AIP Applied Physics Letters

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Citation: Applied Physics Letters **103**, 221907 (2013); doi: 10.1063/1.4834700
View online: http://dx.doi.org/10.1063/1.4834700
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Thermoelectric and mechanical properties of multi-walled carbon nanotube doped $Bi_{0.4}Sb_{1.6}Te_3$ thermoelectric material

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(Received 24 September 2013; accepted 13 November 2013; published online 25 November 2013)

Since many thermoelectrics are brittle in nature with low mechanical strength, improving their mechanical properties is important to fabricate devices such as thermoelectric power generators and coolers. In this work, multiwalled carbon nanotubes (CNTs) were incorporated into polycrystalline $Bi_{0.4}Sb_{1.6}Te_3$ through powder processing, which increased the flexural strength from 32 MPa to 90 MPa. Electrical and thermal conductivities were both reduced in the CNT containing materials, leading to unchanged figure of merit. Dynamic Young's and shear moduli of the composites were lower than the base material, while the Poisson's ratio was not affected by CNT doping. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4834700]

Thermoelectric (TE) materials, which can directly convert thermal energy to electrical energy and vice versa, are useful for solid state cooling/heating applications as well as power generation.[1–5] However, most TE materials are brittle in nature with low fracture strength and toughness.[6] Poor mechanical performance leads to difficulties in manufacturing and can also result in TE device failure in field applications. Therefore, improving mechanical properties of TE materials is highly desired.

One approach is to reduce the grain size of thermoelectric materials by powder processing. Since the fracture strength of brittle materials is inversely proportional to the square root of the critical flaw size that tends to scale with the grain size,[7] powder processing techniques (ball milling, hot pressing, spark plasma sintering, etc.) can effectively enhance the mechanical properties of TE materials to some extent.[6,8–10] As the grain size is further reduced to the micron level, strength improvement becomes marginal, because fracture is controlled by defects introduced during material handling and machining.[7] Further improvement of mechanical properties could be realized by making composite materials, where the reinforcement phase can be particles, whiskers, short and long fibers, etc.[7,11]

One potential drawback of making composite TE materials is their impaired efficiency. Using a variational method, Bergman *et al*. showed that the effective dimensionless figure of merit (ZT) of composite TE materials could not exceed the largest ZT of its constituents[12] unless there is size or interfacial effects.[13] For example, one can reduce the thermal conductivity and thus increase the ZT of PbTe by forming nano inclusions during solid-state synthesis to enhance phonon scattering at the interface between the matrix and the inclusion.[14] Another means is to introduce secondary (usually non-thermoelectric) phases via powder processing, such as adding C_{60} into bismuth telluride-based materials,[15–17] C_{60} into skutterudites,[18,19] single-walled carbon nanotube (CNT) into Bi_2Te_3,[20] and TiN nano particles into skutterudites.[21]

In contrast to the voluminous information on their transport properties, there is limited work regarding the mechanical behavior of nano composite TE materials. Sootsman *et al*. reported that PbTe containing nano-scale Si-rich precipitates was qualitatively stronger than the base material,[22] which was also observed by Zhang and coworkers in Tl-doped PbTe.[23] Duan *et al*.[21] studied $CoSb_{2.875}Te_{0.125}$ and discovered that with 1 vol. % TiN nano particles the flexural strength and the fracture toughness could be improved by as much as 31% and 40%, respectively.

In the current study, multi-walled CNTs were incorporated into Bi-Sb-Te material via powder processing with the objective of improving the mechanical strength of this widely used TE material while maintaining its good TE properties in the application temperature range. Thermoelectric properties and dynamic elastic moduli were studied between room temperature and 498 K (225 °C). Room temperature flexural strength was measured using a ring-on-ring configuration on both undoped and 0.5 wt. % CNT doped materials.

