Strong Reduction of Thermal Conductivity in Nanostructured PbTe Prepared by Matrix Encapsulation

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Developing advanced thermoelectric (TE) materials can impact conversion technologies of waste heat to electrical power. It is well expected that by fabricating TE materials in a nanostructured form their properties can be significantly enhanced.[1] Efficient TE materials must exhibit a large TE figure of merit, ZT, defined as $ZT = \sigma S^2/\kappa$, where S is the TE power (absolute Seebeck coefficient), σ is the electrical conductivity, and κ is the thermal conductivity. The Seebeck coefficient is generally inversely related to the electrical conductivity and as a result maximization of ZT is difficult.

One modality in achieving high performance is through the minimization of the thermal conductivity using nanostructures. Superlattice thin film structures grown by molecular beam epitaxy (MBE) $PbSe_{0.98}Te_{0.02}/PbTe$[2−4] have achieved ZT values > 3.[5] These MBE-grown materials contain pyramidal-shaped "nanodots" of PbSe with uniform size (∼20 nm) embedded inside a matrix of PbTe. This assembly possesses record low values of thermal conductivity (∼0.3−0.4 W/(m·K)) while at the same time retains a high power factor. Therefore, it is of significant interest to devise general, convenient, low cost synthetic methodologies for incorporating similar nanometer scale inclusions into bulk semiconductor materials in an effort to mimic the high ZT superlattice structures. Examples of materials with naturally occurring nanostructuring and enhanced TE properties have been reported.[6,7] Here we describe the intentional preparation of nanometer sized inclusions of Sb, Bi, and InSb in bulk PbTe using a general liquid matrix encapsulation technique. We observe that nanocrystals with large contrast in average mass (e.g., Sb and InSb) with that of the PbTe medium achieve stronger scattering of acoustic phonons than nanocrystals with minimal contrast. We also find that the reduction in lattice thermal conductivity is not monotonic with increasing concentration of nanoparticles, but there is an optimum concentration beyond which the lattice thermal conductivity actually increases. These results are in agreement with theoretical expectations and recent reports that embedded nanocrystals of ErAs promote strong scattering of acoustic phonons in a InGaAs matrix.[8]

There is a plethora of published work on the preparation of stable free-standing semiconductor nanocrystals capped with surfactants,[9] embedded in polymers[10] or glasses.[11] However, there is relatively little effort devoted to preparing nanocrystals inside solid matrices or bulk crystals.[12−14] In general, bulk crystals with nanocrystals embedded in them represent a fascinating set of nanostructured materials whose scope extends beyond the field of thermoelectrics especially when the properties of guest/matrix are chosen for specific functions.

To achieve nanoscale matrix encapsulation of a minority phase A inside a majority phase B, we choose the former to have very low or no solubility in the solid state but to be completely soluble in the liquid state. We choose the major phase B to have an equal or higher melting point than the minor phase (guest or inclusion) so that on rapid cooling it will be first to solidify thereby precipitating and simultaneously encapsulating nanocrystals of phase A. These conditions are akin to what is known in conventional solution chemistry as arrested precipitation.[15] We propose this as a general method to prepare bulk nanostructured materials of TE interest provided the matrix is chosen to be an already promising TE. The minor phase should be a nonreactive material capable of altering the phonon scattering processes of the medium.

The PbTe-x% M system (where M = Sb, Bi, and InSb and $2 \leq x \leq 16$) is amenable to a matrix encapsulation process and can form a nanostructured state. When rapidly cooled from a molten homogeneous solution to the frozen state it can kinetically trap nanocrystals of M inside solid PbTe. Sb, Bi, and InSb were selected because of their low solubility in PbTe.[16] Several molar ratios of Sb in PbTe at 2, 4, 8, and 16% were examined. We expected dilute solutions, for example, <4%, to precipitate small nanoparticles throughout the PbTe matrix. Higher concentrations formed larger particles due to nanoparticle fusion giving rise

