



Full length article

Enhancement of thermoelectric properties in liquid-phase sintered Te-excess bismuth antimony tellurides prepared by hot-press sintering

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ABSTRACT

Various approaches have been applied to improve the thermoelectric performance of bismuth antimony telluride based materials. Here, we prepare the bulk pellets of nominal Te-excess p-type $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_{3+x}$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) samples by a high-temperature solid state reaction followed by a hot-press sintering, and perform structural investigations including X-ray diffraction measurements and a high-resolution transmission electron microscopy analysis as well as a thermoelectric property characterization including electrical resistivity, Seebeck coefficient, thermal conductivity, and Hall effect. We demonstrate that a liquid-phase sintering of Te-excess samples can provide a preferential orientation of a bulk pellet along a measured direction, an improvement in hole carrier concentration, and sub-micron sized Sb precipitates acting as a phonon scattering center, resulting in an enhancement in power factor and a reduction in lattice thermal conductivity compared to the pristine $x = 0$ sample. Consequently, the hot-pressed bulk pellet of the nominal $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_{3.4}$ composition exhibits an impressively high ZT of 1.41 at 417 K along the vertical direction, which is about 31 % enhancement in ZT compared to the pristine $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ sample. The significantly improved values of practical thermoelectric properties such as engineering (ZT)_{eng}, maximum efficiency η_{max} , and output power density P_d indicates a practical applicability in thermoelectric energy harvesting technologies.

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1. Introduction

Air pollution, ozone layer depletion, global warming, and worldwide energy shortage are critical environmental and energy problems caused by a huge combustion of fossil fuels. To overcome these problems, it is necessary to implement an inexpensive, highly reliable, long lasting, and eco-friendly energy source to cope with a future energy crisis. A thermoelectric (TE) device is one of alternative energy-generation devices, converting a waste heat into electricity and vice versa. The performance of TE materials is often characterized according to a dimensionless the figure of merit ZT ,

$$ZT = \frac{S^2}{\rho\kappa} T \quad (1)$$

where S , T , ρ , and κ is Seebeck coefficient, absolute temperature, electrical resistivity, and thermal conductivity, respectively. The numerator term in Eq. (1) is expressed as power factor $PF (= S^2/\rho)$ [1].

New research strategies have been applied to enhance the ZT value of both bulk and thin-film TE materials by various research groups [2–4]. Lead antimony silver telluride (LAST) and skutterudites have been well known to be new bulk materials with a quite improved ZT value, but it is difficult to use them in large-scale energy-conversion applications because of a high production cost and poor heat transfer [5]. Up to date, bismuth telluride and its alloys remain to be the best TE material with $ZT > 1$ near room temperature.

Both bismuth telluride (Bi_2Te_3) and antimony telluride (Sb_2Te_3) adopt the rhombohedral crystal structure with $R\bar{3}m$ space group and they consist of stacked quintuple layers (Te-Bi/Sb-Te-Bi/Sb-Te)

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along its *c*-axis. The adjacent quintuple layers are bonded to each other by a weak van der Waals force and the ratio of lattice parameter *c* to *a* is ~7, indicative of a highly anisotropic crystal structure. Thus, Bi₂Te₃-based single crystals easily become cleaved along a basal plane having a weak van der Waals bonding so that their large-scale TE applications are quite inhibited because of no mechanical robustness of the single crystals [6,7]. To obtain Bi₂Te₃-based material with a high mechanical strength suitable for large-scale applications, various processing techniques including hot pressing [8], hot extrusion [9], pulverized & intermixed sintering [10], and spark plasma sintering have been utilized to prepare polycrystalline Bi₂Te₃-based materials. Compared to other techniques, the hot pressing is simple, widely used, and cost-effective so that the hot pressing enables Bi₂Te₃-based materials to show good mechanical properties with no significant loss of orientation texture.

It has been theoretically reported that significant enhancement in *S*, charge carrier mobility, and electrical conductivity can be achieved in low dimensional TE materials because of the increase of density of states near Fermi energy. The κ can be also reduced by a boundary scattering of phonons at the barrier-well interface of low dimensional TE materials [11–14]. However, the fabrication of low dimensional TE materials are expensive and time-consuming with a low throughput. It has been reported that nanostructuring can enhance a phonon scattering and thus effectively reduce the κ in bulk TE materials. The enhanced *ZT* of 1.56 can be obtained in BiSbTe alloys prepared by a melt-spinning (MS) technique because of the nanostructuring [15]. Also, *ZT* of 1.47 can be achieved for BiSbTe made by using ball-milling and hot-pressing method [3]. Recently, an impressively high *ZT* of 1.86 at 320 K can be reached by a simple liquid-phase compaction process. For the liquid-phase compaction process, the liquid of excess Te between Bi_{0.5}Sb_{1.5}Te₃ grains flows out during the spark plasma sintering process (SPS), leading to the formation of dislocation arrays embedded in grain boundaries and thus a considerable reduction in the lattice thermal conductivity (κ_{lat}) [16].