P-type $Bi_{0.4}Sb_{1.6}Te_3$ materials were synthesized by reacting pure elements in a vacuum sealed fused silica ampoule. The cast ingots were then ball milled and sieved to –325 mesh in an inert atmosphere. Purified multiwalled CNT[24] was first dispersed in ethanol and then mixed with the $Bi_{0.4}Sb_{1.6}Te_3$ powder via ball milling. Powders were then densified via hot pressing at 713 K (440 °C) for 10 min in N_2 under a pressure of 27.6 MPa. In this work, three groups of samples were prepared: 0% CNTs, 0.5 wt. % CNTs, and 1.0 wt. % CNTs. The mass densities of the three materials were 6.33 g/cm^3 for the undoped, 6.36 g/cm^3 for the 0.5% CNT-doped, and 6.28 g/cm^3 for the 1.0% CNT-doped, corresponding to theoretical densities of 92.2%, 94.5%, and 95.2%, respectively.

Electrical resistivity and Seebeck coefficient were measured on a ZEM-3 unit (ULVAC, Methuen, MA). Thermal conductivity was calculated by multiplying the mass density, the heat capacity as estimated from the Dulong-Petit law, and the thermal diffusivity that was measured using a laser flash method (Flashline 5000, Anter Corp. Pittsburgh, PA). Since the temperature range in the current study (300 K–500 K) is well above the Debye temperature of

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p-type bismuth telluride (137 K)[25] the electronic contribution to the heat capacity can be omitted.[26,27] Also, in this temperature range, the Dulong-Petit relationship, which is based on constant-volume heat capacity, can be applied on laser flash-measured constant-pressure heat capacity because of the negligible difference between the two heat capacities.[25]

Dynamic elastic moduli were obtained by the resonant ultrasound spectroscopy (RUS) method[28] using a commercial unit (RUSpec, Magnaflux Quasar Systems, Albuquerque, NM). A ring-on-ring apparatus was used to measure the biaxial flexural strength.[29] The diameters of the loading ring and the supporting ring were 6.4 mm and 12.7 mm, respectively; while the samples were approximately 1 mm thick and 19 mm in diameter. The fractured surfaces were examined by scanning electron microscopy.

All three materials (0% CNTs, 0.5% CNTs, and 1% CNTs) exhibited similar trends in electrical and thermal transport properties between 325 K and 498 K (Fig. 1). CNT doped samples were less electrically conductive compared to the base material while their Seebeck coefficients were enhanced (Fig. 1(a)). The highest power factor of all three materials appeared at room temperature, which decreased nearly linearly with increasing temperature (Fig. 1(b)). Although CNT content had a detrimental effect on the power factor (Fig. 1(b)), it also reduced the thermal diffusivity and thus the thermal conductivity (Fig. 1(c)). Typical measurement uncertainties were ~6% in Seebeck coefficient, ~8% in electrical resistivity, and ~10% in thermal diffusivity.[25,30] Using a simple uncertainty propagation method,[25] the uncertainty in ZT was approximately 15%. Therefore, the ZTs of three different samples were not significantly different in the temperature range involved in this study (Fig. 1(d)). The peak ZT value at 325 K was approaching 1.1, which is typical for good p-type Bi-Sb-Te compounds.[31]

Similar results have been observed on n-type Bi_2Te_3 doped with single-walled CNT,[20] in which Seebeck coefficient was improved and electrical and thermal conductivities were degraded. At a doping level of 0.5 wt. %, the ZT value was slightly improved below room temperature; while over doping (>1 wt. % CNT) seemed to damage the TE properties significantly.[20] When adding fullerene (C_{60}) to $(Bi,Sb)_2Te_3$ compounds, the results were however mixed. While Gothard and coworkers found C_{60} reduced the ZT of $(Bi,Sb)_2Te_3$ compounds,[15] Popov and Blank *et al.* found different trends.[16,17] It is important to note that although Popov and Blank *et al.* claimed C_{60} could increase the ZT of base materials by up to 25%–30%, the highest ZT values achieved in their work were approximately 1.15,[16,17] which were similar to the current study and other literature values for $(Bi,Sb)_2Te_3$ compounds.[31]

Equibiaxial flexural strength was measured on six undoped and six 0.5% CNT-doped materials to demonstrate the effectiveness of CNT doping on strength improvement. Since TE elements used in field applications are cut and assembled without further surface preparation, the coin samples tested in this study were in the as-machined condition.

