#### Identifying the Specific Nanostructures Responsible for the High Thermoelectric Performance of (Bi,Sb)<sub>2</sub>Te<sub>3</sub> Nanocomposites

#### Wenjie Xie,<sup>†,†,⊥</sup> Jian He,<sup>†,⊥</sup> Hye Jung Kang,<sup>†</sup> Xinfeng Tang,<sup>\*,†</sup> Song Zhu,<sup>†</sup> Mark Laver,<sup>§</sup> Shanyu Wang,<sup>†</sup> John R. D. Copley,<sup>||</sup> Craig M. Brown,<sup>||</sup> Qingjie Zhang,<sup>†</sup> and Terry M. Tritt<sup>\*,†</sup>

<sup>†</sup>State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, People's Republic of China, <sup>†</sup>Department of Physics & Astronomy, Clemson University, Clemson, South Carolina 29634-0978, <sup>§</sup>Laboratory for Neutron Scattering, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland, and <sup>II</sup>NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-6102

**ABSTRACT** Herein, we report the synthesis of multiscale nanostructured p-type  $(Bi,Sb)_2Te_3$  bulk materials by melt-spinning single elements of Bi, Sb, and Te followed by a spark plasma sintering process. The samples that were most optimized with the resulting composition  $(Bi_{0.48}Sb_{1.52}Te_3)$  and specific nanostructures showed an increase of ~50% or more in the figure of merit, *ZT*, over that of the commercial bulk material between 280 and 475 K, making it suitable for commercial applications related to both power generation and refrigeration. The results of high-resolution electron microscopy and small angle and inelastic neutron scattering along with corresponding thermoelectric property measurements corroborate that the 10–20 nm nanocrystalline domains with coherent boundaries are the key constituent that accounts for the resulting exceptionally low lattice thermal conductivity and significant improvement of *ZT*.

 $\label{eq:KEYWORDS} KEYWORDS \ (Bi,Sb)_2Te_3, \ thermoelectric \ material, \ multiscale \ nanostructures, \ inelastic \ neutron \ scattering, \ small \ angle \ neutron \ scattering \ sc$ 

s electrical energy will most likely remain the most convenient form of energy in the foreseeable future, sustainable and ecofriendly methods to generate electricity are of extreme importance. On the other hand, more than half of all the energy generated by mankind is lost as heat. The past two decades have witnessed an increasing demand in renewable energy technology, including that of direct thermal-electrical energy conversion via thermoelectricity.<sup>1-4</sup> Thermoelectricity is based on two fundamental thermoelectric effects: the Seebeck effect for power generation and the Peltier effect for refrigeration. Heat from different sources such as solar heat, geothermal heat, and waste heat from automobiles or other industrial processes can be directly converted into electrical energy by a thermoelectric device. The thermoelectric device can also work in reverse as a heat pump. Despite a few niche applications such as in NASA's deep space probe missions, broader applications of thermoelectricity in power generation and refrigeration is currently limited by the low conversion efficiency that is a factor of 2-4 less than that of equivalent mechanical systems. The conversion efficiency of ther-

<sup>⊥</sup> These authors contributed equally to this work. Received for review: 03/5/2010 Published on Web: 08/05/2010 moelectricity depends primarily on the performance of the thermoelectric material, which is gauged by the dimensionless figure of merit, *ZT*. The *ZT* is defined as

$$ZT = \frac{\alpha^2 T}{\rho \kappa} = \frac{\alpha^2 T}{\rho (\kappa_{\rm L} + \kappa_{\rm e})} \tag{1}$$

where  $\rho$  is the electrical resistivity,  $\alpha$  the Seebeck coefficient (i.e., thermopower),  $\kappa$  the thermal conductivity (often separated into the lattice thermal conductivity,  $\kappa_L$ , and the carrier thermal conductivity,  $\kappa_e$ ), and *T* the temperature in kelvin. Per eq 1, a high *ZT* material is a "phonon–glass electron–crystal" (PGEC)<sup>5</sup> system with a large Seebeck coefficient. Apparently, it is difficult to satisfy these criteria in a simple crystal field since the three physical properties ( $\rho$ ,  $\alpha$ , and  $\kappa$ ) that govern the *ZT* are interdependent: a modification to any of these properties often adversely affects the other properties.

