Enhancing room temperature thermoelectric performance of n-type polycrystalline bismuth-telluride-based alloys via Ag doping and hot deformation

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ABSTRACT

Bismuth-telluride-based alloys are the unique thermoelectric materials for state-solid refrigeration around room temperature. For n-type polycrystalline counterparts, maximum figure of merit zTs are often shifted above 400 K due to the increased carrier concentration induced by the donor-like effect during the pulverization of ingots. Herein, we report a synergistic optimization procedure, combining Ag doping with hot deformation, to boost room temperature thermoelectric performance of n-type polycrystalline $Bi_2Te_{2.7}Se_{0.3}$ alloys. The Ag doping optimizes the carrier concentration, contributing to an improved power factor and a reduced electrical thermal conductivity. The hot deformation process improves the carrier mobility due to the enhanced texture. As a consequence, a zT value of 1.0 at 300 K and a peak zT of 1.1 at 350 K are obtained in the twice hot deformed $Ag_{0.011}Bi_2Te_{2.7}Se_{0.3}$ alloy, which makes the n-type polycrystalline $Bi_2(Te,Se)_3$ alloys more suitable for solid-state refrigeration near room temperature.

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1. Introduction

Thermoelectric (TE) materials, which can realize the direct conversion between heat and electricity, have drawn extensive attentions for decades [1–4]. The energy conversion efficiency of a TE device is determined by materials' dimensionless figure of merit $zT = \alpha^2\sigma T/\kappa$, where α is the Seebeck coefficient; σ and κ are the electrical conductivity and thermal conductivity (including the carrier contribution κ_e and the lattice contribution κ_L) and T is the absolute temperature, respectively. Since α, σ and κ_e are inter-coupled via carrier concentration n, an optimal carrier concentration n_{opt} is required for a maximum zT [5,6]. Except for the carrier optimization, further enhancement of zT can be achieved by phonon engineering [7–13] and band engineering [14–17], aiming to reduce lattice thermal conductivity κ_L and boost the electrical power factor ($PF = \alpha^2\sigma$), respectively.

For decades, bismuth-telluride-based alloys have been the best commercial TE materials for solid-state refrigeration near room temperature. Both conventional zone-melted (ZM) p-type and n-type Bi_2Te_3-based alloys exhibit zT ~1 in vicinity of the room temperature [18]. However, their poor mechanical properties lead to easy failure of device fabrication. Polycrystalline Bi_2Te_3-based alloys, prepared by powder metallurgical processing, such as ball milling (BM), melt spinning (MS) and hydrothermal method followed by the hot pressing (HP) or spark plasma sintering (SPS), possess both better mechanical properties and lower κ_L than ZM counterparts, which have drawn much attention in the past years. Nanostructuring strategies, including "bottom-up" approach [7,9,19–21] and "top-down" approach [22–24], have been adopted to achieve high peak $zT > 1.2$ and room temperature $zT > 1.0$ in p-type $(Bi,Sb)_2Te_3$ alloys [7,9,19,21–23].

For n-type $Bi_2(Te,Se)_3$ alloys, zT is often decreased after nanostructuring due to the much degraded carrier mobility μ_H. In the last years, hot deformation (HD) process, which has been widely performed in metallic alloys [25,26], is successfully applied to enhance μ_H of polycrystalline n-type Bi_2Te_3-based alloys. Yan et al. reported an improvement in peak zT from 0.85 to 1.04 at 400 K by repressing the as-pressed $Bi_2Te_{2.7}Se_{0.3}$ alloy [27]; Liu et al. obtained a zT ~1.06 at 400 K in the re-pressed $Cu_{0.01}Bi_2Te_{2.7}Se_{0.3}$ sample [28]. Hu et al. and Pan et al. systematically studied the effects of intrinsic point defects on the TE properties of n-type polycrystalline $Bi_2Te_{3-x}Se_x$ alloys and found that a higher Se content ($x > 0.6$) was

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beneficial for a higher zT [29,30]. By engineering intrinsic point defects in $Bi_2Te_{3-x}Se_x$ alloys, Hu et al. obtained a peak zT ~1.2 at 445 K in the multiply hot deformed $Bi_2Te_{2.3}Se_{0.7}$ alloy [29,31] and Pan et al. reported a peak zT ~1.1 at 473 K in the SPS-forged $Bi_2Te_{2.2}Se_{0.8}$ sample via combining texturing with nanostructuring [32], respectively.