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(1) (a) Chen, G.; Dresselhaus, M. S.; Dresselhaus, G.; Fleurial, J.-P.; Caillat, T. *Int. Mater. Rev.* **2003**, *48*, 45. (b) Hicks, L. D.; Harman, T. C.; Sun, X. S. Dresselhaus, M. S. *Phys. Rev. B* **1996**, *53*, R10493.
(2) Harman, T. C.; Taylor, P. J.; Walsh, M. P.; LaForge, B. E. *Science* **2002**, *297*, 2229−2232.
(3) Beyer, H.; Nurnus, J.; Bottner, H.; Lambrecht, A.; Roch, T.; Bauer, G. *Appl. Phys. Lett.* **2002**, *80*, 1216.
(4) Caylor, J. C.; Coonley, K.; Stuart, J.; Colpitts, T.; Venkatasubramanian, R. *Appl. Phys. Lett.* **2005**, *87*, 23105.
(5) Harman, T. C.; Walsh, M. P.; Laforge, B. E.; Turner, G. W. *J. Electron. Mater.* **2005**, *34*, L19.
(6) 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*, 818−821.
(7) (a) Androulakis, J.; Hsu, K. F.; Pcionek, R.; Kong, H.; Uher, C.; D'Angelo, J. J.; Downey, A.; Hogan, T.; Kanatzidis, M. G. *Adv. Mater.* **2006**, *18*, 1170. (b) Poudeu, P. F. P.; D'Angelo, J.; Downey; A. D. Short, J. L.; Hogan, T. P.; Kanatzidis, M. G. *Angew. Chem., Int. Ed.* **2006**, 45, 1.
(8) Kim, W.; Zide, J.; Gossard, A.; Klenov, D.; Stemmer, S.; Shakouri, A.; Majumdar, A. *Phys. Rev. Lett.* **2006**, *96*, 045901.
(9) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545.
(10) Grubbs, R. B. *J. Polym. Sci., Polym. Chem.* **2005**, *43*, 4323 and references therein.
(11) Ekimov, A. *J. Lumin.* **1996**, *70*, 1.
(12) Heremans, J. P.; Thrush, C. M.; Morelli, D. T. *J. Appl. Phys.* **2005**, *98*, 063703.
(13) Goswami, R.; Chattopadhyay, K. *Acta Mater.* **1996**, *44*, 2421.
(14) Singh, A.; Tsai, A. P. *Scr. Mater.* **2001**, *44*, 2005.
(15) Brus, L. E. *J. Phys. Chem.* **1986**, *90*, 2555.
(16) Henger, G. W.; Peretti, E. A. *J. Less-Common Met.* **1965**, *8*, 124.

10.1021/cm0612090 CCC: $33.50

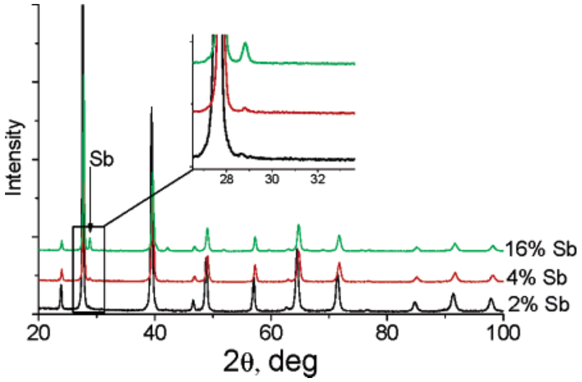

Figure 1. Powder X-ray diffraction pattern for the system PbTe-Sb (2, 4, 16%). The arrow indicates the additional [012] reflection of the Sb phase while the enlarged image shows the [012] Sb reflection is observed in all compositions.

