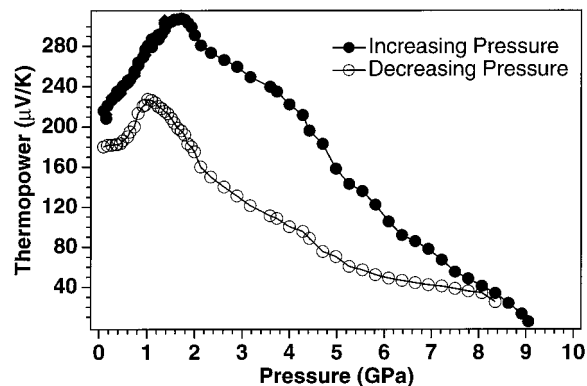


Figure 1. Thermoelectric power versus pressure for $Sb_{1.5}Bi_{0.5}Te_3$. The pressure was initially increased to 1.5 GPa and then released. Upon release of pressure, the thermoelectric power returned to the same ambient pressure value. The data points from this first run in the increasing and decreasing pressure directions are coincident with the low-pressure data in the increasing pressure direction from the second run in which the sample was compressed to 9 GPa. Therefore, the data points from the first run are not indicated separately in the legend.

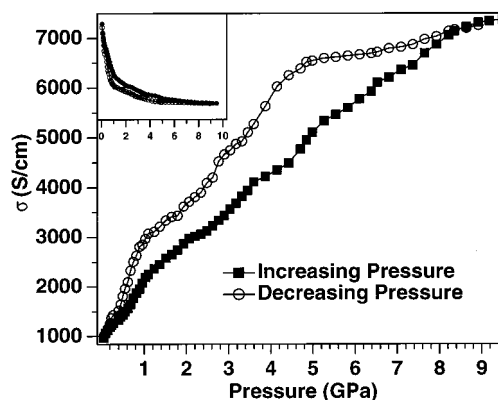


Figure 2. Electrical conductivity versus pressure for $Sb_{1.5}Bi_{0.5}Te_3$. The inset shows the shape of the resistivity curve with pressure as the bottom axis.

magnitude of the peak is less. Similar behavior in which there is hysteresis only after the sample has been compressed above ≈ 2 GPa has also been observed for other samples, such as the $Nd_xCe_{3-x}Pt_3Sb_4$.⁷ This behavior may be associated with the introduction of defects by nonhydrostatic compression or may also be due to changes in the stress conditions surrounding the sample as a result of flow of the ZrO_2 medium surrounding the sample at pressures above where the maximum in the thermoelectric power is observed.

To determine ZT at high pressure, it is also necessary to have the electrical conductivity and the thermal conductivity. Conventional four-probe dc conductivity measurements (in a geometry with four independent leads in contrast to the geometry used to place an upper bound on the contact resistance) were performed on a sample loaded in the same way as the samples loaded for thermoelectric power measurements. The electrical conductivity of $Sb_{1.5}Bi_{0.5}Te_3$ increases by a factor of 2.74 from 967 S/cm at 0.1 MPa to 2650 S/cm upon compression to 1.7 GPa in a diamond anvil cell (Figure 2).

It is possible to measure thermal conductivity at high pressure, but it is challenging and relatively few measurements have been made. Instead, we place an upper

(8) Lifshitz, I. M. *Sov. Phys. JETP* **1960**, *11*, 1130.