Due to the excessively increased carrier concentration n_H induced by donor-like effect during the pulverization of ingots [29,33], the n-type hot deformed Bi_2Te_3-based alloys generally achieve their peak zTs above 400 K. Nevertheless, their room temperature zT values are still less than 1.0, which is adverse for solid-state refrigeration around room temperature. Ag is generally used as an acceptor dopant to increase the hole concentration in p-type $(Bi,Sb)_2Te_3$ alloys [34,35] or reduce the electron concentration in n-type $Bi_2(Te,Se)_3$ alloys [36,37]. Simultaneously, a lower Se content in $Bi_2Te_{3-x}Se_x$ alloy is also required to maintain relatively high carrier mobility and density-of-states effective mass m^* [38]. In this work, Ag doping and hot deformation were applied to the n-type polycrystalline $Bi_2Te_{2.7}Se_{0.3}$ solid solution. The carrier concentration was optimized by Ag doping and the carrier mobility was enhanced by hot deformation, both together contributing to the room temperature zT enhancement of n-type $Bi_2Te_{2.7}Se_{0.3}$ alloy. To further boost the TE performance near room temperature, one more hot deformation was performed subsequently on the as-HD $Ag_{0.011}Bi_2Te_{2.7}Se_{0.3}$ sample. As a result, a zT value of 1.0 at 300 K, and a peak zT of 1.1 at 350 K were obtained in the twice hot deformed $Ag_{0.011}Bi_2Te_{2.7}Se_{0.3}$ alloy, demonstrating the feasibility of the applied synergistic processing for improving TE performance of n-type polycrystalline $Bi_2(Te,Se)_3$ alloys near room temperature.

2. Experimental section

Synthesis

Highly pure element chunks of Bi (5N), Te (5N), Se (5N) and Ag powder (5N) were weighted according to the stoichiometric Ag_x-$Bi_2Te_{2.7}Se_{0.3}$ ($x = 0$, 0.003, 0.005, 0.007, 0.009, 0.011 and 0.014) and sealed into quartz tube at 10^{-3} Pa. The mixtures were subsequently melted at 1073 K for 10 h in a furnace and rocked every several hours to ensure the composition homogeneity. The as-obtained ingots were ball-milled into fine powders and hot pressed into a disk of 12.7 mm diameter at 773 K for 30 min under a uniaxial pressure of 80 MPa, named as HP-Agx ($x = 0$–0.014) samples. Subsequently, a hot deformation process was performed by repressing the HP samples in a larger graphite die of 20 mm diameter at 823 K for 30 min under a uniaxial pressure of 80 MPa (named as HD-Agx samples). Compared to the HP process, the temperature of HD process is elevated, which is better for the enhancement of texture and has been testified in our previous work [39]. Necessarily, a disk of 12.7 mm in diameter was cut from the HD sample and hot deformed again in the graphite die of 20 mm in the same condition, named as HD2-Agx samples.

