Enhanced Thermoelectric Properties Obtained by Compositional Optimization in \( p \)-Type \( \text{Bi}_x\text{Sb}_{2-x}\text{Te}_3 \) Fabricated by Mechanical Alloying and Spark Plasma Sintering

CHEN CHEN,1,2 DA-WEI LIU,1 BO-PING ZHANG,2 and JING-FENG LI1,3

1.—State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China. 2.—Beijing Key Laboratory of New Energy Materials and Technology, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China. 3.—e-mail: jingfeng@mail.tsinghua.edu.cn

\( \text{Bi}_x\text{Sb}_{2-x}\text{Te}_3 \) bulk alloys are known as the best \( p \)-type thermoelectric materials near room temperature. In this work, single-phase \( \text{Bi}_x\text{Sb}_{2-x}\text{Te}_3 \) \( (x = 0.2, 0.25, 0.3, 0.34, 0.38, 0.42, 0.46, \) and \( 0.5) \) alloys were prepared by spark plasma sintering (SPS) using mechanical alloying (MA)-derived powders. A small amount (0.1 vol.\%) of SiC nanoparticles was added to improve the mechanical properties and to reduce the thermal conductivity of the alloys. The electrical resistivity decreases significantly with increasing ratio of Sb to Bi in spite of the weaker decreasing trend in Seebeck coefficient, whereby the power factor at 323 K reaches \( 3.14 \times 10^{-9} \) \( \text{W/mK}^2 \) for a sample with \( x = 0.3 \), obviously higher than that at \( x = 0.5 \) \( (2.27 \times 10^{-9} \text{W/mK}^2) \), a composition commonly used for ingots. Higher thermal conductivities at low temperatures are obtained at the compositions with lower \( x \) values, but they tend to decrease with temperature. As a result, higher \( ZT \) values are obtained for \( \text{Bi}_{0.3}\text{Sb}_{1.7}\text{Te}_3 \), with a maximum \( ZT \) value of 1.23 at 423 K, about twice the \( ZT \) value (about \( 0.6 \)) of \( \text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 \) at the same temperature.

Key words: \( \text{Bi}_x\text{Sb}_{2-x}\text{Te}_3 \), spark plasma sintering, mechanical alloying

INTRODUCTION

Thermoelectric (TE) devices are capable of the direct conversion of electricity and thermal energy for cooling or heating, which can be used to recover waste heat for conversion into electrical power. Therefore, the potential applications of TE devices in waste heat recovery, air conditioning, and refrigeration have attracted increasing interest.1–5 \( \text{Bi}_2\text{Te}_3 \)-based alloys such as \( \text{Bi}_x\text{Sb}_{2-x}\text{Te}_3 \) \((p\text{-type})\) are some of the most important thermoelectric materials for use near room temperature and have been widely used in commercial thermoelectric materials. \( \text{Bi}_x\text{Sb}_{2-x}\text{Te}_3 \) has remarkable crystallographic anisotropy that originates from the rhombohedral structure composed of five atomic layers \([-\text{Te}^{11}\text{-Sb-Te}^{22}\text{-Bi-Te}^{11}]\), stacked by van der Waals interactions along the \( c \)-axis.5,6 Conventionally, zone melting (ZM), Bridgman, and Czochralski methods are often used to prepare \( \text{Bi}_x\text{Sb}_{2-x}\text{Te}_3 \) ingots with excellent TE properties.7 However, it is difficult to fabricate TE modules from such ingots, because of their poor mechanical properties. In recent years, many methods such as shear extrusion, melt spinning, hydrothermal synthesis, and hot pressing have been applied to prepare polycrystalline \( \text{Bi}_x\text{Sb}_{2-x}\text{Te}_3 \) alloys.8–11

The composition of \( \text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 \) was historically thought to have the optimized carrier density, and it has been used for more than 50 years. As many new methods have been used to synthesize \( \text{Bi}_2\text{Te}_3 \)-based alloys, the optimal composition of \( \text{Bi}_x\text{Sb}_{2-x}\text{Te}_3 \) has probably deviated from \( \text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 \). The origin of charge carriers in \( p \)-type \( \text{Bi}_x\text{Sb}_{2-x}\text{Te}_3 \) is related to the antisite defects (\( \text{Sb}\text{Te} \) or \( \text{Bi}\text{Te} \)) where Sb or Bi atoms occupy Te sites.7 Hence, it is possible to get an optimized carrier density for the best electrical properties by changing the Sb-to-Bi ratio. In this study, \( \text{Bi}_x\text{Sb}_{2-x}\text{Te}_3 \) \((x = 0.2, 0.25, 0.3, 0.34, 0.38, 0.42, 0.46, \) and \( 0.5) \) alloys were prepared by spark plasma sintering (SPS) using mechanical alloying (MA)-derived powders. A small amount (0.1 vol.\%) of SiC nanoparticles was added to improve the mechanical properties and to reduce the thermal conductivity of the alloys.
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0.42, 0.46, and 0.5) alloys were prepared by spark plasma sintering (SPS) using mechanical alloying (MA)-derived powders. The influence of the Sb-to-Bi ratio on carrier density was clarified by investigating the microstructure and thermoelectric properties of the Bi$_{x}$Sb$_{2-x}$Te$_3$ alloys.

