Improving thermoelectric properties of p-type Bi$_2$Te$_3$-based alloys by spark plasma sintering

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Abstract: High-performance (Bi$_2$Te$_3$)$_x$(Sb$_2$Te$_3$)$_{1-x}$ bulk materials were prepared by combining fusion technique with spark plasma sintering, and their thermoelectric properties were investigated. The electrical resistivity and Seebeck coefficient increase greatly and the thermal conductivity decreases significantly with the increase of Bi$_2$Te$_3$ content, which leads to a great improvement in the thermoelectric figure of merit ZT. The maximum ZT value reaches 1.33 at 398 K for the composition of 20%Bi$_2$Te$_3$-80%Sb$_2$Te$_3$ with 3% (mass fraction) excess Te.

Key words: ternary-alloy system; electrical resistance; thermoelectric properties

1 Introduction

Thermoelectric (TE) materials are of interest for applications in solid state cooling and electrical power generation devices due to many attractive features such as long life, no moving parts, no emission of toxic gases, low maintenance, and high reliability [1]. However, its present usage is limited to niche applications [2] due to its low conversion efficiency. The efficiency of TE materials is governed by the dimensionless figure of merit, ZT, and is defined as $ZT=S^2\sigma T/\kappa$, where $S$, $\sigma$, $\kappa$, and $T$ are the Seebeck coefficient, electrical conductivity, thermal conductivity, and thermodynamic temperature, respectively. Among various thermoelectric materials, bismuth telluride based alloys [3-4] including n-type Bi$_2$(Te,Se)$_3$ and p-type (Bi,Sb)$_2$Te$_3$ are of great interest today not only as the best thermoelectric materials available near room temperature, but also due to the potential for improving their ZT values by structural and composition modification.

Thermoelectric properties of Bi-Te based alloys were deeply affected by preparation methods. Unidirectional crystal growth by zone melting [5] was used for preparing Bi-Sb-Te system materials, and the maximum ZT of 1.14 was obtained at about 350 K for the composition of 24% Bi$_2$Te$_3$-76% Sb$_2$Te$_3$ with 3% (mass fraction) excess Te. Besides the good thermoelectric properties, it needs long process time and the products are anisotropic and thus mechanically weak. Nano-engineering bulk material is an effect way to improve ZT. POUDEL et al [6] used a commercial bulk material with ZT=1 at RT by an extensive ball milling technique in an inert atmosphere followed by a hot pressing process. They found that the presence of the nanostructure within the bulk matrix led to a significant enhancement in the ZT reaching 1.4 at approximately 380 K, due primarily to a significant reduction in the lattice thermal conductivity. $ZT=1.56$ at 300 K was obtained by melting spinning p-type Bi$_{0.52}$Sb$_{1.48}$Te$_3$ bulk material with $ZT=1$ combined with a subsequent spark plasma sintering process [7]. Besides structure, chemical composition also has influence on thermoelectric properties of Bi$_2$Te$_3$-Sb$_2$Te$_3$ solid solutions, for ZT could be changed by adjusting the ratio of Bi and Sb due to change of carrier concentration and thermal conductivity. KIM et al [8] prepared (Bi$_2$Te$_3$)$_x$(Sb$_2$Te$_3$)$_{1-x}$ materials in the composition range of $x=0.15-0.25$ and found that the (Bi$_2$Te$_3$)$_{0.5}$(Sb$_2$Te$_3$)$_{0.5}$ alloy exhibits a maximum thermoelectric figure of merit Z of 3.05×10$^{-3}$ K$^{-1}$. JIANG et al [5] studied the influence of the variations of Bi$_2$Te$_3$ contents on the thermoelectric properties of Bi$_2$Te$_3$-Sb$_2$Te$_3$ and

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found the maximum ZT obtained in the composition of 24% Bi$_2$Te$_3$-76% Sb$_2$Te$_3$. However, there are many discrepancies in the published work. YANG et al [9] found ZT is less composition sensitive with Bi$_2$Te$_3$ contents.

As discussed above, excellent Bi-Te based bulk material is the guarantee that ZT could be further improved. In the present study, p-type (Bi$_2$Te$_3$)$_x$(Sb$_2$Te$_3$)$_{1-x}$ thermoelectric materials in the composition range of $x=0.18$−0.26 are prepared by the fusion method together with spark plasma sintering. The influence of the Bi$_2$Te$_3$ content on thermoelectric properties is studied.

2 Experimental

Elemental Bi (99.99%, Alfa Aesar), Sb (99.5%, Sigma Aldrich) and Te (99.999%, Alfa Aesar) granules were weighed according to the formula of (Bi$_2$Te$_3$)$_x$(Sb$_2$Te$_3$)$_{1-x}$ ($x=0.18, 0.19, 0.20, 0.22, 0.24$ and $0.26$ for sample B6, B5, B4, B3, B2 and B1, respectively) doped with 3% Te (mass fraction). The powder mixture was loaded into quartz ampoule sealed under vacuum at 10$^{-2}$ Pa, and then heated at 800°C for 10 h. Then the ingot was grinded and compacted by spark plasma sintering at a pressure of 50 MPa in a vacuum. The sintering temperature and heating rate were 673 K and 373 K/min, respectively. The crystal phase of sample was confirmed by X-ray diffraction at room temperature using Cu K$_\alpha$ radiation.