Over the past decade, the efforts of pursuing higher *ZT* materials have culminated into a new paradigm,<sup>6,7</sup> namely, nanocomposite (NC) thermoelectric materials. In NC thermoelectric materials, the characteristic length scale of at least one constituent is on the nanometer scale; the resulting classical and quantum size effects help ease the interdependence of those properties.<sup>8</sup> This new paradigm started several years ago with the speculation that low dimensional

<sup>\*</sup> To whom correspondence should be addressed,  ${\tt tangxf} @{\tt whut.edu.cn}$  and  ${\tt ttritt} @{\tt clemson.edu}.$ 

materials should have enhanced thermoelectric properties compared to similar materials in bulk form.<sup>9</sup> This assertion was confirmed with the advent of the "custom nanoengineered" systems of quantum dot and superlattice materials,<sup>10</sup> and more recently in several "self-assembled" NC thermoelectric materials.<sup>11–15</sup> It is instructive to note that the main contribution to enhancing *ZT* in these NC thermoelectric materials is from the significant reduction of lattice thermal conductivity,  $\kappa_{L}$ , despite the variety of materials systems and synthesis methods.

In solids, heat is carried by phonons that access a broad range of energies (frequency) and momenta (wavelength). To effectively scatter phonons, the size of the scattering centers needs to be comparable to the wavelength of the heat-carrying phonons, typically on the order of nanometers. Since the phonon spectrum is temperature dependent, it entails the appropriate implementation of multiscale nanostructures and combined phonon scattering mechanisms such as mass fluctuation, grain boundary, and strain field scattering.<sup>16</sup> On the other hand, not *all* nanostructures are favorable since these nanostructures simultaneously need to have a minimal detrimental impact on the electrical properties.

An inherent and added practical concern of the NC thermoelectric materials is the stability of nanostructures at elevated temperatures; hence it is more viable to develop NC thermoelectric materials that operate in the vicinity of room temperature since diffusion and grain growth will be minimal there. Bi2Te3-based bulk materials are the most widely used thermoelectric material that operates in the temperature range of 200-400 K. The high ZT p-type (Bi,Sb)<sub>2</sub>Te<sub>3</sub> nanocrystalline bulk materials have been prepared from a commercial ingot<sup>17</sup> and elemental chunks<sup>18</sup> by a combined ball milling and hotpressing procedure in an inert atmosphere. Herein, we report a novel two-stage, time and cost efficient, melt-spin and spark-plasma-sintering synthesis procedure of high-performance p-type (Bi,Sb)<sub>2</sub>Te<sub>3</sub> NC thermoelectric materials from single elements of Bi, Sb, and Te, which builds upon our previous work.<sup>19,20</sup> The present paper is organized as follows. First, we show that melt spinning is an effective way to create a wide spectrum of multiscale nanostructures and that the spark plasma sintering process can then control the as-formed nanostructures in the final product. Next, we present the results of the thermoelectric property and inelastic neutron scattering measurements to show that the significantly reduced  $\kappa_{\rm L}$  is due to strong phonon scattering rather than an altered phonon spectrum. Finally, the small angle neutron scattering measurements help pinpoint which specific nanostructures account for the observed low  $\kappa_{\rm L}$  and significantly enhanced ZT values over a broad temperature range.

**Experimental Procedure.** The single elements Bi, Sb, and Te powder (99.999%, 99.999%, and 99.99%, Alfa Aesar) were mixed in an optimized molar ratio<sup>21</sup> of 0.48:1.52:3.00, cold-pressed into chunks, and loaded into a quartz tube with

a 0.5 mm diameter nozzle. In a standard 0.06 MPa argon atmosphere, the chunks were inductively melted and sputtered onto a fast-rotating water-cooled copper roller. The melt spin process takes  $\approx 1$  min for a load of 5 g of powder. We found that higher rotation speed led to finer nanostructures, so we adopted a 4000 rpm, i.e., a tangential linear speed of 40 m/s. The products of the melt spin process were in the form of ribbons with a typical size of  $10 \times 2 \times$ (0.005-0.01) mm<sup>3</sup>. The ribbons were then hand-ground for a few minutes into raw powders; no protective atmosphere was needed at this stage. Finally, the raw powders were densified into pellets using a spark plasma sintering (SPS) technique in vacuum. The SPS System is a Dr. Sinter SPS-1500 A from Metal Processing Systems in the US and Sunimoto Mining in Japan. In order to preserve the thermoelectrically favored nanostructures, an optimal SPS temperature of 773 K, pressure of 15 MPa, and total sintering time of 5 min were adopted. The sample prepared by singleelement-melt spinning followed by a spark plasma sintering (SPS) procedure is designated as SE-MS-SPS. Zone-melted p-type Bi<sub>0.48</sub>Sb<sub>1.52</sub>Te<sub>3</sub> ingots obtained from Shenhe Thermo-Magnetics Co. Ltd. (Shanghai, China) were used as the comparison.

