High thermoelectric performance of fullerene doped $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloys

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In this paper, we report our recent experimental findings on the enhancement of thermoelectric performance of C_{60} doped $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ bulk alloys. Incorporation of a small amount of C_{60} significantly reduces the crystalline particle size and leads to closely packed nanostructure, whilst slightly improve the electric conductivity in the measured temperature range. In addition, a minimum thermal conductivity of 0.4 W/(mK) at 358 K was observed, which is identified to be caused by the strong lattice phonon scattering at grain boundaries, yielding a high figure-of-merit $ZT = 1.47 \pm 0.07$ at 358 K. Our results demonstrate that the materials can be used for the development of advanced thermoelectrics.

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1. Introduction

Thermoelectricity is a direct conversion of thermal energy to electrical energy.(1) The limitation to its application is due to its low efficiency.(2) In the past five decades, it has been challenging to improve the dimensionless thermoelectric figure-of-merit (ZT). (3-4) Most of the commercial materials currently in use, such as p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$, have ZT around 1.(5) The ZT is defined as $S^2\sigma T/\kappa$, where S is the Seebeck coefficient; σ is the electrical conductivity; κ is the thermal conductivity; and T is the absolute temperature in Kelvin. $S^2\sigma$ is the power factor. The aforementioned parameters are interdependent and thus are difficult to be optimized separately without negatively impacting on the other.

In the last several years, studies have shown that a significant enhancement of ZT is possible by utilizing a nano-structuring approach to reduce the thermal conductivity by scattering phonons more effectively than electrons.(3, 6) It has also been reported that quantum dot superlattice (QDSL) structures offer the potential for better thermoelectric devices, due to three-dimensional quantum confinement, a potentially more favorable carrier scattering mechanism, and a much lower lattice thermal conductivity.(7) Very recently, it has been reported that SnSe single crystal shows very high ZT along the b-axis at 923 K.(8) However, it has been demonstrated to be difficult to practically use QDSL structures for large scale applications because of their delicate fabrication process and high cost. Traditional $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ -based materials still dominate, in particular near room temperature (323-523 K) applications.(9-13)

We hereby report the significant improvement of ZT by mechanically alloying C_{60} with $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$. The thermal conductivity of typical carbon allotropes, such as diamond and single crystal graphite (along ab plane), lie in the range between 10^1 - 10^3 W/(mK) above room temperature. In these single crystal phases, heat transport by lattice waves (phonons) is observed.(14-16) However, the thermal conductivity of compressed $\text{C}_{60}/\text{C}_{70}$ pallet considerably lie far below that of diamond and graphite, i.e. as low as 10^{-3} W/(mK).(17) Origin of this behavior is ascribed to a different mechanism for the heat transport, which is believed to be caused by vibrational motions of the rigid C_{60} molecules.(17) The exceptionally low thermal conductivity of $\text{C}_{60}/\text{C}_{70}$ compact and their chemically stable cage-like close structure offer the possibility to potentially improve ZT of existing materials. It has been reported that the addition of C_{60} could increase ZT of thermoelectric materials, however, the reported ZT still remain lower than 1 near room temperature.(18-21)

2. Experimental details

In this work, $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ powder was synthesized by mechanical alloying from elemental shots of Bi, Sb, and Te, using a ball milling method in Argon environment.(22) To make nanopowders, appropriate amounts of elemental chunks Bi (99.999%),

Sb (99.999%) and Te (99.999%), which are obtained from Sigma Aldrich, were weighted with the *mol* proportion of Bi:Sb:Te=1:3:6 and loaded into a ball mill jar with balls and then subjected to mechanical alloying for 40 hrs. The material of the ball and vial is harden tool steel, which can reasonably prevent impurities peeled from the balls and vial during the ball milling. After ball milling, the prepared nano powder was doped with 0.35 wt.% C60 and ball milled again for 1 hour for mechanical alloying. During sample preparation, two steps were implemented to diminish the effect of the oxidization of the nano powders. The first step was performing the ball milling for 40 hrs in a glove box in the environment of argon gas. The second step was performing the hydrogen reduction after the ball milling for the alloyed nano powders for 10 hrs at 653 K by using tube furnace. A cold isostatic pressing machine (MTI Corporation) with the dry pressing dies of inner diameters of 12.7 and 19.1 mm were used to cold press the prepared nano powders to obtain 1mm and 3mm thick bulk disk samples.