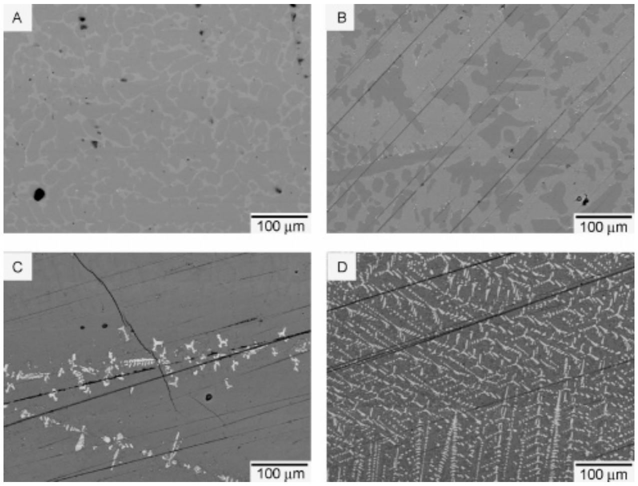

Figure 2. Scanning electron micrographs of (A) PbTe-Sb(2%), (B) PbTe-Sb(4%), (C) PbTe-Sb(8%), and (D) PbTe-Sb(16%). At Sb fractions of >4%, micrometer-sized precipitates (Sb concn > 95%) are observed. Black lines or dots are artifacts of polishing or holes in the surface of the material.

to micrometer-sized structures. Larger features are not expected to be important from the point of view of reducing thermal conductivity.

Figure 1 shows typical X-ray diffraction patterns for a series of PbTe-Sb nanocomposites. Indeed, with rising concentration of Sb, the diffraction pattern indicated additional peaks corresponding to bulk Sb. Each peak in the diffraction pattern was indexed according to those of PbTe and Sb. Energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) confirmed the presence of nanoparticles and the bulk composition in each of the composite materials. In each of the nanocomposite systems the only phases present were PbTe and inclusions of Sb, Bi, or InSb.

SEM of these samples revealed microscale islands of the minor phase within the matrix of PbTe. Backscattered electron imaging was used to detect compositional differences within the sample, and EDS was used to identify the local composition. In the case of the PbTe-Sb system, the number and size of the nanoparticles increased with concentration of Sb to a point where a network of bulk Sb within the PbTe matrix began to emerge (at >4%), Figure 2b. SEM observations indicated that the samples had two distinct types of regions. One with a smooth featureless composition and one with clearly visible islands of the guest phase. As TEM