(9) Polvani, D. A.; Meng, J. F.; Hasegawa, M.; Badding, J. V. *Rev. Sci. Instrum.* **1999**, *70*, 3586.

bound on the increase in the thermal conductivity under pressure. The electronic contribution to the thermal conductivity can be estimated from the Wiedemann–Franz law: $L_0 T = \kappa/\sigma$ ($L_0 T = 5 \times 10^{-6}$ W/S·K at 298 K).^{10,11} In semiconductors the value of the Lorenz number, L_0 , is dependent on both the position of the Fermi level and the mechanism by which the carriers are scattered. Here, we employ a value of L_0 appropriate for the case that the Fermi level is at the band edge and the carriers are scattered predominantly by acoustic phonons. At ambient pressure and 298 K the electronic contribution is $967 \text{ S/cm} \times (5 \times 10^{-6} \text{ W/S}\cdot\text{K}) = 4.8 \times 10^{-3} \text{ W/cm}\cdot\text{K}$. This is about a third of the total thermal conductivity of the doped $\text{Sb}_{1.5}\text{Bi}_{0.5}\text{Te}_3$ sample at ambient pressure, which is $14.9 \times 10^{-3} \text{ W/cm}\cdot\text{K}$. The remaining contribution is due to phonons ($10.1 \times 10^{-3} \text{ W/cm}\cdot\text{K}$). Upon compression to 1.7 GPa the electronic contribution to the thermal conductivity should increase by 2.74, the same factor as that for the electrical conductivity, to approximately $13.2 \times 10^{-3} \text{ W/cm}\cdot\text{K}$. Many materials also exhibit an increase in the phonon contribution upon compression because phonon frequencies often shift to higher values. CsI is softer than Bi_2Te_3 and is likely to exhibit a larger increase in phonon frequencies and lattice thermal conductivity upon compression. The thermal conductivity of CsI has been determined to increase by a factor of about 2 upon compression to 1.7 GPa.¹² If we assume a factor of 2 increase in the lattice thermal conductivity of $\text{Sb}_{1.5}\text{Bi}_{0.5}\text{Te}_3$, it becomes $20.2 \times 10^{-2} \text{ W/cm}\cdot\text{K}$. (This may be a considerable overestimation; see below.) The total thermal conductivity is then $13.2 \times 10^{-3} + 20.2 \times 10^{-3} = 33.4 \times 10^{-3} \text{ W/cm}\cdot\text{K}$, a factor of 2.2 larger than the ambient pressure thermal conductivity. This upper bound on the thermal conductivity appears conservative in view of measurements on the thermal conductivity under pressure for doped p-type Sb_2Te_3 that shows an increase by a factor of 1.1 at 1.6 GPa.¹³ Using the maximum value of the thermoelectric power at 1.7 GPa, $305 \mu\text{V/K}$, ZT is 2.2. This is significantly larger than any reported ZT value at ambient pressure.

Sharp maxima in the thermoelectric power that resemble the behavior observed for $\text{Sb}_{1.5}\text{Bi}_{0.5}\text{Te}_3$ have been observed in metallic elements, intermetallic compounds, and heavily doped semiconductors that undergo an electronic topological transition (ETT).¹⁴ An ETT occurs when a band extremum, which is associated with a Van Hove singularity in the density of states, crosses the Fermi energy, resulting in a change in the topology of the Fermi surface^{8,15} and a strong energy dependence to the electronic density of states near the Fermi energy. At 0 K there are singularities in the thermoelectric power and thermodynamic potentials associated with an ETT.⁸ At finite temperatures, the singularity becomes more diffuse, but significant maxima can still be

observed.⁸ Metallic AuIn_2 , for example, exhibits a peak in its thermoelectric power associated with an ETT at 2 GPa at room temperature.¹⁶ There is a sharp maximum in the thermoelectric power of doped Bi_2Te_3 upon hydrostatic compression at liquid helium temperature as a result of an ETT,¹⁴ suggesting that it is plausible for an ETT to occur in the isoelectronic doped alloy $\text{Sb}_{1.5}\text{Bi}_{0.5}\text{Te}_3$. Furthermore, there are similarities between the behavior of the conductivity under compression of materials undergoing an ETT, such as AuIn_2 , and the conductivity reported here for $\text{Sb}_{1.5}\text{Bi}_{0.5}\text{Te}_3$. When plotted as resistivity curves (Figure 2 inset),¹⁶ the data exhibit a strong decrease in the resistivity at pressures below that of the maximum in the thermoelectric power.