Typical loading curves during the ring-on-ring tests are illustrated in Fig. 2(a), in which the CNT-doped samples exhibited different behavior than the base material. For the CNT-doped sample, following a slow initial increase, the load rapidly rose in a linear manner until the ultimate value was reached (Fig. 2(a)). In contrast, the load vs. extension curve of the undoped sample had "tailed down" after reaching the peak value, indicating some plastic deformation occurred prior to fracture (Fig. 2(a)). Although the extension at failure was comparable, the ultimate load of the CNT-doped material was much higher than the undoped (Fig. 2(a)). The mean flexural strength of the CNT-doped material was 90 ± 8 MPa, which was approximately twice higher than the flexure strength of the base material of 32 ± 6 MPa.

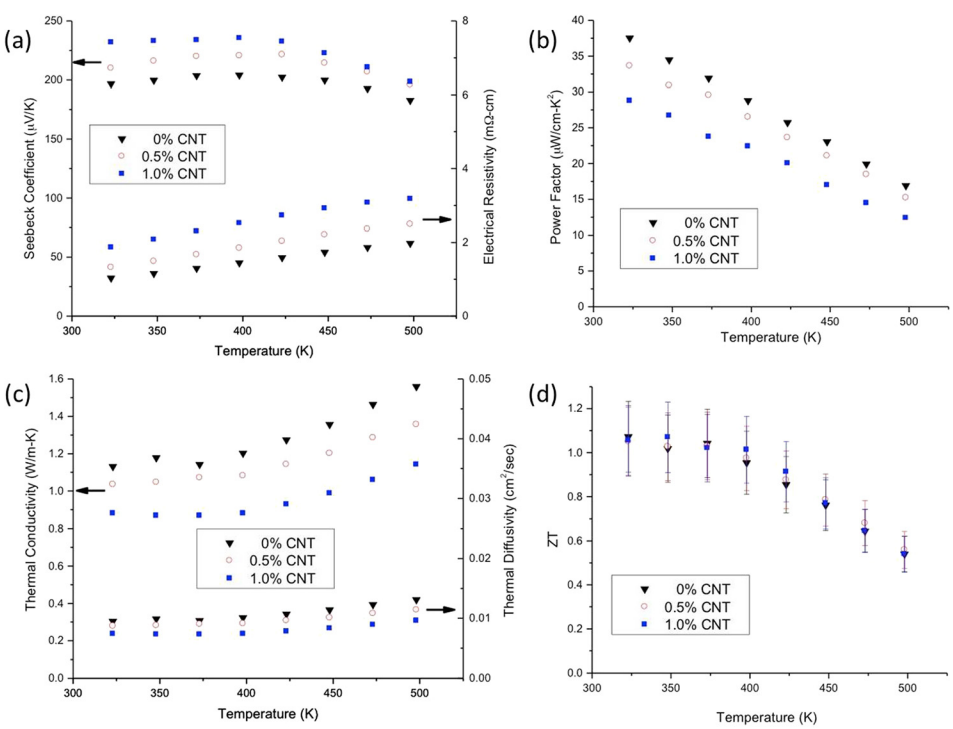

FIG. 1. Thermoelectric properties of $Bi_{0.4}Sb_{1.6}Te_3$ doped with 0% (triangle) 0.5 wt. % (circle), and 1.0 wt. % (square) multi-walled carbon nanotube: (a) Seebeck coefficient and electrical resistivity, (b) power factor, (c) thermal diffusivity and conductivity, and (d) ZT. A 15% uncertainty in ZT was estimated based on uncertainties involved in individual measurements.