X-ray powder diffraction (XRD, Rigaku Miniflax), field emission scanning electron microscopy (FESEM) (Hitachi S-4800) with an energy-dispersive X-ray spectroscopy (EDS) option, and transmission electron microscopy (HRTEM) (JEM-2100F) were performed at each stage of the preparation to monitor the possible change in phase, crystallinity, and micromorphology.

All thermoelectric properties were measured on the same sample. The results of supplemental transport measurements indicated an anisotropy <3 % in the SE-MS-SPS sample. The low-temperature Seebeck coefficient ( $\alpha$ ) and electrical resistivity (p) data were collected on a custom-designed measurement system<sup>22</sup> from 10 to 300 K. The high-temperature Seebeck coefficient ( $\alpha$ ) and electrical resistivity ( $\rho$ ) data were collected on commercial equipment (ZEM-2, Ulvac Riko, Inc.) in a helium atmosphere from 300 to 540 K. The low temperature thermal conductivity ( $\kappa$ ) data were collected using a steady-state technique on a custom-designed measurement system<sup>23</sup> from 10 to 300 K. The thermal diffusivity (D) was measured by the laser flash method using a Netzsch LFA457 system. Specific heat  $(C_p)$  was determined by differential scanning calorimetry using a Netzsch DSC-404C. The density  $(\rho_D)$  was determined by the Archimedes technique. The high-temperature  $\kappa$  was calculated from *D*,  $C_p$ , and  $\rho_{\rm D}$  from the relationship:  $\kappa = DC_p \rho_{\rm D}$ . The results of lowtemperature and high-temperature measurements match very well. Uncertainties in the electrical conductivity and thermal conductivity are  $\pm (5-7)\%$  due in large part in determination of the sample dimensions; the uncertainties in thermopower are  $\pm 5\%$ . It should be noted that the uncertainty in the area of the sample is eliminated (since the area cancels out) in the ZT calculation if the electrical

3284

conductivity and thermal conductivity are measured on the same sample. Thus the uncertainty in the *ZT* is around 10%. Repeated measurements up to 540 K on the SE-MS-SPS sample did not show any degradation; the variations were within a few percent for the samples made by the same procedure.

In the data analysis, the total thermal conductivity is separated into contributions from the electron thermal conductivity ( $\kappa_e$ ) and the lattice thermal conductivity ( $\kappa_L$ ) by the relationship:  $\kappa = \kappa_e + \kappa_L$ , where  $\kappa_e$  is estimated by the Wiedemann–Franz relation,  $k_e = LT/\rho$ , and the Lorenz number  $L = 2.0 \times 10^{-8} \text{ V}^2/\text{K}^2$  for a heavily doped semiconductor. The Hall coefficient measurements were preformed on a Quantum Design Physical Properties Measurement System (PPMS) using a five-probe configuration by sweeping the magnetic field between  $\pm 0.5$  T over a temperature range of 5–310 K. The carrier concentration (*n*) and Hall mobility ( $\mu_H$ ) were estimated from the Hall coefficient by the relation  $n = -1/R_He$  and  $\mu_H = R_H/ne$ , respectively, where  $R_H$  is the Hall coefficient and *e* the electron charge.