An ETT is not associated with a structural phase transition. High-pressure powder X-ray diffraction patterns collected by means of a laboratory-based focusing diffraction system¹⁷ and an energy-dispersive diffraction system at the CHESS synchrotron on $\text{Sb}_{1.5}\text{Bi}_{0.5}\text{Te}_3$ compressed under both hydrostatic conditions with a methanol–ethanol–water medium and nonhydrostatic compression conditions with a ZrO_2 medium reveal that no structural phase transitions occur up to at least 6.5 GPa. Interestingly, the hexagonal c axis has approximately the same compressibility as the a axis. This observation is surprising in view of the weak van der Waals bonding between the layers perpendicular to the c axis.

Anomalies in the phonon spectrum are predicted for materials undergoing an ETT.^{18,19} When an electron pocket is created, for example, new Kohn anomalies appear at small but finite wave vectors that may induce a long wavelength acoustic instability. The phonon spectrum softens for values of the wave vector \mathbf{q} along the direction where new Fermi surface appears. It also depends on the polarization and the localization of \mathbf{q} on the Fermi surface. Some of the Raman modes of $\text{Sb}_{1.5}\text{Bi}_{0.5}\text{Te}_3$ ²⁰ soften when compressed either hydrostatically with a methanol–ethanol medium or nonhydrostatically with a ZrO_2 medium (Figure 3). The softening of some of the phonons is consistent with an ETT in compressed $\text{Sb}_{1.5}\text{Bi}_{0.5}\text{Te}_3$. Furthermore, because there is relatively little change in the frequencies of all the observed modes, which are likely important to thermal transport, it is possible that the thermal conductivity of $\text{Sb}_{1.5}\text{Bi}_{0.5}\text{Te}_3$ may not increase much under pressure, which would be favorable for increased ZT .

The results reported here demonstrate that in principle improved ZT values are possible. It would be desirable to now reproduce the improved thermoelectric behavior observed at high pressure at ambient pressure. Electronic topological transitions can be induced not only by pressure but also by means of alloying.²¹ Metallic lithium–magnesium alloys, for example, can exhibit a peak in the thermoelectric power at temperatures below 78 K, which is associated with an electronic

(10) Ashcroft, N. W.; Mermin, N. D. *Solid State Physics*; Holt, Rinehart, and Winston: New York, 1976.

(11) Goldsmid, H. J. *Electronic Refrigeration*; Pion Ltd: London, 1986.

(12) Gerlich, D.; Andersson, P. *J Phys. C: Solid State Phys.* **1982**, *15*, 5211.

(13) Averkin, A. A.; Zaporov, Z. Z.; Sil'bens, L. S. *Sov. Phys. Semicond.* **1972**, *5*, 1954.

(14) Itskevich, E. S.; Kashirskay, L. M.; Kraidenov, V. F. *Semiconductors* **1996**, *31*, 276.

(15) Blanter, Y. M.; Kaganov, M. I.; Pantsulaya, A. V.; Varlamov, A. A. *Phys. Rep.* **1994**, *245*, 159.

(16) Godwal, B. K.; Jayaraman, A.; Meenakshi, S.; Rao, R. S.; Sikka, S. K.; Vijayakumar, V. *Phys. Rev. B* **1998**, *57*, 773.

(17) Atou, T.; Badding, J. V. *Rev. Sci. Instrum.* **1995**, *66*, 4496.

(18) Dagens, L. *J. Phys. F: Met. Phys.* **1978**, *8*, 2093.

(19) Dagens, L.; Lopez-Rios, C. *J. Phys. F: Met. Phys.* **1979**, *9*, 2195.

(20) Richter, W.; Kohler, H.; Becker, C. R. *Phys. Stat. Sol. (b)* **1977**, *84*, 619.

(21) Bruno, E.; Ginatempo, B.; Giuliano, E. S.; Ruban, A. V.; Vekilov, Y. K. *Phys. Rep.-Rev. Sec. Phys. Lett.* **1994**, *249*, 353.