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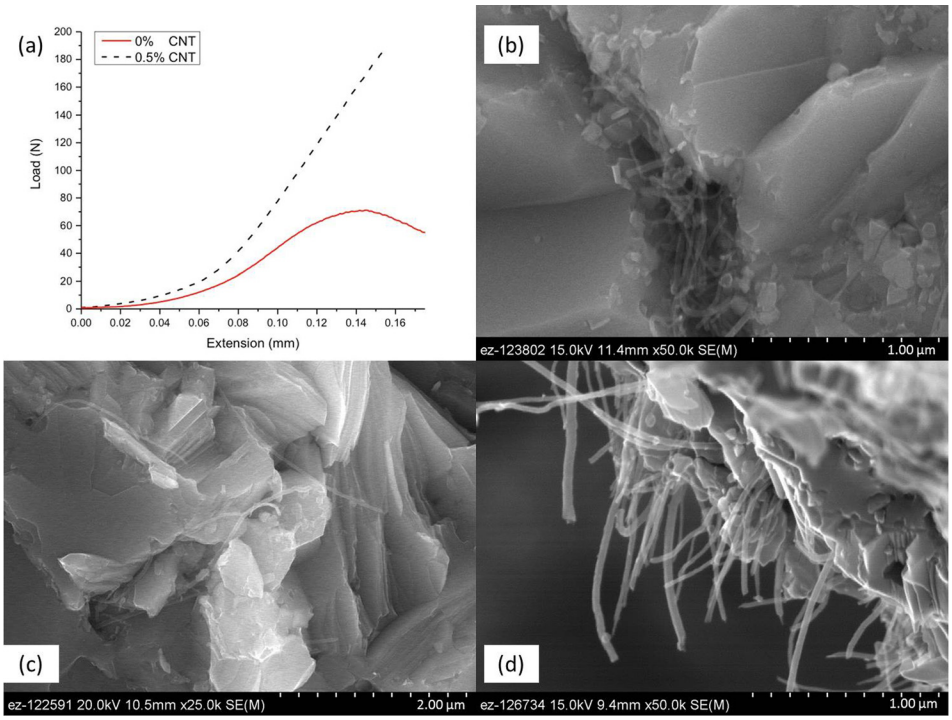

FIG. 2. (a) Comparison of loading curves between $Bi_{0.4}Sb_{1.6}Te_3$ samples with and without CNT doping. SEM images showing (b) CNTs distributed at the grain boundary, (c) CNTs attached to grains, and (d) CNT pullout on the fracture surface.

Mechanical strength reported in open literature showed large variation on bismuth telluride-based materials,[32] ranging from <25 MPa to over 100 MPa. This range is a result of variations in composition, processing, testing method, and sample preparation (e.g., polishing). With other parameters being equal, polishing help to remove surface flaws and thus lead to higher measured fracture strength. In the current study, although surface polishing was not performed for the reason stated above, the flexural strength of 90 MPa is among the highest values measured for this material family.[32]

Carbon nanotubes have been used as reinforcement in many material systems including ceramics.[33–37] Wei and coworkers[33] found that the addition of 3 vol. % CNT can improve the bending strength and fracture toughness of alumina by 13% and 79%, respectively. They believed CNTs residing at the grain boundary as well as embedded inside grains were responsible for the observed improvement.[33] Meanwhile, Pasupuleti *et al.*[34] reported a 1 wt. % CNT did not induce significant change in bending strength of Si_3N_4 while the fracture toughness was increased due to crack deflection, crack bridging, and CNT pullouts. On the other hand, Shimoda *et al.* found the bending strength of SiC was decreased when the CNT doping was increased from 0 to 10 wt. %.[35] They also discovered the indentation fracture toughness increased with increasing CNT content to 5 wt. % then decreased, which might be due to CNT agglomeration at higher concentrations.[35]

In this study, in addition to those distributed in the grain boundary regions (Fig. 2(b)), some CNTs seemed to have reacted and attached to $Bi_{0.4}Sb_{1.6}Te_3$ grains (Fig. 2(c)). As mentioned above, Wei *et al.*[33] believed CNTs embedded inside grains were the cause of the 13% enhancement in the bending strength of alumina, where CNT pullouts from the matrix contributed to the reinforcement/fracture toughness. It is likely that the strength improvement observed in this work was, at least partially, due to pullout of CNTs attached to $Bi_{0.4}Sb_{1.6}Te_3$ grains. From post mortem examination, a large number of CNTs pointing out from the fracture surface were discovered (Fig. 2(d)), which could be evidence of CNT pullout during flexural testing.

At room temperature, the Young's modulus of the undoped $Bi_{0.4}Sb_{1.6}Te_3$ was 47.1 ± 0.1 GPa, while the CNT-doped samples showed lower Young's modulus of 44.8 ± 0.3 GPa with 0.5% CNT doping and 40.8 ± 0.3 GPa with 1% CNT doping (Fig. 3(a)). The shear modulus also decreased with increasing CNT concentration (Fig. 3(a)). In contrast, Poisson's ratio was not significantly different between undoped and doped samples (Fig. 3(b)). It is unclear why CNT doping played different roles such that it decreased the Young's modulus and shear modulus but improved the fracture strength. All samples prepared in this study had similar mass density: 6.33 g/cm^3 for pure $Bi_{0.4}Sb_{1.6}Te_3$, 6.36 g/cm^3 for samples with 0.5% CNT, and 6.28 g/cm^3 for samples with 1.0% CNT. Therefore, the decrease in Young's and shear moduli was due to other mechanisms.