Inelastic neutron scattering measurements were performed with the time-of-flight instrument, DCS,<sup>24</sup> at the NIST Center for Neutron Research (NCNR). The detector array of the time-of-flight instrument covers a wide range of scattering angle and allows for the energy and momentum to be probed at the same time. The generalized phonon density of states (GDOS) were obtained by averaging the momentum over both the direction and the magnitude using available software.<sup>25</sup> For our measurements, an incident neutron wavelength of 4.8 Å was selected, which gives an elastic energy resolution of about 0.1 meV. The sample was sealed in an aluminum can filled with helium gas for heat exchange with its temperature controlled using a closed cycle refrigerator. The same measurement on an identical helium-filled can without a sample was performed to obtain a background. To probe the nanostructuring-induced microstructure change, small angle neutron scattering (SANS) measurements were performed using the NG3-SANS instrument at the NIST Center for Neutron Research.<sup>26</sup> Neutrons of average wavelength 8.4 Å were collimated over distances 3-16 m before the sample. The scattering was measured using a two-dimensional detector of  $128 \times 128$  pixels, each  $5.08 \text{ mm} \times 5.08 \text{ mm}$ , placed at distances 2-14 m after the sample. In addition, the lowest scattering vectors were attained through the use of focusing biconcave MgF<sub>2</sub> lenses. The error bars in neutron scattering data are  $\pm \sigma$ .

Thermoelectric Properties of  $(Bi,Sb)_2Te_3$  Nanocomposites. The temperature dependences of the electrical resistivity ( $\rho$ ) and Seebeck coefficient ( $\alpha$ ) are presented in parts a and b of Figure 1, respectively. For comparison, a sample directly cut from the commercial zone melting (ZM) ingot along the ZM direction is designated as ZM. Both the ZM and SE-MS-SPS samples exhibit typical semimetallic behavior in electrical resistivity and Seebeck coefficient. Despite the similar resistivity behavior, they display a different Seebeck



FIGURE 1. Thermoelectric properties of ZM and SE-MS-SPS bulk materials: (a) electrical resistivity; (b) Seebeck coefficient; (c) lattice thermal conductivity inserted by total thermal conductivity; (d) figure of merit ZT values.

behavior in several important aspects. The SE-MS-SPS sample has as much as 10% higher Seebeck value than the ZM sample between  $\approx$ 270 and 540 K. Furthermore, the Seebeck coefficient of SE-MS-SPS sample peaks at  $T \approx 450$  K, significantly higher than that of the ZM sample. The results of Hall coefficient measurements indicated that both samples have a carrier concentration on the order of  $10^{19}$  cm<sup>-3</sup> and within  $\pm 10\,\%$  of each other between 5 and 300 K (see Figure S2 in Supporting Information). Furthermore, the  $T^{-3/2}$  dependence of Hall mobility is consistent with a predominant electron-phonon scattering near room temperature. The concomitant enhancement and the upshift of the Seebeck coefficient peak with temperature strongly suggest that the nanostructuring process induced a favorable change in the Fermi surface topology. This argument is further supported by the temperature dependence of the lattice thermal conductivity. As shown in the main panel and inset of Figure 1 c, the minima of lattice thermal conductivity ( $\kappa_1$ ) and total thermal conductivity ( $\kappa$ ) are close to the temperature where the Seebeck coefficient peaks, a signature of bipolar thermal conduction. The MS-SPS nanostructuring procedure thus alters the band structure and shifts the impact of the detrimental bipolar effects to higher temperatures. As a result, the adopted two-stage nanostructuring procedure led to a slightly higher resistivity, moderately enhanced Seebeck coefficient, and significantly reduced lattice thermal conductivity in the SE-MS-SPS sample. In particular, the SE-MS-SPS sample has a lattice thermal conducitivity,  $\approx 0.4-0.5$ W/(m K) between 300 and 400 K, as compared to a  $\approx\!0.8{-}0.9$  W/(m K) of the ZM sample. An increase of 50 % or more in the ZT values between 280 and 540 K over the ZM sample has been attained, and the maximum ZT value is  $\approx$ 1.5 at 390 K (Figure 1d).

3285



FIGURE 2. Generalized phonon density of states (GDOS) for ZM and SE-MS-SPS samples at 300 K. For clarity, we do not show the data taken at 100 K.