EXPERIMENTAL PROCEDURES

Commercial high-purity powders of 99.99% Bi (under 100 mesh), 99.99% Te (under 200 mesh), 99.99% Sb (under 200 mesh), and 99% SiC (average diameter $\sim$100 nm) were used as raw materials. Since dispersion of SiC nanoparticles in Bi$_2$Te$_3$ can reduce the thermal conductivity and improve the mechanical properties, as found in our previous studies,$^{12}$ a small amount (0.1 vol.%) of SiC nanoparticles was dispersed into Bi$_{x}$Sb$_{2-x}$Te$_3$ in the present study.

Powders with chemical compositions of Bi$_{x}$Sb$_{2-x}$Te$_3 + 0.1$ vol.% SiC ($x = 0.2$, 0.25, 0.3, 0.34, 0.38, 0.42, 0.46, and 0.5) were prepared after MA at 450 rpm for 3 h in purified argon atmosphere using a planetary ball mill (QM-3SP2, Nanjing University, China). A stainless-steel vessel and balls were used with the weight ratio of balls to powders kept at 20:1. Subsequently, the as-milled powders were sintered under an axial compressive stress of 50 MPa at 673 K in vacuum using a spark plasma sintering (SPS) system (Sumitomo SPS 1050, Japan) as reported elsewhere.$^{12-14}$

Phase structure of the bulk samples was characterized by x-ray diffraction (XRD, Cu K$_\alpha$, D/Max-2500; Rigaku, Japan). Fractographs of the bulk samples were observed by scanning electron microscopy (SEM, JSM-6460, Japan). The Seebeck coefficient and electrical resistivity were evaluated along the sample section perpendicular to the SPS pressing direction, while the thermal diffusivity was evaluated along the sample section parallel to the SPS pressing direction. The Seebeck coefficient and electrical resistivity were measured using a Seebeck coefficient/electrical resistivity measuring system (ZEM-2; Ulvac-Riko, Japan) under helium atmosphere in the temperature range from 323 K to 473 K. The thermal diffusivity ($D$) was measured by the laser flash method using a TC-9000 apparatus (Ulvac-Riko, Japan). The specific heat ($C_p$) was measured by using a thermal analysis apparatus (DSC-60, Shimadzu, Japan). The density ($d$) of the samples was measured by the Archimedes method. The thermal conductivity ($\kappa$) was calculated from the density ($d$), specific heat ($C_p$), and thermal diffusivity ($D$) using the relationship $\kappa = DC_pd$.\(^5\)

RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of sintered bulk samples with compositions of Bi$_{0.5}$Sb$_{1.5}$Te$_3 + 0.1$ vol.% SiC ($x = 0.3$ and 0.5). All the diffraction peaks of the bulk materials were obtained from the section perpendicular to the pressing direction. The standard diffraction peaks cited for Bi$_{0.5}$Sb$_{1.5}$Te$_3$ (PDF#49-1713) are indicated by vertical lines for comparison. Regardless of the different $x$ values, the characteristic peaks of all the sintered bulk materials matched up well with the standard pattern, indicating the formation of single-phase Bi$_{x}$Sb$_{2-x}$Te$_3$ compounds. No characteristic peaks of SiC were found in the XRD patterns owing to the low SiC content (0.1 vol.%).

Figure 2 presents XRD patterns of Bi$_{0.5}$Sb$_{1.5}$Te$_3 + 0.1$ vol.% SiC from sections parallel and perpendicular to the pressing direction for comparison. The relative intensities of (00$l$) planes from the sections perpendicular to the pressing direction, including (006), (009), (0015), and (0018), are slightly higher than those from the sections parallel to the pressing direction. This indicates that the sections perpendicular to the pressing direction are slightly orientated on (00$l$) planes. The electrical and thermal conductivities in the c-plane are about four and two times larger than those along the c-axis in Bi$_2$Te$_3$-based alloys, respectively.$^5$ The orientation degree of the (00$l$) planes, termed $F$, was calculated by the Lotgering method using the following equations:$^6$

$$F = \frac{P - P_0}{1 - P_0}, \quad (1)$$

$$P_0 = \frac{I_0(00l)}{\sum I_0(hkl)}, \quad (2)$$