There is very limited information concerning the effect of CNT addition to the elastic properties of brittle materials such as ceramics. Chintapalli and coworkers observed a 15% increase in indentation fracture toughness of 2 vol. % CNT doped ZrO_2 (3Y-TZP) but no significant change in elastic modulus.[36] Kobayashi *et al.*[37] however found the elastic modulus of B_4C decreased with increasing CNT concentration, which they argued was due to the elastic mismatch between CNT and the matrix and the orientation distribution of CNTs. Similarly, Mukhopadhyay *et al.*[38] also observed a decrease in Young's modulus when 2.5 wt. % of CNT was added into alumino-borosilicate glass matrix. Assuming randomly oriented, only one third of CNTs aligned along the stress direction could effectively bear the load and the other two third acted as pores that lowered the effective Young's modulus of the composite.[38]

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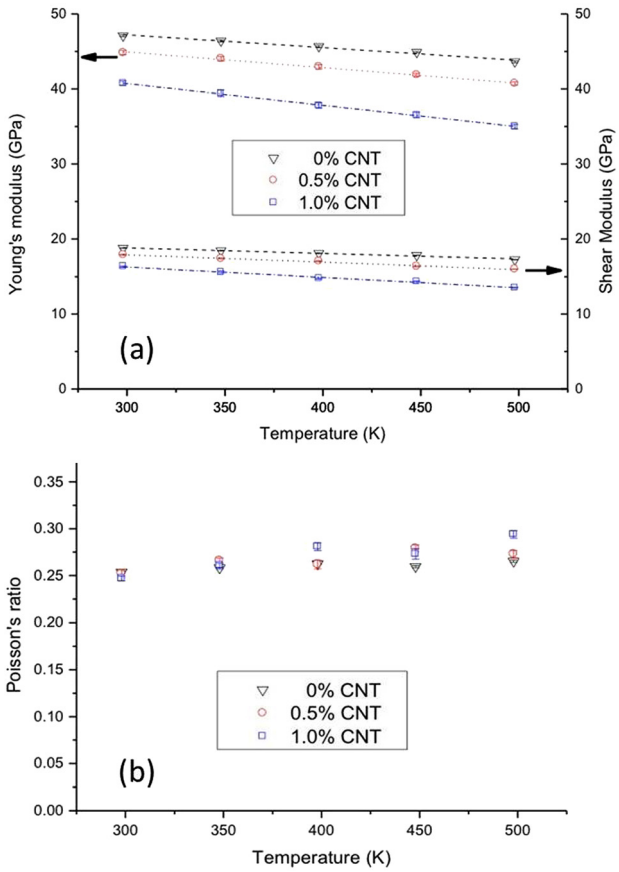

FIG. 3. Temperature dependent (a) Young's modulus, shear modulus, and (b) Poisson's ratio.

Young's modulus is sensitive to and can be reduced by microstructural flaws such porosity, microcracks, grain boundaries, etc.[39] In this study, CNTs aggregated in the grain boundary region can be regarded as a defect phase that reduced the Young's modulus of the undoped material, similar to those observed by Kobayashi and coworkers[37] and Mukhopadhyay *et al.*[38] This effect also corresponded to the reduced thermal conductivity (Fig. 1(c)) where the phonon transportation was impaired by CNT additions.

As the temperature increased, both Young's modulus and shear modulus for all samples decreased in a linear fashion which was faster when the CNT concentration was increased (Fig. 3(a)). For all samples, Poisson's ratio showed similar values, which slightly increased with rising temperature (Fig. 3(b)).