Relation between Microstructures and Transport **Properties.** In view of the trivial differences in the packing density, overall composition, and XRD patterns between the two samples, the drastic reduction of the lattice thermal conductivity in the SE-MS-SPS sample is somewhat unexpected. From a kinetic point of view, it is an open question whether such a reduction in  $\kappa_{\rm L}$  is due to a drastically altered phonon spectrum and/or a strong scattering of the phonons. To address this question, we performed inelastic neutron scattering experiments and present the results in Figure 2. The generalized phonon densty of states (GDOS) in the energy range of 0-30 meV was measured at 100 and 300 K for both materials. The resulting GDOS of the SE-MS-SPS and the ZM samples are virtually identical. Although, we are fully aware that the GDOS is not sensitive enough to monitor small changes of each phonon mode, the overall change in GDOS is nonetheless too small to account for the reduction of lattice thermal conductivity. Hence, the drastic reduction of lattice thermal conductivity is more likely due primarily to the diminishing phonon mean free path arising from some strong scattering processes. In additon, the GDOS exhibited a quadratic energy dependence in the energy range of 0-4.5 meV, the data fitting in this range yielded a velocity of sound  $\nu \approx 900$  m/s and a Debye temperature  $\theta_{\rm D}$ pprox 120 K in the context of the Debye model. The characteristic wavelength of heat-carrying phonons, mostly acoustic phonons, was estimated to be on the order of 1-10 nm from the values of energy and velocity of sound.

At this point, it is instructive to estimate the minimum lattice thermal conductivity ( $\kappa_{min}$ ) using a model developed by Cahill et al.<sup>27</sup>

$$k_{\min} = \left(\frac{\pi}{6}\right)^{1/3} k_{\rm B} n_{\rm a}^{2/5} \sum_{i} v_i \left(\frac{T}{\theta_i}\right)^2 \int_0^{\theta_i/T} \frac{x^3 e^x}{(e^x - 1)^2} \,\mathrm{d}x$$
(2)

where the summation is over the three polarization modes and  $k_{\rm B}$  is the Boltzmann constant. The cutoff frequency (in units of kelvin) is  $\theta_i = v_i (\hbar/k_{\rm B}) (6\pi^2 n_{\rm a})^{1/3}$ , where  $n_{\rm a}$  is the number density of atoms,  $\hbar$  the reduced Planck constant,  $v_i$  the sound velocity for each polarization mode. The supplemental study showed that the SE-MS-SPS sample is an isotropic phonon media: the anisotropy in total thermal conductivity is <3%. The Cahill model is in the context of a random walk of Einstein oscillators of varying sizes and is valid for amorphous or highly disordered materials, where the phonon mean free path is close to the average interatomic spacing. Substituting the *v* and  $\theta$  values in eq 2 yields  $\kappa_{\rm min}$  as shown in the main panel of Figure 1c. Between 300 and 400 K, the lattice thermal conductivity of SE-MS-SPS sample is close to  $\kappa_{\rm min}$ , indicating a "phonon glass" like heat conduction despite the well-defined crystalline nature.

Now we proceed to the electron microscopy results in order to more clearly establish the correlation between the microstructures and the thermoelectric properties. We first examine the microstructures of the melt spun ribbons. Owing to the rapid solidification and low thermal conductivity of melts in the melt spin process, the contact surface (where the melts touch the copper roller) and the free surface are expected to have drastically different temperatures, critical radii for nucleation, and growth speed for nucleation sites. In order to verify these speculations, high-resolution transmission electron microscopy (HRTEM) was utilized to investigate the microstructures of the two surfaces and the cross section of SE-MS ribbon. The results show that the contact surface is characterized by 5-10 nm nanocrystalline domains embedded in amorphous phase (parts a and b of Figure 3), whereas the free surface features microsize dendritic crystals (Figure 3c). More interestingly, we have identified nanoscale modulations within the dendritic crystals (Figure 3d), the Fourier analysis yielded a periodicity close to 1.0 nm—about 5 times that of the  $d_1 = d_{0015}$  spacing. The microstructures observed on the cross section of ribbon are shown in Figure 4. Note that a gradient of multiscale microstructures was formed along the thickness direction of ribbon during the melt spin process ((Figure 4a): from the amorphous phase near the contact surface (Figure 4b), to the 5-10 nm randomly oriented nanocrystalline domains with coherent boundary in the midpart of the ribbon (Figure 4c), and to the microsize dendritic crystals near the free surface (Figure 4d). The selected area electron diffraction (SAED) confirmed that the nanocrystalline domains could be indexed as  $\mathrm{Bi}_2\mathrm{Te}_3$  and the orientation of domains appeared to be random. Besides, the EDS taken on seven different locations along the thickness of the ribbon showed that the composition was uniform on the micrometer scale and above, but the Bi and Te concentrations were not homogeneous on the nanoscale (Figure 4e).