Characterization

X-ray diffraction (XRD) was applied to examine the phase structure of all samples on a Rigaku D/MAX-2550P diffractometer. The freshly fractured surfaces of samples were observed by field-emission SEM using an S-4800 microscope (Hitachi, Japan). The electrical conductivity σ and Seebeck coefficient α were simultaneously measured on a commercial Linseis LSR-3 system. The thermal diffusivity D was measured on a Netzsch LFA 467 laser flash apparatus using the method introduced by Xie et al. [40]. The specific heat C_P was calculated by the Dulong-Petit law and the density ρ was measured by an ordinary dimension-and-weight

method. The thermal conductivity was then calculated as $\kappa = D\rho C_P$. The Hall coefficient R_H at 300 K was obtained on a Quantum Design PPMS-9T instrument using a four-probe configuration, with the magnetic field sweeping between ±4.0 T. Then the Hall carrier concentration n_H and Hall mobility μ_H were calculated via $n_H = 1/eR_H$ and $\mu_H = \sigma R_H$, respectively. To be noted, all thermoelectric properties were measured along the in-plane direction.

3. Results and discussion

No secondary phases are observed in the XRD pattern of all samples and the phase structure of five typical $Ag_xBi_2Te_{2.7}Se_{0.3}$ bulk samples (HP-Ag0, HP-Ag0.011, HD-Ag0, HD-Ag0.011, HD2-Ag0.011) is shown in Fig. 1. It is obvious that the (00l) diffraction intensity increases in the HD samples, indicating a preferred orientation after hot deformation. To investigate the texture degree more clearly, the orientation factor F of the (00l) plane is calculated according to the Lotgering method [41] and presented in Table 1. The F values of HP-Ag0.011, HD-Ag0.011 and HD2-Ag0.011 samples are 0.02, 0.19 and 0.33 respectively, demonstrating that the texture is enhanced during hot deformation, which is consistent with our previous work [42]. Meanwhile, the samples with different Ag content have the similar F values. The enhanced texture after hot deformation is also observed in the SEM images of typical samples in Fig. 2: the HP sample almost has an isotropic distribution of fine grain (Fig. 2a) while the grains become larger and the orientation is more preferred in the HD samples (Fig. 2b–c).

Fig. 3a displays that the Hall carrier concentration n_H of HP and HD $Ag_xBi_2Te_{2.7}Se_{0.3}$ samples is continuously decreased with increasing x, indicating that Ag atoms forms the substitutional defects Ag''_{Bi} and increase the hole concentration (or decrease the
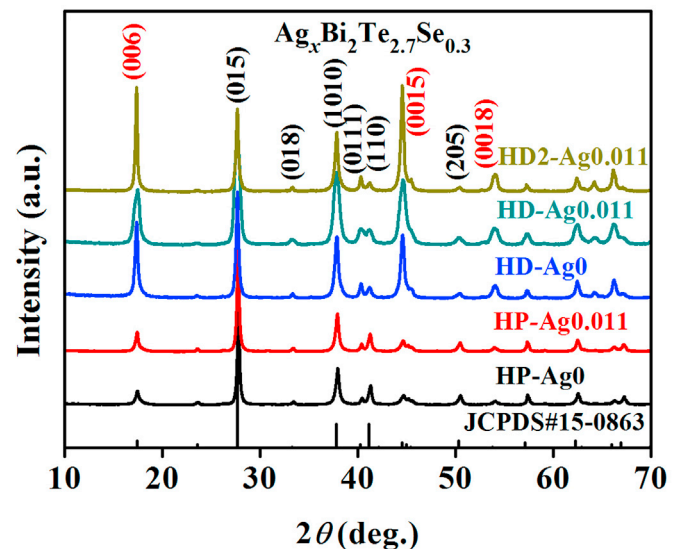

Fig. 1. In-plane XRD patterns of $Ag_xBi_2Te_{2.7}Se_{0.3}$ ($x = 0$, 0.011) bulk samples before and after hot deformation.

Table 1
The orientation factor F of (00l) plane in $Ag_xBi_2Te_{2.7}Se_{0.3}$ bulk samples before and after hot deformation.

x	0	0.003	0.005	0.007	0.009	0.011	0.014
F-HP	0.02	0.01	0.01	0.01	0.01	0.02	0.01
F-HD	0.20	0.17	0.21	0.17	0.18	0.19	0.20
F-HD2	–	–	–	–	–	0.33	–