J Materiomics xxx (2018) 1–7

Contents lists available at ScienceDirect

J Materiomics

journal homepage: www.journals.elsevier.com/journal-of-materiomics/

# Enhanced thermoelectric performance of n-type bismuth-telluride-based alloys via In alloying and hot deformation for mid-temperature power generation

Feng Li, Renshuang Zhai, Yehao Wu, Zhaojun Xu, Xinbing Zhao, Tiejun Zhu*

*State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, China*

ARTICLE INFO

*Article history:*
Received 14 April 2018
Received in revised form
16 May 2018
Accepted 23 May 2018
Available online xxx

*Keywords:*
Bismuth telluride
Thermoelectric materials
Hot deformation
Alloying

ABSTRACT

Bismuth telluride-based alloys are the most widely used commercial thermoelectric (TE) material for room temperature refrigeration. Here, we successfully shift up the optimum figure of merit of n-type bismuth-telluride-based TE materials for mid-temperature power generation. $SbI_3$ doping is used to regulate the carrier concentration and Indium alloying to increase the bandgap, suppressing the detrimental bipolar conduction in the mid-temperature range. The lattice thermal conductivity is significantly reduced due to the multiscale microstructures induced via hot deformation. As a result, a peak $zT$ of ~1.1 was attained at 625 K for $Bi_{1.85}In_{0.15}Te_2Se$ + 0.25 wt% $SbI_3$ alloy after hot deformation, showing a great application prospect of this alloy in mid-temperature TE power generation.



## 1. Introduction

Thermoelectric (TE) materials, which are capable of directly inter-converting heat and electricity, have received widespread attention due to the growing energy needs of fossil fuels over the past two decades [1]. The conversion efficiency of a TE device strongly depends on the dimensionless figure of merit $zT = \alpha^2\sigma T/\kappa$, where $\alpha$ is the Seebeck coefficient, $\sigma$ and $\kappa$ are the electrical conductivity and the total thermal conductivity (including the lattice contribution $\kappa_L$ and the carrier contribution $\kappa_e$) respectively, and $T$ is the operating temperature [2,3]. Recently, band engineering [4–6] and phonon engineering [7,8] have been used separately to optimize the electronic and the thermal transport properties in order to maximize the figure of merit, including band convergence, hierarchical phonon scattering, nanostructuring and introducing point defects.

For power generation, some good TE materials have exhibited excellent TE performance with the optimal operating temperatures over 700 K, such as PbTe [9,10], half-Heusler alloys [11,12], and filled skutterudes [13,14]. However, the promising TE materials are rarely reported for the waste heat harvesting in the temperature range of 400–700 K. Therefore, developing high-efficiency TE materials operating in the range 400–700 K is significant in practice.

In the past decades, zone-melted (ZM) bismuth telluride ($Bi_2Te_3$) based alloys have become the best commercial TE materials. ZM $Bi_2Te_3$-based alloys are mainly used in the solid-state refrigeration because of high $zT$ values of ~1 near room temperature [15]. With the increasing energy consumption, $Bi_2Te_3$ based alloys have drawn increasing interest for power generation applications below 700 K. P-type $Bi_2Te_3$-based alloys for this purpose have exhibited high TE performance. For example, Hu et al. obtained a high $zT$ of ~1.3 at 380 K for p-type polycrystalline $Bi_{0.3}Sb_{1.7}Te_3$ alloys [16] and a maximum $zT$ of ~0.92 at 710 K for p-type $Ag_{0.01}Sb_{1.85}In_{0.15}Te_3$ alloy [17]. Xu et al. successfully upshifted the service temperature of p-type $(Bi,Sb)_2Te_3$, and a peak value of $zT$ of ~1.4 was attained at 500 K in $Bi_{0.3}Sb_{1.625}In_{0.075}Te_3$ [18]. As for n-type $Bi_2Te_3$-based alloys for power generation, Pan et al. fabricated textured n-type $Bi_2(Te,Se)_3$ materials with a maximum $zT$ exceeding 1.1 at 473 K [19]; Wang et al. reported a peak $zT$ value of ~0.86 at 600 K in n-type zone melted $Bi_2Te_{1.5}Se_{1.5}$ [20]; Meanwhile, Liu et al. achieved a high $zT$ of ~0.8 at 573 K in n-type $Bi_2Te_2S$ prepared by ball-milling and hot-pressing [21]. However, the current n-type performance cannot match the p-type counterparts in the range of 500–700 K. Therefore, this work is focused on high performance n-type $Bi_2Te_3$-based alloys for power generation at higher temperatures.