Next, we examine the impact of the SPS process on these multiscale microstructures. As shown in panels a and b of Figure 5, the typical microstructures after the SPS process contained some 10-20 nm nanocrystals embedded in the bulk matrix (SE-MS-SPS). These 10-20 nm nanocrystals are



FIGURE 3. Microscopy images of the melt spin ribbon: (a) TEM image of near contact surface; (b) HRTEM image of nanocrystalline domains; (c) TEM image of free surface that is featured by microsize dendritic crystals; (d) HRTEM image of nanoscale modulation in the dendritic crystal shown in (c). The scale bars for (a), (b), (c), and (d) are 20, 5, 200, and 5 nm, respectively. (e) Diagram of the MS process denoting the free surface (FS) and contact surface (CS). (f) Schematic structure distribution in the ribbon from contact surface to free surface.



FIGURE 4. (a) TEM image of the cross section of ribbon, positions 7 and 1 are near the contact surface and free surface, respectively. (b) HRTEM image of amorphous phase. (c) HRTEM image of nanocrystalline domains with mostly coherent boundary. (d) TEM image of microsize crystals. (e) EDS results of related position in (a). The scale bars for (a), (b), (c) and (d) are 0.5, 10, 5, and 50 nm, respectively. The insets of panel d are the HRTEM image of the nanoscale modulation, and the scale bar is 2 nm.

probably derived from the amorphous phase and the 5-10 nm nanocrystals that are shown in Figures 3 and 4. It is interesting to note that these nanostructures give rise to only a slight increase in resistivity but significantly reduce the resulting lattice thermal conductivity. In other words, the boundaries among the nanocrystalline domains and the bulk matrix scatter phonons more effectively than they scatter electrons. Panels a and b of Figure 5 present a representative grain boundary between nanocrystalline domains. We found that most grain boundaries are coherent despite some nanodomains without clear boundaries. Importantly, the nanoscale modulations found in the microsize dendrite crystals survive the SPS process, as shown in panels c and d of Figure 5.

In general, the microstructures of the as prepared SE-MS-SPS sample are featured by closely packed microsized

crystals with nanoscale modulations, a small amount of amorphous phase, and a large population of 10-20 nm nanocrystalline domains with coherent boundaries. The characteristic length scales of these nanostructures are comparable to the estimated wavelength of heat-carrying phonons, and the mostly coherent grain boundaries render a minimum degradation of the carrier mobility. To supplement the microscopy study of nanostructures, we performed SANS measurements on ZM and SE-MS-SPS bulk materials.<sup>28</sup> SANS is a well-established technique for characterizing microstructures on the length scales from a few nanometers to a few hundred nanometers, which greatly supplements the electron microscopy study. In Figure 6 we present the SANS intensity (I) as a function of momentum transfer (Q) for the SE-MS-SPS and ZM samples. The plot is in double*logarithmic* scale. Due to the complexity of microstructures,

3287



FIGURE 5. Representative TEM images of SE-MS-SPS sample: (a) and (b) HRTEM images of typical microstructures contained 10-20 nm nanocrystals embedded in the bulk matrix; (c) and (d) HRTEM images of nanoscale modulations. The scale bars for (a), (b), (c), and (d), are 2, 5, 100, and 2 nm, respectively.



FIGURE 6. SANS intensities as a function of momentum transfer Q in a *double-logarithmic* plot. The SE-MS-SPS sample is fitted with a  $Q^{-a}$  in all Q range with a = 3.7 (black line).

we shall restrict our data analysis to the comparison of the Q dependence of scattered intensity in the two samples. First of all, the scattered intensity for SE-MS-SPS sample exhibits a salient power-law behavior with an exponent, a = 3.7between  $Q_{\min} = 0.001 \text{ Å}^{-1}$  and  $Q_{\max} = 0.1 \text{ Å}^{-1}$ , i.e.,  $I \sim Q^{-a}$ with  $a = 3.70 \pm 0.01$ . This observation is consistent with a broad distribution of microstructures over a decade or more in length scale,<sup>29</sup> as well as the observed multiscale microstructures in the electron microscopy study (Figures 3-5). In addition, the observed power-law exponent close to 4 indicates that the interfaces among nanostructures and bulk matrix in the SE-MS sample are mostly homogeneous or  $coherent.^{30,31}$  In sharp contrast, the Q dependence of the scattered intensity for the ZM sample deviates from the power law in the ranges, (i)  $Q < 0.007 \text{ Å}^{-1}$  and (ii) Q > 0.05Å<sup>-1</sup>, the overall downward curvature suggesting a less polydisperse distribution of microstructures. As a rough estimate,