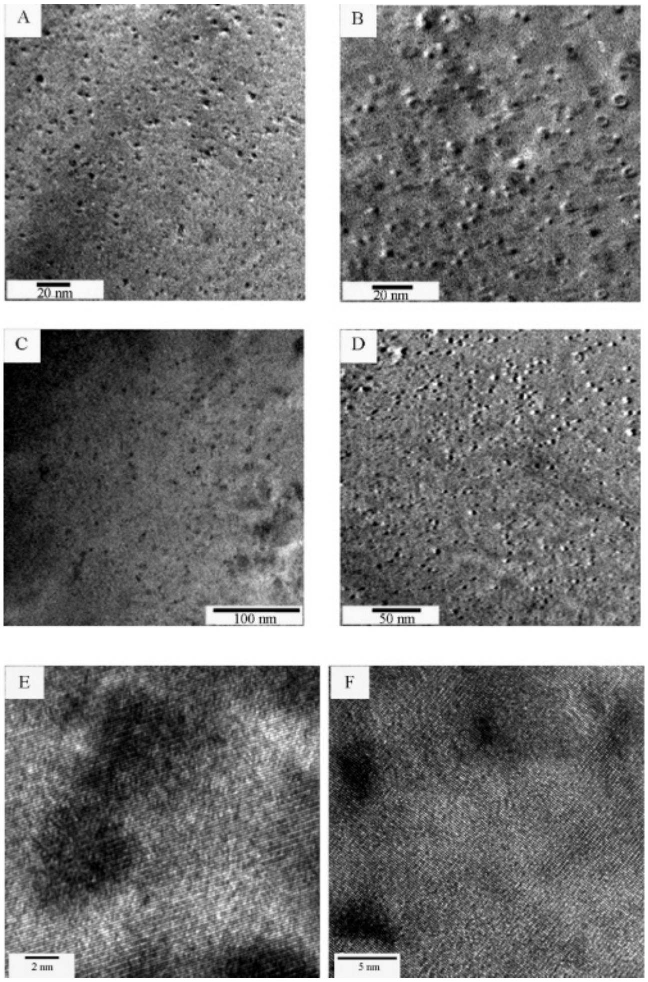

Figure 3. TEM images showing dispersed nanoparticles in samples of (A) PbTe-Sb(2%), (B) PbTe-Sb(4%), (C) PbTe-Sb(8%), and (D) PbTe-Sb(16%). Because the 8 and 16% samples contain distinct Sb regions the images shown in parts C and D are from the PbTe rich region. (E) High-resolution transmission electron micrograph showing several nanoprecipitates of Sb coherently embedded within the matrix of PbTe. (F) High-resolution micrograph of the PbTe-Bi(4%) system also showing embedded particles in PbTe.

examination shows (see above) both of these regions are nanostructured with the smooth featureless regions containing the smallest nanoparticles. Figure 2a-d shows SEM images for the series of PbTe − Sb (2, 4, 8, 16%). SEM images for the samples containing Bi and InSb showed similar behavior in which isolated nanocrystals were observed at lower concentration (e.g., < 4%) which began to agglomerate into larger micrometer-scale structures and even networks as the concentration increased. Therefore, it appears that exclusively nanostructured material is formed at concentrations lower than ∼4%. With larger concentrations the system seems to saturate, and further additions of the second phase accumulate as bulk component.

TEM revealed that the systems contain well-dispersed nanocrystals of Sb, Bi, and InSb, respectively. The frequency and size of these nanocrystals seem to depend on concentration where higher concentration favored on average larger nanocrystals. Figure 3a−d shows a series of TEM micrographs for the series of PbTe-Sb (2, 4, 8, 16%). The images were taken from the smooth PbTe-rich region of the samples where the presence of nanoparticles throughout the sample is readily visible. The 2−6 nm sized particles had a modest

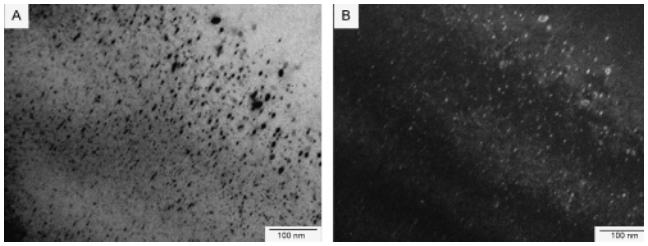

Figure 4. Corresponding bright (A) and dark field (B) images for a sample of PbTe-InSb(4%) clearly showing the embedded InSb phase as nanometer-sized inclusions within the PbTe matrix. Scale bars indicate 100 nm length.

size distribution and were evenly dispersed through the matrix. High-resolution TEM images of PbTe-Sb(4%) and PbTe-Bi(4%), Figure 3e−f, suggest that the nanoparticles are probably coherently imbedded in the matrix although more work is needed to verify this.

The PbTe-Bi and the PbTe-InSb systems were also clearly nanostructured. A bright and dark field image from the PbTe-InSb(4%) sample is shown in Figure 4. The dark field image clearly indicates that the second phase is truly incorporated into the PbTe matrix as nanocrystals. Investigation by TEM and SEM after annealing the composite below the melting point of the guest phase for several hundred hours showed little change in the nano- and microstructure of the samples. This indicates that the formation of the nanoparticles occurs via precipitation from the liquid and not through a nucleation growth mechanism in the solid state[17] brought about by annealing.

To probe the effect of nanostructuring on the thermal transport properties of PbTe the thermal conductivity was measured using the laser flash diffusivity−specific heat method (see Supporting Information). The lattice thermal conductivity was obtained by subtracting the electronic component[18] of the thermal conductivity from the total using the Wiedemann−Franz law.