The bulk samples were loaded into a hot-press cell and then placed in a furnace for heat treatment and annealing in hydrogen environment. In order to obtain good crystallinity of the samples, a low heating rate with 2 K/min was set for three-step continuous annealing at 553 K for 2h, 603 K for 2h and 653 K for 5h, respectively. Finally, bar-shape samples were cut from the fabricated sample with 19.1 mm diameter and burnished to a size of about $3\times4\times15\text{ mm}^3$ for the measurements of thermoelectric properties, using commercial ZEM-3 equipment (Ulvac-Riko, Inc., Japan) from 323-523 K. The thermal conductivity was determined by using a Laserflash 5000 thermal properties analyzer (Anter Corporation, USA). All sample preparation and material characterization experiments in the paper were repeated several times to verify the reliability and repeatability.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) pattern, the data of Differential Scanning Calorimetry (DSC), Field Emission Scanning Electron Microscopy (FE-SEM) and Transmission Electron Microscopy (TEM) images of the materials. The XRD patterns in Fig. 1(a) confirm that the material is in a single phase, which is well matched with $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ (PDF 49-1713, Jade, Materials Data Inc.).(23) This is also verified by the single endothermic peak around 878 K from in the DSC data (Fig. 1(b)) that agrees well with the melting point of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$. The C60 doped sample is based on the undoped material and they have the same crystalline phase, except some doping effect that will be discussed below. Several peaks, such as (110), (205) and (125), slightly shift to low angle and show changes of intensity after C60 doping. A plausible explanation is that the increase of grain boundaries of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ after C60 doping results in peak shift, which will be further discussed in the following. The broadened XRD peaks suggest the materials contain small particles; however, the mechanically alloyed

materials have a large range of particle size distribution as shown in the SEM images of Fig. 1(c) and (d), and the data of the XRD peak width may not be sufficient for the determination of the particle size in the sample, due to the complex particle size distributions in the materials.

SEM images in Fig. 1(c) verify that the particles have the sizes ranging from a few hundred nanometers up to 4 μm and show clear crystallinity and random orientation in the undoped $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloy sample. This indicates that through the cold press and heat treatment, the mechanically assisted reaction and high temperature treatment allow the growth of alloy crystals based on elemental shots Bi, Sb and Te. These structures could be the reason that alloyed compounds have high electrical conductivity, but low thermal conductivity.(24-25) After doping with C_{60} , the particle sizes in the sample have a large range of distribution as shown in the SEM image of Fig. 1(d). Some small particles in the alloy powder were observed, in addition to some larger ones (see Fig. 1(d)). In addition, for the undoped sample, crystalline particles have sharp edges (see Fig. 1(c)); for the C_{60} doped sample, the crystalline particles are more rounded (see Fig. 1(d)). Some small particles, which embed between alloy crystalline particles, can reach to about 50 nm. The TEM image of C_{60} doped sample in Fig. 1 (e) shows the fine structure of the material at nm scale. Small crystalline particles at about 50 to 200 nm as well as large number of grain boundaries can be seen from the TEM image. The morphology of the alloy sample with C_{60} doping as shown in Fig. 1(d) is significantly different from those without C_{60} (Fig. 1(c)), that correlate with their thermoelectric properties as discussed in the following sections. The chemical stability of C_{60} inhibits the crystalline growth and reduces the size of micro-particles.(9) Gothard et al. reported that C_{60} can actively prompt the microstructural refinement of bismuth telluride alloys even when present in small quantities and the resulting materials are highly crystalline, which are in satisfactory agreement with our results.(21) This demonstrates that C_{60} can be used as an effective structure refinement agent.

To obtain excellent electric conductivity in the material, extreme care was taken to prevent oxidation in the fabrication and measurement processes. The electric conductivity of the sample doped with C_{60} is similar to or slightly higher than that of undoped sample, depending on the temperature (Fig. 2(a)). Although the incorporation of C_{60} is believed to decrease the electric conductivity since the crystalline particle size is significantly reduced, the formation of a much more compact structure with considerably clean boundary (Fig. 1(d)) overcomes this effect and leads to a slight enhancement of electric conductivity. This behavior is similar to published report that the electrical properties of hot pressed compacts of heavily doped alloys are unaffected by grain boundary scattering effects.(26) In our case, the significant increase in the number of grain boundaries does not deteriorate the electric properties, rather it increases the degree of phonon scattering.(6, 21)