One advantage of lowering Young's modulus is that it can improve the thermal shock resistance according to the following relationship:[40]

$$R = \frac{\sigma_f(1-\nu)k}{\alpha E}, \quad (1)$$

where R is the thermal shock resistance, σ_f is the fracture strength, υ is Poisson's ratio, k is the thermal conductivity, α is the thermal expansion coefficient, and E is the Young's modulus. In addition to increasing the fracture strength, the current finding provides an additional path to enhanced thermal shock resistance by lowering the Young's modulus. As demonstrated above, CNT doping can also increase the fracture strength. Therefore, the thermal shock resistance of the CNT-doped material could be enhanced.

Using a powder processing approach, multi-walled CNTs were incorporated into bulk $Bi_{0.4}Sb_{1.6}Te_3$ thermoelectric material, where CNTs were observed along grain boundaries. The addition of CNT increased the Seebeck coefficient and electrical resistivity, but decreased the thermal conductivity, leading to an unchanged ZT. The fracture strength was significantly improved by the CNT addition, from 32 MPa for 0 wt. % CNT samples to 90 MPa for samples with 0.5 wt. % CNT. The dynamic Young's modulus and shear modulus were reduced by incorporating CNTs, which is not yet fully understood but could be related to the elastic mismatch between CNT and the matrix and the "defect" effect of CNTs in the grain boundary region. With enhanced strength and decreased Young's modulus, CNT is expected to improve the thermal shock resistance, which is important for application of thermoelectric materials subject to thermal cycling and rapid temperature change.

The research was sponsored by the ORNL Laboratory Directed Research and Development Seed Money Program, under DOE Contract No. DE-AC05-00OR22725 with UT-Battelle, LLC.

[1]L. E. Bell, Science **321**, 1457 (2008).
[2]J. Sharp, J. Bierschenk, and H. B. Lion, Jr., Proc. IEEE **94**(8), 1602 (2006).
[3]B. C. Sales, Int. J. Appl. Ceram. Technol. **4**(4), 291 (2007).
[4]J.-P. Fleurial, JOM **61**(4), 79 (2009).
[5]S. B. Riffat and X. Ma, Appl. Therm. Eng. **23**, 913 (2003).
[6]E. D. Case, J. Electron. Mater. **41**(6), 1811 (2012).
[7]J. B. Wachtman, *Mechanical Properties of Ceramics* (Wiley-Interscience, 1996).
[8]L. D. Zhao, B.-P. Zhang, J.-F. Li, H. L. Zhang, and W. S. Liu, Solid State Sci. **10**, 651 (2008).
[9]F. Ren, B. D. Hall, J. E. Ni, E. D. Case, J. Sootsman, M. G. Kanatzidis, E. Lara-Curzio, R. M. Trejo, and E. J. Timm, *in Thermoelectric Power Generation*, edited by T. P. Hogan, J. Yang, R. Funahashi, and T. Tritt (Mater. Res. Soc. Symp. Proc., 2008), Vol. 1044, p. 121.
[10]D. Kenfaui, G. Bonnefont, D. Chateigner, G. Fantozzi, M. Gomina, and J. G. Noudem, Mater. Res. Bull. **45**, 1240 (2010).
[11]D. Hull and T. W. Clyne, *An Introduction to Composite Materials*, 2nd ed. (Cambridge University Press, 1996).
[12]D. J. Bergman and O. Levy, J. Appl. Phys. **70**(11), 6821 (1991).
[13]D. J. Bergman and L. G. Fel, J. Appl. Phys. **85**(12), 8205 (1999).
[14]M. G. Kanatzidis, Chem. Mater. **22**, 648 (2010).
[15]N. Gothard, G. Wilks, T. M. Tritt, and J. E. Spowart, J. Electron. Mater. **39**(9), 1909 (2010).
[16]M. Popov, S. Buga, P. Vysikaylo, P. Stepanov, V. Skok, V. Medvedev, E. Tatyanin, V. Denisov, A. Kirichenko, V. Aksenenkov, and V. Blank, Phys. Status Solidi A **208**(12), 2783 (2011).
[17]V. D. Blank, S. G. Buga, V. A. Kulbachinskii, V. G. Kytin, V. V. Medvedev, M. Yu. Popov, P. B. Stepanov, and V. F. Skok, Phys. Rev. B **86**, 075426 (2012).
[18]X. Shi, L. Chen, J. Yang, and G. P. Meisner, Appl. Phys. Lett. **84**(13), 2301 (2004).
[19]X. Shi, L. D. Chen, S. Q. Bai, X. Y. Huang, X. Y. Zhao, Q. Yao, and C. Uher, J. Appl. Phys. **102**, 103709 (2007).
[20]Y. Zhang, X. L. Wang, W. K. Yeoh, R. K. Zeng, and C. Zhang, Appl. Phys. Lett. **101**, 031909 (2012).
[21]B. Duan, P. Zhai, P. Wen, S. Zhang, L. Liu, and Q. Zhang, Scr. Mater. **67**, 372 (2012).
[22]J. R. Sootsman, J. He, V. P. Dravid, S. Ballikaya, D. Vermeulen, C. Uher, and M. G. Kanatzidis, Chem. Mater. **22**, 869 (2010).
[23]Q. Zhang, H. Wang, Q. Zhang, W. Liu, B. Yu, H. Wang, D. Wang, G. Ni, G. Chen, and Z. Ren, Nano Lett. **12**, 2324 (2012).
[24]T. R. Hendricks, I. N. Ivanov, D. A. Schaeffer, P. A. Menchhofer, and J. T. Simpson, Nanotechnology **21**, 115301 (2010).

