

Microstructure and properties of p-type $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ fabricated by spark plasma sintering

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Received 15 July 2007; accepted 10 September 2007

Abstract: P-type thermoelectric material $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ was sintered by spark plasma sintering (SPS) process in the temperature range of 320–420 °C. The microstructures of sintered materials were found to be well aligned, particularly when sintered at lower sintering temperatures. The electrical conductivity of the material became larger as the sintering temperature increased. The Seebeck coefficient showed a general decreasing tendency with an increase in sintering temperature. In terms of the power factor, the optimum sintering temperature was found to be 380 °C for a maximum value of around 2.6 mW/K.

Key words: $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$; thermoelectric material; spark plasma sintering (SPS); sintering temperature

1 Introduction

Thermoelectric materials, which can make direct and mutual conversion between electrical energy and thermal energy, are promising for the applications in the power generators and the cooling devices [1–2]. The thermoelectric devices possess remarkable advantages such as light in mass, reliable, friendly to environment and etc [3]. However, they have not been widely applied due to the low energy conversion efficiency. The efficiency of a thermoelectric device can be represented by the figure of merit ZT which is defined as $ZT = \alpha^2 \sigma T / \kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity and T is the absolute temperature [4].

At present, bismuth telluride based alloys shows the most satisfied thermoelectric properties around room temperature [5–6]. Bismuth telluride based alloys have a rhombohedra crystal structure. Along the c -axis, the atom layers array in the structure of $-\text{Te}^{(1)}-\text{Bi}-\text{Te}^{(2)}-\text{Bi}-\text{Te}^{(1)}$ -, the $-\text{Te}^{(1)}-\text{Te}^{(1)}$ - atomic layers are bonded with van der Waals force, so they are liable to cleavage, which lead to poor mechanical performance [7].

Bismuth telluride based alloys are generally fabricated by zone melting methods owing to the high

figure of merit along the crystal growth direction. However, these unidirectional solidified materials usually behaves poor mechanical properties due to the weak bonding between $-\text{Te}^{(1)}-\text{Te}^{(1)}$ - layers and the coarse grain size. In order to obtain the materials with excellent thermoelectric performance as well as high mechanical properties, varies of powder metallurgy methods such as pressureless sintering, hot pressing sintering and hot extrusion have been introduced in fabricating the bismuth telluride based alloys recently [8–10]. However, these methods have some drawbacks, for example, time consuming, procedures complicating and high production costs [11–12]. Spark plasma sintering (SPS) is a rapid sintering method for fabricating bulk materials at relatively lower temperatures in much shorter time, which can suppress elements evaporation and restrain the crystal grain growth. These characteristics contribute to its potential application advantages in fabricating the thermoelectric materials, such as bismuth telluride based alloys [13–14].

In the present work, ball milling method is used to prepare p-type $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ powders from the zone-melting ingots. Then SPS method is adopted to consolidate the powders into bulk materials. The texture and thermoelectric properties of the sintered materials are investigated, and the variation of thermoelectric pro-

properties with the sintering temperature is discussed.

2 Experimental

The alloy powders under 150 μm sieves were sintered in the temperature range of 593–693 K in vacuum at the pressure of 40 MPa. During the sintering process, the heating rate is 50 K/min, the temperature and pressure was held for 10 min. The sintered samples were cut into different sizes for the thermoelectric measurements. The directions parallel and perpendicular to the pressing axis during the sintering process are named as longitudinal and transverse directions, respectively.

The phase structures were identified by the X-ray diffraction(XRD), the micro-morphology and chemical compositions were analyzed by the cold field emission scanning electric microscope(SEM) and the energy diffraction spectrometer(EDS). The Seebeck coefficient α and electric conductivity σ were measured at room temperature. The mechanical properties were measured by the three-point bending test.

3 Results and discussion

3.1 Evaluation of microstructure

Bismuth telluride based alloys have a rhombohedra structure with space group $R3m$, so their performances relate to the orientation of grains. To investigate the preferred orientation of grains, XRD analyses were made in the sections of both longitudinal and transverse direction. Figs.1(a) and (b) show the corresponding XRD patterns of the sample sintered at 80 $^{\circ}\text{C}$ and 40 MPa. The diffraction lines of (00l) planes, including (0015), (0018) and (0021), could be observed and their intensities in the transverse direction are higher than that in the longitudinal one. It means that the c -axis of the grains are preferentially oriented parallel to the pressing direction.