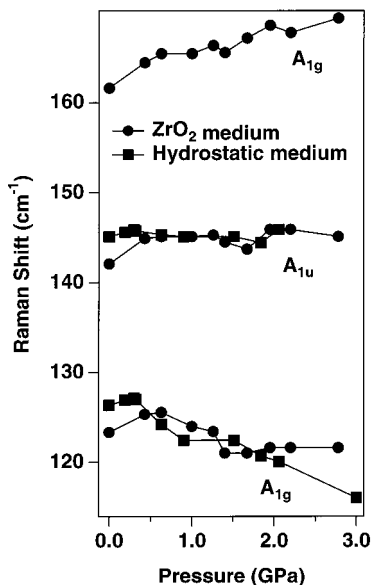


Figure 3. Raman spectra for $Sb_{1.5}Bi_{0.5}Te_3$ under both hydrostatic and nonhydrostatic compression. The Raman modes are labeled using assignments for isostructural Bi_2Te_3 . Raman spectra were collected with a Dilor XY microfocus Raman spectrometer with 514.5-nm excitation.

topological transition.²² This peak broadens and becomes less pronounced at higher temperatures. However, as mentioned previously, peaks in thermoelectric power associated with an ETT have been observed in compressed metals at ambient temperature,¹⁶ indicating that it may be possible for similar behavior to occur in alloys. Such compounds might exhibit improved thermoelectric properties. Whether an ETT can be induced in Sb_2Te_3 or Bi_2Te_3 by means of alloying remains an open question, but this approach could also be applied to many other semiconductor materials.

Uniaxial stress was observed to enhance the thermoelectric power of $Nd_xCe_{3-x}Pt_3Sb_4$.⁷ It may play a similar role in the increase in the thermoelectric power of compressed $Sb_{1.5}Bi_{0.5}Te_3$ and other small band gap semiconductors. The large effect that stress can have on properties such as superconductivity, which like thermoelectricity are dependent on the detailed nature of the electronic structure, is well documented. Epitaxial

stress in deposited layers of the oxide superconductor $La_{1.9}Sr_{0.1}CuO_4$ can double T_c .²³ Deposition of strained layers of semiconducting thermoelectric materials could mimic the high-pressure behavior reported here, although this approach would likely not be viable for $Sb_{1.5}Bi_{0.5}Te_3$ because it has a layered structure. However, it might be viable for three-dimensionally bonded semiconductors that also exhibit an ETT. Lead telluride, for example, is a thermoelectric material that does not have weak layered bonding. The effects of hydrostatic compression can often be mimicked at ambient pressure by introduction of smaller atoms into the lattice, which might also be used to induce an ETT.

Finally, we note that it would be valuable to have independent control over the hydrostatic and uniaxial stress components to obtain a more complete understanding of the role of uniaxial stress in the observed increase in thermoelectric power. The only means to vary the proportions of uniaxial and hydrostatic stress with a conventional diamond cell is through the choice of gasket geometry and sample medium. However, a hybrid diamond cell/gas pressure apparatus that allows independent control of uniaxial and hydrostatic stress components has recently been constructed.²⁴ When compared with conventional types of pressure apparatus, this device provides another degree of freedom in pressure-tuning experiments on thermoelectric materials, which is the ability to control interatomic distance in a particular direction in addition to the control over interatomic distance in three dimensions afforded by hydrostatic compression.

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(23) Locquet, J. P.; Perret, J.; Fompeyrine, J.; Machler, E.; Seo, J. W.; Van Tendeloo, G. *Nature* **1998**, *394*, 453.

(24) Widulle, F.; Held, J. T.; Huber, M.; Hochheimer, H. D.; Kotitschke, R. T.; Adams, A. R. *Rev. Sci. Instrum.* **1997**, *68*, 3992.

(22) Egorov, V. S.; Fedorov, A. N. *Sov. Phys. JETP* **1983**, *58*, 959.