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High thermoelectric performance of fullerene doped $Bi_{0.5}Sb_{1.5}Te_3$ alloys

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ABSTRACT

In this paper, we report our recent experimental findings on the enhancement of thermoelectric performance of C_{60} doped $Bi_{0.5}Sb_{1.5}Te_3$ 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.

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 $Bi_{0.5}Sb_{1.5}Te_3$, 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 $Bi_xSb_{2-x}Te_3$-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 $Bi_{0.5}Sb_{1.5}Te_3$. The thermal conductivity of typical carbon allotropes, such as diamond and single crystal graphite (along ab plane), lie in the range between 10^1 and 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 C_{60}/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 C_{60}/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].

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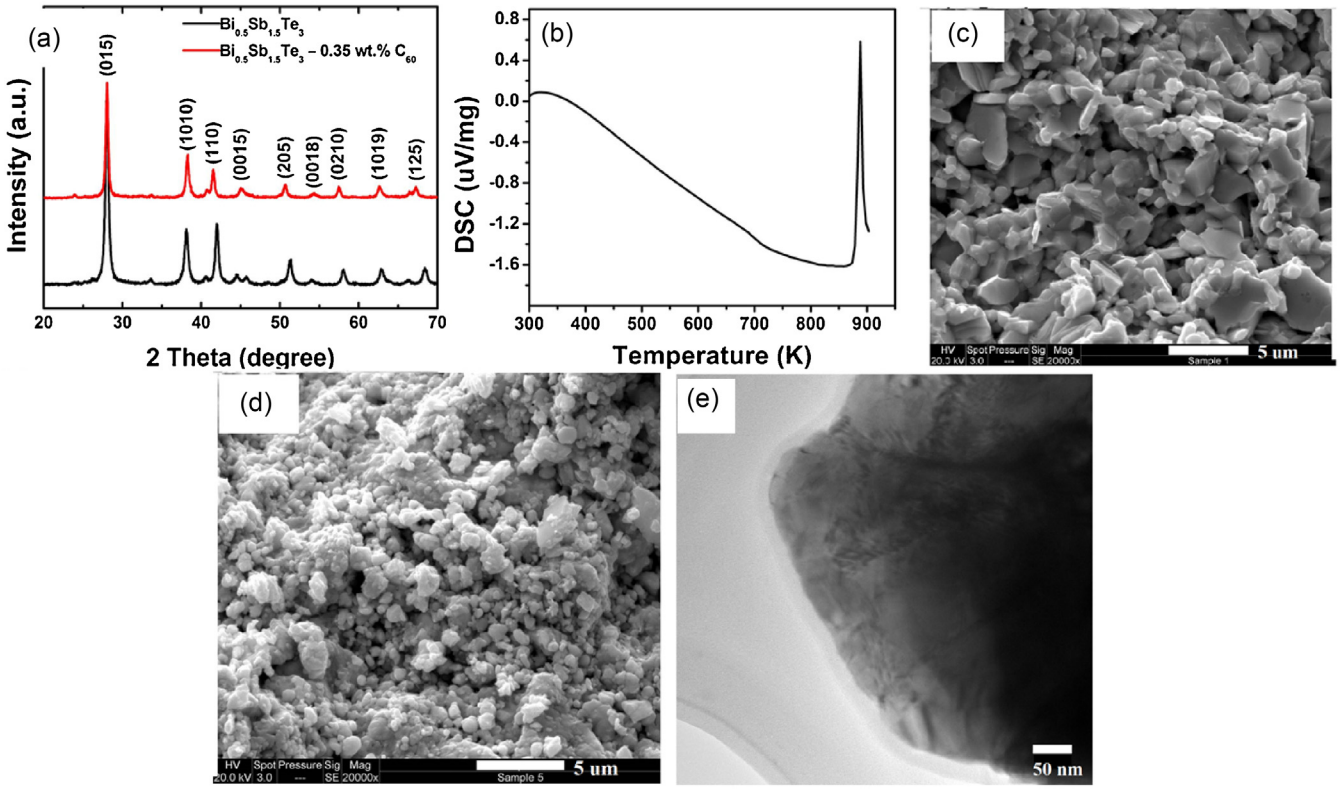

Fig. 1. (a) XRD of undoped and 0.35 wt.% C_{60} doped $Bi_{0.5}Sb_{1.5}Te_3$; (b) DSC of $Bi_{0.5}Sb_{1.5}Te_3$ powder sample; SEM images of (c) undoped and (d) 0.35 wt.% C_{60} doped $Bi_{0.5}Sb_{1.5}Te_3$; (e) TEM image of 0.35 wt.% C_{60} doped $Bi_{0.5}Sb_{1.5}Te_3$.

2. Experimental details

In this work, $Bi_{0.5}Sb_{1.5}Te_3$ 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 h. 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 h 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 h 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 h 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 1 mm and 3 mm 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 2 h, 603 K for 2 h and 653 K for 5 h, respectively. Finally, bar-shape samples were cut from the fabricated sample with 19.1 mm diameter and burnished to a size of about 3 mm × 4 mm × 15 mm for the measurements of thermoelectric properties, using commercial ZEM-3 equipment (Ulvac-Riko, Inc., Japan) from 323 to 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 $Bi_{0.5}Sb_{1.5}Te_3$ (PDF 49-1713, Jade, Materials Data Inc.).[23] This is also verified by the single endothermic peak around 878 K from the DSC data (Fig. 1(b)) that agrees well with the melting point of $Bi_{0.5}Sb_{1.5}Te_3$. 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 (1 1 0), (2 0 5) and (1 2 5), slightly shift to low angle and show changes of intensity after C60 doping. A plausible explanation is that the increase of grain boundaries of $Bi_{0.5}Sb_{1.5}Te_3$ 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 $Bi_{0.5}Sb_{1.5}Te_3$ alloy sample. This indicates that through the cold