 $Q < 0.007 \text{ Å}^{-1}$  and  $Q > 0.05 \text{ Å}^{-1}$  translate to characteristic length scales of a few hundred nanometers and a few tens of nanometers, respectively. The difference in the range (i) may be attributed to the presence of dendritic crystals in the SE-MS-SPS sample (Figure 2c) and their absence in the ZM sample. However, the associated length scale in the range (i) is too large, compared to the wavelength of heat-carrying phonons, to substantially affect the lattice thermal conductivity. That leaves us with the only option, i.e., the range (ii) that corresponds to the nanostructures on the order of a few to a few tens of nanometers. In light of the absence of 10-20nm nanocrystalline domains in the ZM sample and the estimated 1-10 nm phonon wavelength, we thus attribute the difference in the range (ii) along with the drastic reduction of lattice thermal conductivity to the presence of 10-20 nm nanocrystalline domains with coherent boundaries. We note that similar features of microstructures have been also reported in the ball-milled nanocrystalline bulk p-Bi<sub>2</sub>Te<sub>3</sub> that exhibited high ZT values.<sup>17,18</sup>

Summary. Nanocomposite thermoelectric materials can be a cost-effective and scalable alternative to the "custom nanoengineered" systems, such as superlattices or quantum dots, in order to achieve higher ZT materials. Herein, we reported a nanostructuring procedure in p-type Bi<sub>2</sub>Te<sub>3</sub> by combining high-speed melt spinning and spark plasma sintering processes to yield a bulk TE nanocomposite from the precursor single elements. The unique multiscale microstructures, in particular the 10-20 nm nanocrystals with mostly coherent grain boundaries, are believed to account for the significant reduction of thermal conductivity without degrading the electrical properties. Compared to the commercial zone melting material, as much as a 50% enhancement in the ZT over a wide temperature range has been attained by a sample prepared from the single elements at a 4000 rpm melt spin speed followed by spark plasma sintering at 15 MPa of pressure and at 773 K for 1 min.

Acknowledgment. We acknowledge the support of the National Basic Research Program of China (Grant No. 2007CB607501) and the Natural Science Foundation of China (Grant No. 50731006 and 50672118) along with 111 Project (Grant No. B07040). The work at Clemson University is supported by DOE/EPSCoR Implementation Grant (#DE-FG02-04ER-46139), and the SC EPSCoR cost sharing program. The work at NIST was supported in part by the National Science Foundation under Agreement No. DMR-0454672. W.J. Xie would also like to thank the China Scholarship Council (CSC) for support in the form of a partial fellowship (No. 2008695022).

**Supporting Information Available.** Figures showing dimensionless thermoelectric figure of merit *ZT* as a function of Bi content and carrier concentration and carrier mobility as a function of temperature for SE-MS-SPS and ZM bulk

materials. This material is available free of charge via the Internet at http://pubs.acs.org.