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[25]H. Wang, W. D. Porter, H. Böttner, J. König, L. Chen, S. Bai, T. Tritt, A. Mayolett, J. Senawiratne, C. Smith, F. Harris, P. Gilbert, J. Sharp, J. Lo, H. Kleinke, and L. Kiss, J. Electron. Mater. **42**(6), 1073 (2013).
[26]E. S. R. Gopal, *Specific Heats at Low Temperatures* (Plenum Press, 1996), pp. 61–63.
[27]C. Kittle, *Introduction to Solid State Physics*, 5th ed. (John Wiley & Sons, 1976), pp. 164–166.
[28]F. Ren, E. D. Case, J. Sootsman, M. G. Kanatzidis, H. Kong, C. Uher, E. Lara-Curzio, and R. M. Trejo, Acta Mater. **56**(20), 5954 (2008).
[29]Standard Test Method for Monotonic Equibiaxial Flexural Strength of Advanced Ceramics at Ambient Temperature, C 1499-09, ASTM International, West Conshohocken, PA, 2009.
[30]H. Wang, W. D. Porter, H. Böttner, J. König, L. Chen, S. Bai, T. M. Tritt, A. Mayolet, J. Senawiratne, C. Smith, F. Harris, P. Gilber, J. W. Sharp, J. Lo, H. Kleinke, and L. Kiss, J. Electron. Mater. **42**(4), 654 (2013).
[31]J. Jiang, L. Chen, S. Bai, Q. Yao, and Q. Wang, Scr. Mater. **52**, 347 (2005).
[32]B. D. Hall, J. L. Micklash, J. R. Johnson, C.-I. Wu, T. P. Hogan, and E. D. Case, "A review of mechanical properties of thermoelectric materials," in *paper presented at Materials Science and Technology Conference*, Detroit, MI, September 16–20, 2007.
[33]T. Wei, Z. Fan, G. Luo, and F. Wei, Mater. Lett. **62**, 641 (2008).
[34]S. Pasupuleti, R. Peddetti, S. Santhanam, K.-P. Jen, Z. N. Wing, M. Hecht, and J. P. Halloran, Mater. Sci. Eng., A **491**, 224 (2008).
[35]K. Shimoda, T. Hinoki, and A. Kohyama, Compos. Sci. Technol. **70**, 387 (2010).
[36]R. K. Chintapalli, F. G. Marro, B. Wilson, M. Reece, and M. Anglada, Mater. Sci. Eng., A **549**, 50 (2012).
[37]T. Kobayashi, K. Yoshida, and T. Yano, J. Nucl. Mater. **440**, 524 (2013).
[38]A. Mukhopadhyay, B. T. T. Chu, M. L. H. Green, and R. I. Todd, Acta Mater. **58**, 2685 (2010).
[39]E. D. Case, *in Thermo-Mechanical Fatigue and Fracture*, edited by M. H. Alibadi (WIT Press, Southampton, 2002), pp. 137–208.
[40]W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, 2nd ed. (Wiley-Interscience, New York, 1976).

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