The dependence of the lattice thermal conductivity of the PbTe-Sb system was studied as a function of Sb concentration. It is interesting to observe that among three samples with 2%, 4%, and 16% Sb concentration, respectively, it is the lowest concentration of 2% that exhibits the lowest room temperature thermal conductivity of ∼0.8 W/(m·K), as shown in Figure 5. This is the sample that has the lowest average nanoparticle size and lacks any micrometer-sized network domains of Sb. It is also interesting that the 16% sample which possesses an extensive network of micrometer-sized Sb phase exhibits the highest lattice thermal conductivity closer to that of PbTe itself. The high thermal conductivity of the 16% sample could be due to a percolation phenomenon. These results indicate that a very significant decrease in the thermal conductivity in these materials can be achieved provided the nanosized phase is chosen judiciously to cause increased phonon scattering at the nanoparticles−PbTe interface, and it is present at an optimum (not maximum) concentration. We have reason to believe that the optimum concentration of Sb is below 2%. Theoretical analysis suggests that nanoparticles scatter mid-to-long wavelength phonons, while atomic scale defects effectively scatter the Brillouin zone edge phonons.[8]

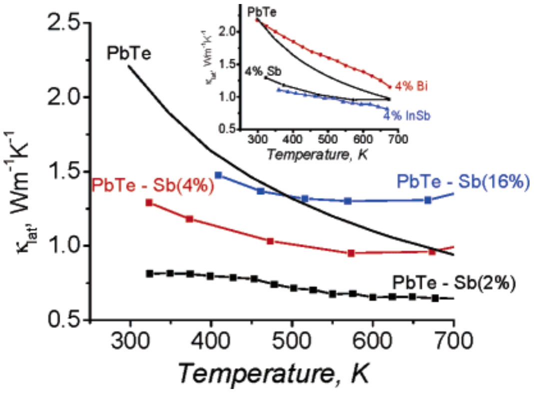

Figure 5. (A) Lattice thermal conductivity for 4% inclusion phase Sb, Bi, and InSb compared to pristine PbTe. (B) Lattice thermal conductivity for PbTe-Sb at 2%, 4%, and 16% concentrations.

A plot of lattice thermal conductivity in the 300−700 K range of samples with 4% Sb, Bi, and InSb, respectively, is shown in Figure 5 (inset). The InSb-containing samples, which have the largest atomic mass difference with the PbTe matrix, exhibit the lowest lattice thermal conductivity, ∼45% lower than pristine PbTe at room temperature.[19] The 4% Sb nanocrystals cuased a reduced thermal conductivity ∼ 27% relative to PbTe. The PbTe-Bi nanocomposites showed no reduction with a value very close to that of PbTe. This is attributed to the fact that the Bi nanophase and the PbTe matrix have very little acoustic mismatch given that Bi and Pb have nearly the same mass. The Sb and InSb nano-inclusions of the observed size distribution act as effective scatterers over a wide spectral range of phonons within the matrix.

The results reported here underscore the important role the nanoparticles play in enhancing phonon scattering in PbTe. If the observed reduction in lattice thermal conductivity were simply due to a disruption of the PbTe matrix caused by introducing into it a second phase, then we would expect either the opposite trend with nano-inclusion concentration (i.e., higher nanoparticle concentration causing greater reduction in the thermal conductivity) or a trend consistent with the law of mixtures[20] (i.e., the thermal conductivity would be an average of the two individual components). In the current case all three materials Sb, InSb, and Bi have considerably larger lattice thermal conductivity than PbTe and thus no reduction or even a slight increase in this property would be expected were they to be regarded as simple mixtures. The results reported here demonstrate that nanostructuring enhances acoustic phonon scattering in PbTe without the need to prepare solid solutions.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Porter, D. A. Easterling, K. E. *Phase Transformations in Metals and Alloys*; Chapman and Hall: New York, 1981.

(18) The electronic component was determined from electrical conductivity measurements performed from 300−700 K.

(19) Fedorov, V. I.; Machuev, V. I. *Sov. Phys. Solid State, USSR* **1969**, *11*, 1116−1120.

(20) Odolevski, V. J. *J. Tech. Phys.* **1951**, *21*, 667−677.