* Corresponding author.
*E-mail address:* zhutj@zju.edu.cn (T. Zhu).
Peer review under responsibility of The Chinese Ceramic Society.

https://doi.org/10.1016/j.jmat.2018.05.008

Owing to the intrinsically small band gap $E_g$ ~0.13 eV [22,23], $Bi_2Te_3$-based alloys show a significant degradation in TE performance when applied to mid-temperature power generation. On account of bipolar conduction, the excitation of minority carriers not only decreases the Seebeck coefficient but also increases the thermal conductivity, which result in a decreased $zT$ [24]. Therefore, suppressing bipolar conduction of $Bi_2Te_3$ based alloys is crucial, and an apparent solution is to increase the band gap. Fig. 1 shows the composition dependence of band gap for n-type $Bi_2Te_{3-x}Se_x$. The previous results reach a consensus that the $E_g$ reaches a maximum at $x = 1$ ($Bi_2Te_2Se$) whereas they disagree at $x = 3$ ($Bi_2Se_3$) [26–28]. Therefore, we choose $Bi_2Te_2Se$ as the matrix composition in this work.

$Bi_2Te_2Se$ ingots prepared by zone-melting exhibit very low carrier concentrations because the concentration of antisite defects near this composition is close to that of anion vacancy [28–30]. For the purpose of increasing carrier concentration, $SbI_3$ is generally used as a donor dopant in the n-type $Bi_2(Te,Se)_3$ alloys [31]. In our previous work, Xu et al. demonstrated that the band gap could be broadened by In doping in p-type $(Bi,Sb)_2Te_3$ and thus suppressed the detrimental bipolar effect [18]. Besides, hot deformation (HD) processing could create multiscale phonon scattering centers to optimize the thermal conductivity [8].

Thus, in this work we fabricate n-type $Bi_2Te_2Se$ alloys by $SbI_3$ doping and In alloying, combining with zone-melting and HD techniques. $SbI_3$ doping can effectively regulate the carrier concentration via providing extra electrons, In alloying inhibits the intrinsic excitation by increasing the band gap of $Bi_2Te_2Se$, and HD processing reduces the lattice thermal conductivity. As a result, a peak $zT$ of ~1.1 at 625 K was obtained, with an average $zT_{av}$ of ~1.03 between 500 and 700 K in $Bi_{1.85}In_{0.15}Te_2Se$ + 0.25 wt% $SbI_3$ fabricated by zone-melting and HD procedure, demonstrating its great potential for mid-temperature (500–700 K) power generation.

## 2. Experimental

### 2.1. Preparation

Commercial high-purity elemental chunks of 99.999% Bi, 99.999% Te, 99.999% Se, 99.99% In and 99.999% $SbI_3$ were used as raw materials. Appropriate quantities of materials were weighed according to stoichiometric $Bi_2Te_2Se$ + $x$ wt% $SbI_3$ ($x = 0.15$, 0.20, 0.25, 0.30), mixed and sealed into a quartz tube at $10^{-3}$ Pa. The mixtures were then melted in a rocking furnace at 1023 K for 10 h. After melting, the ingots were zone-melted at 973 K with a temperature gradient of 30 K $cm^{-1}$ and a growth rate of 20 mm $h^{-1}$. The resulting ingots with $SbI_3$ content $x$ were named ZM-$SbI_3$-$x$, and all thermoelectric properties were tested along the growth direction of the ingot unless otherwise noted. Of these ZM samples, 0.25 wt% $SbI_3$ showed the best TE performance with a peak $zT$ of ~0.65 at 575 K as presented in Fig. S1, and other TE properties are shown in Figs. S1–S2. Room temperature physical parameters of zone melted sample of $Bi_2Te_2Se$ + 0.25 wt% $SbI_3$ are displayed in Table S1. It is obvious that the band gap needs to be further increased and the high lattice thermal conductivity needs to be reduced. Based on these results, then we prepared ZM $Bi_{2-x}In_xTe_2Se$ + 0.25 wt% $SbI_3$ ($x = 0$, 0.005, 0.01, 0.015, 0.02) ingots, and these ingots were named ZM-In$x$.