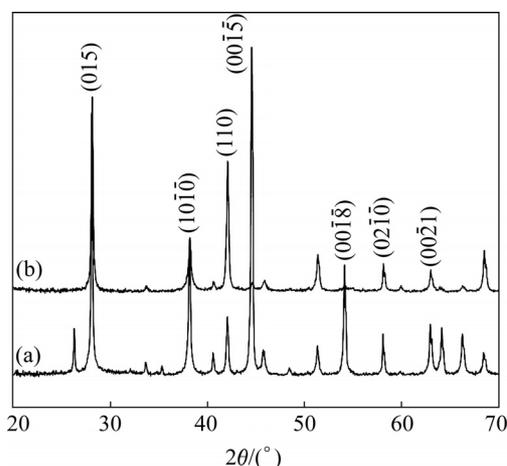


Fig.1 XRD patterns of $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ sintered at 380 $^{\circ}\text{C}$ under 40 MPa: (a) Transverse direction; (b) Longitudinal direction

The microstructure can be clearly verified by the observation on the fracture surfaces of the materials, as shown in Fig.2. The SEM microstructure of the material sintered at 380 $^{\circ}\text{C}$ under 40 MPa and in the direction perpendicular to the pressure shows that the fracture surface of the sample demonstrates a layered structure, which is in good consistence with the XRD results.

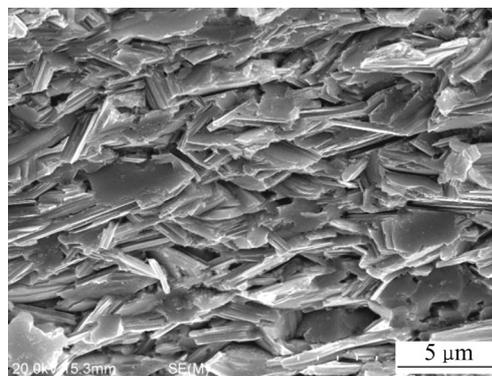


Fig.2 SEM image of $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ sample sintered at 380 $^{\circ}\text{C}$ under 40 MPa in transverse direction

The considerable preferential orientation in the microstructure in the as-sintered condition is somewhat a surprise. Actually, an isotropic microstructure was expected after sintering, as the powders were randomly filled into the mold. However, the powders used in this study are in platelet shape, the c -axis of the crystal is perpendicular to the platelet. Apparently this platelet shape of the powders results in the preferred orientation. On the other hand, during sintering, mechanical pressure of 40 MPa was applied. It is not unreasonable that the particles with basal planes bonded with van der Waals' force rotate perpendicular to the pressure. Besides, the pulse discharge sintering, inevitably inducing a high electric field to the materials during sintering, may also affects the orientation of the final material microstructure. This point of view is to be clarified, not only for this material but also for any other ones. With the increase in the sintering temperature, the preferential orientation is reduced.

3.2 Mechanical properties

The relative densities of the sintered samples are about 90%. The mechanical properties of both the zone-melted and SPS-sintered ones were measured by a three-point bending test method in the longitudinal direction. The result shown in Fig.3 indicates that as the sintering temperature increases, the bending strength of the samples firstly enhances because the density is improved; but then slightly reduces due to the evaporations in higher temperatures. The average value is about 40 MPa, which is about 3 times larger than that

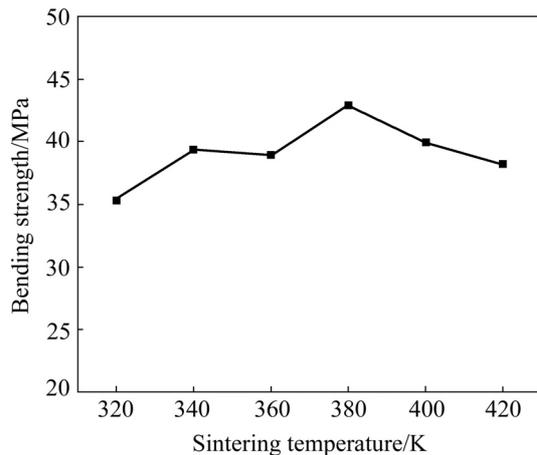


Fig.3 Bending strength of SPS-sintered samples as function of sintering temperature

of the zone-melted material which is 13.9 MPa. The improvement of mechanical strength is considered to be attributed to the bonding between powders. It is believed that such high mechanical strengths could provide sufficient ability to bear the cutting load and improve the reliability for the applications in thermoelectric modules.

3.3 Thermoelectric properties

The room temperature electrical conductivities of the materials in both longitudinal and transverse directions are shown in Fig.4(a), as functions of sintering temperature. With data shown by the two curves, the electrical conductivity increases with the sintering temperature. That's because as the sintering temperature increases, not only the carrier concentration and mobility grows larger, but also the carrier scattering is reduced due to the reduction of pore density. It is obvious that the average electrical conductivities in the transverse direction are much higher due to the orientation of the platelet grain is parallel to this direction and so the carrier scattering is lower.