In this work, we prepare a series of nominal p-type polycrystalline Te-excess Bi_{0.4}Sb_{1.6}Te_{3+x} (*x* = 0, 0.2, 0.4, 0.6, 0.8, 1) samples by a high-temperature solid state reaction followed by a hot-press sintering. TE properties are measured in both horizontal and vertical direction of a hot-press sintered bulk pellet. Very impressively, the *x* = 0.4 sample exhibits the highest *ZT* of 1.41 at 417 K along the vertical direction of the hot-press sintered bulk pellet, which is 31% improvement in *ZT* compared to the *x* = 0 sample. We demonstrate that enhanced *ZT* values in liquid-phase sintered Te-excess samples should be attributed to both the reduction in κ_{lat} by Sb precipitates and the increase in hole carrier concentration through the compensation of antisite Bi/Sb_{Te} defects by Te-excess. Furthermore, we estimate an engineering power factor *PF*_{eng}, *ZT*_{eng}, TE efficiency, and output power density with various temperature gradients to simulate the TE performance of TE modules prepared by our samples.

2. Experimental detail

The nominal Bi_{0.4}Sb_{1.6}Te_{3+x} (*x* = 0, 0.2, 0.4, 0.6, 0.8, 1) polycrystalline samples were prepared by a high-temperature solid state reaction using a stoichiometric mixture of elemental Sb (99.999%), Bi (99.999%), and Te (99.999%). A quartz tube, in which the elements were loaded, was sealed under a high vacuum (10⁻⁵ Torr) and then the tube was heated to 923 K for 24 h followed by water quenching. The quenched ingot taken out from the tube was pulverized into the powders, the powders were put into a graphite die for a hot-press sintering, and then the hot-press sintering was performed at 753 K under the pressure of 50 MPa. All TE

properties were measured along both the horizontal and vertical direction of hot-press sintered bulk pellets.

The x-ray diffraction (XRD) measurement were performed using Cu K α radiation (D8 Advance, Bruker) and the electrical resistivity and Seebeck coefficient were simultaneously measured using a thermoelectric measurement system (ZEM-3, ULVAC, Japan) under a helium atmosphere in the temperature range of 300 K–450 K. The thermal conductivity was calculated by the relation $\kappa = dC_p\lambda$, where *d* is the density of sample, *C_p* is the specific heat and λ is the thermal diffusivity. The thermal diffusivity λ was measured using a laser flash method (LFA-447, NETZSCH, Germany). The Hall carrier concentration were measured using the physical property measurement system (PPMS, Quantum Design, USA).

We observed nano-scale morphologies using Transmission Electron Microscopy (TEM) images. In order to get clean surfaces, we performed ion etching of the surfaces by Nova 600 nanolab Focused Ion Beam (FIB) using 5–30 kV. TEM images (High Resolution images/STEM/ED pattern) were collected using a JEOL 2100F at 200 kV. Energy dispersive x-ray spectrometer (EDS) analysis were obtained using Oxford Instruments (INCA platform) detector equipped on JEOL 2100F.

3. Results and discussion

Fig. 1a shows X-ray diffraction (XRD) patterns of the powder samples of Bi_{0.4}Sb_{1.6}Te_{3+x} before hot-press sintering. Most of diffraction peaks can be assigned to the rhombohedral structure of Bi_{0.4}Sb_{1.6}Te₃ [17] and additional peaks from elemental Te are observed as marked, indicative of the presence of excess Te before hot-press sintering. We fabricated bulk pellets by hot-press sintering Te-excess Bi_{0.4}Sb_{1.6}Te_{3+x} (*x* = 0, 0.2, 0.4, 0.6, 0.8, 1) samples at 753 K under 50 MPa and thus the liquid of excess Te can be easily expelled out. The XRD measurements are performed on both horizontal and vertical planes of hot-press sintered bulk pellets (Fig. 1b and c) and there exist no extra peaks from elemental Te. The peak intensity of (110) on vertical planes is higher than that on horizontal planes, indicating that (110) planes is preferentially oriented on vertical planes. Furthermore, a remarkably enhanced peak intensity of (00l) on horizontal planes is observed compared to that on vertical planes, which should be attributed to a plate morphology of powders caused by a layered crystal structure of Bi₂Te₃-based materials [18]. It has been well known that the preferential orientation in Bi₂Te₃-based materials can affect their electrical transport properties so that the ρ is generally lower along a horizontal direction than along a vertical direction of bulk pellets and the *S* shows an opposite trend with the ρ [19–21].

Fig. 2a shows a high-resolution transmission electron microscopy (HRTEM) image of Bi_{0.4}Sb_{1.6}Te₃, showing a clear lattice fringe of (001) planes from the rhombohedral structure of Bi_{0.4}Sb_{1.6}Te₃. An electron diffraction (ED) pattern is shown in inset of Fig. 2a, indicative a typical ED pattern of Bi₂Te₃-based materials in the zone axis of [0–10]. However, we can clearly observe a precipitate in the Bi_{0.4}Sb_{1.6}Te₃ matrix for the Bi_{0.4}Sb_{1.6}Te_{3+x} (*x* = 0.4) sample in a bright filed image of HRTEM (top inset of Fig. 2b) and the corresponding selected area ED (SAED) pattern of a red square box in Fig. 2b indicates a sub-micron sized Sb precipitate in the matrix (the bottom inset of Fig. 2b). Furthermore, a dark field image of HRTEM in the top inset of Fig. 2c and a EDS line scan across a precipitate (yellow arrow) in the bottom inset of Fig. 2c reveal that there is an interface between a Bi_{0.4}Sb_{1.6}Te₃ matrix and the precipitate being determined to have more Sb and less Te/Bi than the matrix. A high angle annular dark field (HAADF) image (HAADF) coupled with TEM-EDS elemental maps confirms that there exists the Sb precipitate having no Bi and Te in the matrix (Fig. 2d–g). We believe that the Sb precipitate could influence the electrical and

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