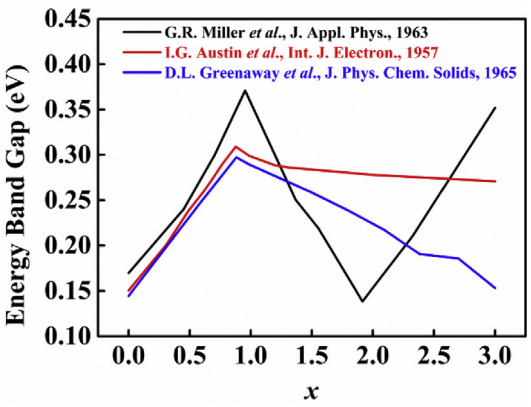


**Fig. 1.** Previous study on band gap of $Bi_2Te_{3-x}Se_x$ [25–27].

HD processing was performed subsequently. Rods with a diameter of 16 mm and a height of 20 mm were cut along the growth direction of the as-grown ZM-In$x$ ingots, and then HD processing was performed in a graphite die of ϕ 20 mm at 823 K for 30 min under the pressure of 80 MPa. More details can be found elsewhere [32–34]. Finally, the disk-shaped hot deformed samples of 20 mm (HD-In$x$) were obtained. All the samples have similar relative densities of ~96% and all their TE properties were tested along the pressure direction.

### 2.2. Characterization

The phase identification of all the samples was investigated by X-ray diffraction on a Rigaku D/MAX-2550 P diffractometer. The actual chemical compositions were characterized by electron probe microanalysis (EPMA) on JEOL JXA-8100 with a wave dispersive spectrometer (WDS). Transmission electron microscope (TEM) observation was performed on JEOL 2100 F and FEI TF30 microscopes and the thin TEM specimens were prepared by the conventional standard methods.

### 2.3. Thermoelectric measurements

The electrical conductivity $\sigma$ and the Seebeck coefficient $\alpha$ were simultaneously measured on a commercial Linseiss LSR-3 system. The thermal diffusivity $D$ and the specific heat capacity $C_p$ were tested on A Netzsch LFA 457 laser flash apparatus with a Pyroceram standard. The thermal conductivity is then calculated according to the relation $\kappa = D\rho C_p$, where $\rho$ is estimated by the usual dimension and weight measurement procedures. The Hall coefficient $R_H$ was measured at 300 K using a four-probe configuration on a Quantum Design PPMS-9T instrument. The carrier concentration $n_H$ and the carrier mobility $\mu_H$ were computed by $n_H = 1/eR_H$ and $\mu_H = \sigma R_H$, respectively.

## 3. Results and discussion

### 3.1. Electrical transport properties

No secondary phases were observed in the ZM $Bi_{2-x}In_xTe_2Se$ +0.25 wt% $SbI_3$ bulk samples with x = 0–0.20, as indicated in the XRD patterns (Fig. 2). During the preparation of n-type $Bi_2Te_2Se$ zone melted ingot, Se and Te atoms tend to be more deficient than Bi due to their lower boiling points (Table S2), resulting in the anion vacancies $V_{Te}^{\bullet\bullet}$ and $V_{Se}^{\bullet\bullet}$. Excess Bi atoms can occupy Te and Se vacancies to form the negatively charged antisite defects $Bi'_{Te}$ and $Bi'_{Se}$, resulting in the increase of hole concentration [16].

Fig. 3(a) shows the variation of carrier concentration $n_H$ with In content in $Bi_{2-x}In_xTe_2Se$ + 0.25 wt% $SbI_3$ before and after hot deformation. With the increase of In content, the carrier concentration firstly increases and then decreases. Substituting In at Bi sites does not produce more holes or electrons because of the

Please cite this article in press as: Li F, et al., Enhanced thermoelectric performance of n-type bismuth-telluride-based alloys via In alloying and hot deformation for mid-temperature power generation, J Materiomics (2018), https://doi.org/10.1016/j.jmat.2018.05.008