Disks of 8.3 mm in diameter and 1.5 mm thick and bars of about 1.5 mm × 3 mm × 12 mm were cut and polished from the pressed disks for the thermoelectric properties characterization. The electrical conductivity of the sample was measured by a four-point direct current (dc) current-switching technique, and the Seebeck coefficient was measured by a static dc method based on the slope of the voltage versus temperature-difference curves, using commercial equipment (ZEM-3(M8), Ulvac Riko, Inc.) under low pressure helium environment in the temperatures ranging from 300 K to 470 K. The thermal diffusivity, $D$, was measured using the laser flash method (Netzsch, LFA 457). The specific heat capacity, $c_p$, was determined by a commercial instrument (Pyris Diamond DSC, Perkin-Elmer). The density, $\rho$, was measured by the Archimedes method. The resulting thermal conductivity was calculated from the measured thermal diffusivity $D$, specific heat capacity $c_p$, and density $\rho$ from the relationship $\kappa=D\rho c_p$.

3 Results and discussion

The XRD patterns of Bi$_x$Sb$_{2-x}$Te$_3$ are shown in Fig. 1. It can be seen that all the main diffraction peaks correspond to those of standard JCPDS card of Bi$_2$Te$_3$ with rhombohedral structure (crystal group R3m). As compared with that of Bi$_2$Te$_3$, no obvious changes are observed in XRD patterns for Bi$_x$Sb$_{2-x}$Te$_3$ samples, suggesting that all the substituted specimens have the same crystallographic structure as that of Bi$_2$Te$_3$.

![Fig. 1 XRD patterns (Cu K$_\alpha$ irradiation) for (Bi$_2$Te$_3$)$_x$(Sb$_2$Te$_3$)$_{1-x}$ ($x=0.18, 0.19, 0.20, 0.22, 0.24$ and $0.26$)](image)

Temperature dependence of electrical resistivity with various Bi$_2$Te$_3$ contents was shown in Fig. 2. The electrical resistivity increases with increasing temperature, which indicates that the bulk materials exhibit a temperature dependence of the electrical resistivity that is described by metal-like or degenerated semiconductor behavior. It was also found that $\rho$ decreased with increasing Bi$_2$Te$_3$ content. For instance, $\rho$ decreased from about $6\times10^{-5}$ Ω m to $1.4\times10^{-5}$ Ω m with increasing Bi$_2$Te$_3$ content from $x=0.18$ to $x=0.26$ at 300 K.

![Fig. 2 Temperature dependence of electrical resistivity for (Bi$_2$Te$_3$)$_x$(Sb$_2$Te$_3$)$_{1-x}$ ($x=0.18, 0.19, 0.20, 0.22, 0.24$ and $0.26$)](image)
The positive values of the Seebeck coefficient for (Bi$_2$Te$_3$)$_x$(Sb$_2$Te$_3$)$_{1-x}$ ($0.18 \leq x \leq 0.26$) determined over the temperatures ranging from 300 K to 470 K, as shown in Fig. 3, means that the major charge carriers in all the samples are holes. The Seebeck coefficient for (Bi$_2$Te$_3$)$_x$(Sb$_2$Te$_3$)$_{1-x}$ samples was observed to increase with increasing temperature, and at a certain temperature, it showed a slight decrease with increase in temperature. This behavior has been reported previously [10] and may be due to excitation of carrier at high temperature. The Seebeck coefficient at 300 K increased from about 170 to 216 $\mu$V/K by increasing the Bi$_2$Te$_3$ content from $x=0.18$ to 0.26. Since the Seebeck coefficient and the electrical resistivity strongly depend on carrier concentration, their changes are well explained by the variation of the carrier concentration $n$. The electrical resistivity ($\rho$) and Seebeck coefficient ($S$) can be expressed in terms of the carrier concentration ($n$), as follows:

$$\rho = \frac{1}{ne\mu} \quad (1)$$

$$S = \pm \frac{k_B}{e} [(r + 2) + \ln \frac{2(2\pi m^* k_B T)^{3/2}}{h^3 n}] \quad (2)$$

where $k_B$ is Boltzmann’s constant; $e$ is the electron charge; $r$ is the scattering factor; $m^*$ is effective mass; $h$ is the Planck constant; and $\mu$ is the carrier mobility. As is known [11], in the p-type (Bi$_2$Te$_3$)$_x$(Sb$_2$Te$_3$)$_{1-x}$ ($0.18 \leq x \leq 0.26$) alloys, the holes are generally created by the antistructure defects generated by the occupation of Te sites with Bi and Sb atoms. A decrease of difference in electronegativity between the component atoms ($\chi_{Bi}=1.9$, $\chi_{Te}=1.8$ and $\chi_{Sb}=2.1$) will be favorable for an increase in the ability to form the antistructure defects. Hence, carrier (holes) concentration in (Bi$_2$Te$_3$)$_x$(Sb$_2$Te$_3$)$_{1-x}$ decreases with increasing Bi$_2$Te$_3$ content resulting from lower antistructure defects due to larger difference in electronegativity between Bi and Te than that between Sb and Te, which causes decrease in Seebeck coefficient and the electrical resistivity. Similar phenomena were also observed in Bi$_2$Sb$_2$Te$_5$ [12].