The Seebeck coefficient and power factor of the doped sample show quite similar trend in temperature dependence as the

undoped sample, however, they are much enhanced in comparison with that of undoped sample between 323 and 523 K, with a peak at 358 K (Fig. 2(b) and (c)). This behavior is very desirable for material finding applications near room temperature. It is reported that zero-dimensional C_{60} nanoparticles allow quantum confinement during carrier transport, and thus improves the Seebeck coefficient.⁽⁶⁾ In addition, considering the Seebeck coefficient is the energy difference between the average energy of moving electrons and the Fermi level.⁽²⁷⁾ Another possible reason could be that the doping of C_{60} in the $Bi_{0.5}Sb_{1.5}Te_3$ alloy is capable of pushing the Fermi level away from the valence band, and this leads to a further enhancement of Seebeck coefficient.⁽²⁸⁻²⁹⁾

High ZT requires considerable reduction of thermal conductivity while maintaining good electric conductivity. We found that the thermal conductivity of C_{60} doped sample is significantly lower (reduced by one half in the measured temperature range) than that of undoped one (Fig. 2(d)). The minimum thermal conductivity of the doped sample is as low as 0.4 W/(mK) at 358 K.

It has been conceived that the micro/nano size grain interfaces/boundaries scatter phonon more effectively than electrons, and are responsible for the significant decrease in thermal conductivity.⁽³⁰⁻³¹⁾ As mentioned above, the C_{60} doped sample consists of compact nanosize crystals. The reason for the low thermal conductivity is believed to result from the large amount of nanosize grain boundaries, at which effective phonon scattering appears to occur in the closely packed nanostructure.⁽³²⁾ Although it has been observed that the presence of heavy point defects in pressure-sintered alloys would greatly reduce the thermal conductivity,⁽³³⁾ this effect appears to be unimportant in our samples, considering the excellent electric conductivity of the sample and the compact nanostructure as confirmed by XRD and SEM. Note that most of the published data on the minimum thermal conductivity of $Bi_{0.5}Sb_{1.5}Te_3$ -based materials are found in the range of 0.4-0.9 W/(mK) between 300 and 380 K,^(19, 23, 25, 34-38) which are quite similar to ours 0.4 W/(mK) at 358 K. This suggests that C_{60} by itself does not noticeably contribute to the thermal conductivity due to its small concentration in the sample (molecular ratio: $C_{60}/Bi_{0.5}Sb_{1.5}Te_3$ is 1/305), although C_{60} compact pallet shows extremely low thermal conductivity near room temperature.⁽¹⁷⁾

The considerable decrease of thermal conductivity leads to significantly enhanced ZT . Between 323 and 523 K, the ZT of doped sample is 1.06 ± 0.04 at the starting temperatures of our measurements and rapidly increases to a peak value 1.47 ± 0.07 at 358 K, which lies considerably above that of undoped one (Fig. 3). Although the thermoelectric performance of the undoped sample may not be the best among the reported data in literature, but the improvement of the thermoelectric properties of the C_{60} doped sample, in comparison with the undoped one, is quite significant. The considerable improvement

of ZT indicates that the C_{60} doped materials have the potential as high performance thermoelectric materials, in particular for near room temperature applications. On the basis of thermal conductivity measurements, we conclude that the significant enhancement of ZT is predominantly as a result of the closely packed nanosized crystalline structure, which is capable of scattering mid-to-long wavelength phonons at grain boundaries more effectively.(32, 39) Our results demonstrate that mechanical doping of C_{60} in the sample is more cost effective, and it can be potentially applied to other thermoelectric materials for improving ZT .

4. Conclusions

In conclusion, we report the enhanced thermoelectric performance of C_{60} doped $Bi_{0.5}Sb_{1.5}Te_3$ alloys. The C_{60} doped material consists of highly crystalline and closely packed grain particles, which are responsible for the significant improvement of phonon scattering at grain boundaries leading to the considerably high $ZT = 1.47 \pm 0.07$ at 358 K. The significantly enhanced thermoelectric properties of the material enable the potential development of high performance thermoelectric materials for near room temperature applications.

Acknowledgments

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Fig. 1

Fig. 1 (a) XRD of undoped and 0.35 wt.% C_{60} doped $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$; (b) DSC of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ powder sample; SEM images of (c) undoped and (d) 0.35 wt.% C_{60} doped $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$; (e) TEM image of 0.35 wt.% C_{60} doped $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$.

Fig. 2

Fig. 2 (a) Electric conductivity, (b) Seebeck coefficient, (c) power factor, and (d) thermal conductivity of undoped and 0.35 wt.% C₆₀ doped Bi_{0.5}Sb_{1.5}Te₃.

Fig. 3 Figure-of-merit ZT of undoped and 0.35 wt.% C_{60} doped $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$.