The Seebeck coefficient first increases but then decreases as the sintering temperature increases. It shows the highest value at 244 $\mu\text{V}/\text{K}$ in the longitude direction when the sintering temperature is 380 $^{\circ}\text{C}$. In the entire sintering temperature range, the sintered samples in the longitudinal direction show higher Seebeck coefficient values than those in the transverse direction. The Seebeck coefficient α of the p-type of thermoelectric materials in the extrinsic conduction region can be expressed as[15]

$$\alpha = \frac{k_B}{e} \left[\delta + 2 + \ln \frac{2(2\pi m \cdot k_B T)^{2/3}}{h^3 n} \right] \quad (1)$$

where k_B is the Boltzmann constant, δ is the scattering related factor, h is the Plank constant. At a constant temperature T , thus, the Seebeck coefficient of p-type

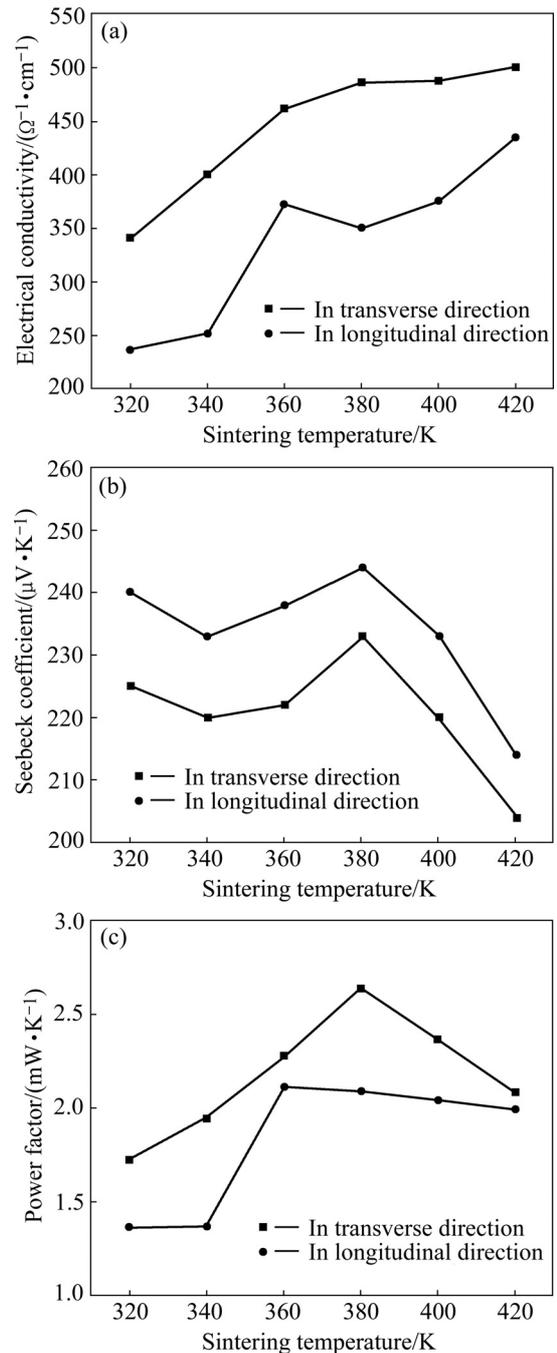


Fig.4 Electric performances of electric conductivity (a), Seebeck coefficient (b) and power factor (c) for $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ sintered at 40 MPa as function of sintering temperature

thermoelectric materials can be simplified as

$$\alpha = k_B/e[\delta + C - \ln n] \quad (2)$$

where C is a constant. According to the function, the high Seebeck coefficient of the material is attributed to the low carrier concentration in this sample. And the reduction of Seebeck coefficients at higher sintering temperature is attributed to the formation of anti-structural defects owing to the Te evaporation.

The power factor $\alpha^2\sigma$ increases with increasing sintering temperature in both longitudinal and transverse directions, though slight decreasing occurred at highest temperature, the highest value reaches to 2.6 mW/K of the sample sintered at 380 °C. In comparison to the longitudinal direction, the samples in the transverse direction shows higher power factor, which is attributed to the higher electrical conductivity.

4 Conclusions

The p-type $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ was crushed to powder with particle size below 150 μm . The powder was sintered by SPS process under 40 MPa for 10 min at various temperatures. The mechanical properties and the thermoelectric properties were investigated and the following conclusions are drawn from the experimental data:

1) After spark plasma sintering (SPS), the microstructures of sintered materials are well aligned along the basal planes on the transverse direction.

2) The sintering temperature has an important influence on the properties of $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$. As the sintering temperature increases, the electricity is improved but the Seebeck coefficient firstly enhances and then decreases.

3) The experimental results show that the p-type $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ with good thermoelectric performance and mechanical property has achieved, the maximum power factor ($\alpha^2\sigma$) reaches to 2.6 mW/K at 380 °C, the bending strength is enhanced to 40 MPa, which equals to three times more than that of the samples prepared by zone melting method. This indicates that SPS is a promising method for fabricating p-type $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ and it may also be applied in the preparations of similar thermoelectric materials.

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(Edited by LAI Hai-hui)