The temperature dependence of power factor PF ($\mathcal{P} = \rho S^2/\mu$) for (Bi$_2$Te$_3$)$_x$(Sb$_2$Te$_3$)$_{1-x}$ ($0.18 \leq x \leq 0.26$) is shown in Fig. 4. It can be seen that the PF of (Bi$_2$Te$_3$)$_x$(Sb$_2$Te$_3$)$_{1-x}$ decreased with increasing temperature. The PF obtained here for B$_x$, B$_2$, and B$_6$ is larger than that of B1, B2 or B3 in the whole temperature range investigated. The room temperature PF for B$_x$, B$_1$ and B$_6$ is around $4.91 \times 10^{-3}$ W/(m·K$^2$), $4.64 \times 10^{-3}$ W/(m·K$^2$) and $4.84 \times 10^{-3}$ W/(m·K$^2$), which is larger than that ($\sim 4.5 \times 10^{-3}$ W/(m·K$^2$)) reported by POUDEL et al [6].

The total thermal conductivity consists of a phononic contribution $\kappa_p$ and a contribution of mobile charge carriers, $\kappa_C$, i.e. $\kappa = \kappa_p + \kappa_C$. Usually, $\kappa_C$ can be estimated by the Wiedemann-Franz law, which relates $\kappa_C$ to the electrical resistivity $\rho$ according to $\kappa_C = L_0 T/\rho$, where $L_0=2.0 \times 10^{-8}$ V$^2$/K$^2$ is the Lorentz number for a degenerate semiconductor [13] and $T$ is the temperature in Kelvin. The effects of temperature on the thermal conductivity of the (Bi$_2$Te$_3$)$_x$(Sb$_2$Te$_3$)$_{1-x}$ ($0.18 \leq x \leq 0.26$) compounds is shown in Fig. 5. As seen in Fig. 5(a), the temperature behavior of the thermal conductivity for the five samples is similar: it decreases with increasing temperature and then increases with further increasing temperature. Such behavior is typical for crystalline materials. It can be seen from Fig. 5(b) that the carrier thermal conductivity in the temperature range investigated decreased with increasing Bi$_2$Te$_3$ content from $x=0.18$ to 0.24, which is originated from the increase in electrical resistivity due to the decrease in carrier concentration. By comparison of Fig. 5(a) with Fig. 5(c), one can find that the smaller thermal conductivity with decreasing Bi$_2$Te$_3$ content originates.
Fig. 5 Variation of thermal conductivity $\kappa$, $\kappa_C$ and $\kappa_L$ with temperature for (Bi$_2$Te$_3$)$_x$(Sb$_2$Te$_3$)$_{1-x}$ ($x=0.18, 0.19, 0.20, 0.22, 0.24$ and $0.26$)

mainly from the reduction in its lattice thermal conductivity.

Based on the data obtained above, the temperature dependence of ZT for (Bi$_2$Te$_3$)$_x$(Sb$_2$Te$_3$)$_{1-x}$ compounds is shown in Fig. 6. As seen in Fig. 6, the temperature behavior of ZT for the five samples is similar: it increases with increasing temperature, and after reaching a maximum, ZT value decreases with further increasing temperature. The ZT value for B5 and B6 sample exhibits a ZT of $\approx1.05$ at 300 K, its maximum ZT is 1.25. The sample B4 corresponding to the composition of 20%Bi$_2$Te$_3$-80%Sb$_2$Te$_3$ with 3% excess Te has the best thermoelectric properties: its room temperature ZT reaches 1.05 and the ZT value exceeds 1.3 in the temperature range of 330-400 K. Specially, ZT value for B4 reaches a maximum value of 1.33 at 398 K. The good thermoelectric properties for B4 originate from the relatively large power factor and low thermal conductivity.

4 Conclusions

p-type (Bi$_2$Te$_3$)$_x$(Sb$_2$Te$_3$)$_{1-x}$ crystals with various chemical compositions ($x=0.18, 0.19, 0.20, 0.22, 0.24$ and $0.26$) were fabricated through fusion method combined with spark plasma sintering. Thermoelectric properties, including Seebeck coefficient, electrical resistivity and thermal conductivity, were measured in the temperature range of 300–470 K. The influence of the Bi$_2$Te$_3$ content ($x$) on the thermoelectric properties was studied. The results show that the increase in Bi$_2$Te$_3$ content ($x$) led to a decrease in thermal conductivity and the increases in electrical resistivity and Seebeck coefficient due to the decreased hole concentration. As a result, the maximum figure of merit ZT of 1.33 was obtained at about 398 K for the composition of 20%Bi$_2$Te$_3$-80%Sb$_2$Te$_3$ with 3% excess Te.

References