#### **REFERENCES AND NOTES**

- (1) *MRS Bull.* **2006**, *31*, special issue edited by T. M. Tritt and M. A. Subramanian.
- (2) Tritt, T. M.; Bottner, H.; Chen, L. D. MRS Bull. 2008, 33, 366.
- (3) Snyder, G. J.; Toberer, E. S. Nat. Mater. 2008, 7, 105.
- (4) Bell, L. E. Science **2008**, *321*, 1457.
- (5) Slack, G. A. In *CRC Handbook of Thermoelectrics*; Rowe, D. M., Ed.; CRC Press: Boca Raton, FL, 1995; pp 407–440.
- (6) Kanatzidis, M. G. Chem. Mater. 2010, 22 (3), 648.
- (7) Sootsman, J. R.; Chung, D. Y.; Kanatzidis, M. G. Angew. Chem., Int. Ed. 2009, 48, 8616.
- (8) Heremans, J. P. Acta Phys. Pol. 2005, 4, 609.
- (9) Hicks, L. D.; Dresselhaus, M. S. Phys. Rev. B: Condens. Mater. 1993, 47, 12727.
- (10) Hsu, K. F.; Loo, S.; Guo, F.; Chen, W.; Dyck, J. S.; Uher, C.; Hogan, T.; Polychroniadis, E. K.; Kanatzidis, M. G. *Science* **2004**, *303*, 818.
- (11) Kim, W.; Zide, J.; Gossard, A.; Klenov, D.; Stemmer, S.; Shakouri, A.; MajumdarA., *Phys. Rev. Lett.* **2006**, *96*, No. 045901.
- (12) Zhang, Q.; He, J.; Zhu, T. J.; Zhang, S. N.; Zhao, X. B.; Tritt, T. M. Appl. Phys. Lett. 2008, 93, 102109.
- (13) Li, H.; Tang, X. F.; Su, X. L.; Zhang, Q. J. Appl. Phys. Lett. 2008, 92, 202114.
- (14) Androulakis, J.; Lin, C. H.; Kong, H. J.; Uher, C.; Wu, C. I.; Hogan, T.; Cook, B. A.; Caillat, T.; Paraskevopoulos, K. M.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2007**, *129*, 9780.
- (15) Dresselhaus, M. S.; Chen, G.; Tang, M. Y.; Yang, R. G.; Lee, H.; Wang, D. Z.; Ren, Z. F.; Fleurial, J. P.; Gogna, P. Adv. Mater. 2007, 19, 1043.
- (16) Kim, W.; Wang, R.; Majumdar, A. Nano Today 2007, 2, 40.

- (17) Poudel, B.; Hao, Q.; Ma, Y.; Lan, Y.; Minnich, A.; Yu, B.; Yan, X.;
  Wang, D.; Muto, A.; Vashaee, D.; Chen, X.; Liu, J.; Dresselhaus,
  M. S.; Chen, G.; Ren, Z. F. *Science* **2008**, *320*, 634.
- (18) Ma, Y.; Hao, Q.; Poudel, B.; Lan, Y.; Yu, B.; Wang, D.; Chen, G.; Ren, Z. F. *Nano Lett.* **2008**, *8*, 2580.
- (19) Xie, W. J.; Tang, X. F.; Yan, Y. G.; Zhang, Q. J.; Tritt, M. T. Appl. Phys. Lett. 2009, 94, 102111.
- (20) Xie, W. J.; Tang, X. F.; Yan, Y. G.; Zhang, Q. J.; Tritt, M. T. J. Appl. Phys. 2009, 105, 113713.
- (21) Dimensionless thermoelectric figure of merit *ZT* as a function of Bi content is shown in Figure S1 in Supporting Information. The results show that the optimized molar ratio is 0.48:1.52:3.00 for Bi, Sb, and Te.
- (22) Pope, A. L.; Littleton IV, R. T.; Tritt, T. M. *Rev. Sci. Instrum.* **2001**, 72, 3129.
- (23) Pope, A. L.; Zawilski, B.; Tritt, T. M. Cryogenics 2001, 41, 725.
- (24) Copley, J. R. D.; Cook, J. C. Chem. Phys. 2003, 292, 477.
- (25) Azuah, R. T.; Kneller, L. R.; Qiu, Y.; Tregenna-Piggott, P. L. W.; Brown, C. M.; Copley, J. R. D.; Dimeo, R. M. J. Res. Natl. Inst. Stand. Technol. 2009, 114, 341.
- (26) Glinka, C. J.; Barker, J. G.; Hammouda, B.; Krueger, S.; Moyer, J. J.; Orts, W. J. J. Appl. Crystallogr. 1998, 31, 430.
- (27) Cahill, D. G.; Watson, S. K.; Pohl, R. O. *Phys. Rev. B* **1992**, *46*, 6131.
- (28) The ZM sample used in SANS measurement is prepared as follows. The ingots were hand ground into coarse grains with the size of  $600-3000 \ \mu m$  and pelletized by a SPS process at 823 K and 15 MPa for 20 mins in vacuum.
- (29) Beaucage, G.; Rane, S.; Schaefer, D. W.; Long, G.; Fischer, D. J. Polym. Sci., Part B: Polym. Phys. **1999**, 37, 1105.
- (30) Beaucage, G. J. Appl. Crystallogr. 1995, 28, 717.
- (31) Beaucage, G.; Kammler, S. K.; Pratsinis, S. E. *J. Appl. Crystallogr.* **2004**, *37*, 523.