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Synthesis of micro/nanostructured p-type $Bi_{0.4}Sb_{1.6}Te_3$ and its thermoelectrical properties

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ABSTRACT

Micro/nanostructured p-type $Bi_{0.4}Sb_{1.6}Te_3$ alloy was prepared by hot-pressing at 703 K. From the measurements of Seebeck coefficient, electrical resistivity and thermal conductivity, the calculated ZT value up to 1.15 was achieved at room temperature. The achieved higher ZT value is attributed to the unique micro/nanostructures which reduce the thermal conductivity effectively. The as-prepared micro/nanostructured p-type $Bi_{0.4}Sb_{1.6}Te_3$ alloy can serve as a high performance thermoelectric material.

1. Introduction

Recently, thermoelectric materials have attracted much attention on the applications of functional devices, such as power generators, coolers, and thermal sensors , for their particular capability of mutual conversion between temperature gradient and electricity [1–5]. The performance of thermoelectric materials is characterized by a dimensionless figure of merit $ZT = \alpha^2 T/\rho\kappa$, where α, ρ, κ, and T are Seebeck coefficient, electrical resistivity, thermal conductivity and absolute temperature, respectively. An optimization to achieve a higher ZT value is still a challenge due to the interdependence of α, ρ and κ.

Bi_2Te_3-based alloys doped with Sb, Sn, In, and Pb have been extensively adopted to make thermoelectric devices, owing to the high atomic weights reducing the speed of sound in the material and thereby decreasing the thermal conductivity [5–8]. So far, based on these thermoelectric materials, great interests were focused on how to selectively allow charge carriers to flow across them, while blocking heat flow by lattice vibrations or phonons, and such a process was conceived as an effective approach to improve the thermoelectric performance. Thus, nanostructured materials became attractive for the capability of enhancing charge carriers flow but blocking heat flow, and remarkable breakthroughs have been achieved; for instance, a ZT value up to 2.4 has been obtained in Bi_2Te_3/Sb_2Te_3 superlattices [9]. A high ZT value of 1.4 has also been achieved in bulk materials with nanoscaled grains, which can be used in large-scale energy-conversion [10]. Besides the nanostructures, micro/nanostructures also attracted much attention because they combine the advantages of nanostructures and microstructures [11–14]. As for the synthesis of thermoelectric materials, a variety of methods were proposed such as epitaxial growth, hydrothermal synthesis and electrodeposition method. [15–18]. Herein, we prepared micro/nanostructured p-type $Bi_{0.4}Sb_{1.6}Te_3$ alloys by hot-pressing approach and the influences of hot-pressing conditions on the microstructures and thermoelectric properties of as-prepared $Bi_{0.4}Sb_{1.6}Te_3$ were investigated.

2. Experimental procedure

Elemental powders of Bi (5N), Sb (5N) and Te (5N) were weighed in the atomic ratios of $Bi_{0.4}Sb_{1.6}Te_3$ and charged with amount of excess Te addition into a quartz tube at 10^{-3} Pa. The elemental mixtures were melted at 1023 K using a rocking furnace to ensure the composition homogeneity, and then were cooled to room temperature in the furnace. The crystal growth was performed in a zone melting furnace at a temperature gradient of 25 K/cm and a growth rate of 6 mm/h and then the zone-melted crystal was subjected to a high-energy ball milling technique under Ar atmosphere to acquire fine powders. The powders were hot-pressed at 200 MPa in a vacuum of 10^{-3} Pa for 2 h at temperatures ranging from 643 K to 733 K.

The phase structure and microstructure were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The Seebeck coefficient (α) and electrical resistivity (ρ) were measured by using ZEM-3 (ULVAC Co., Ltd.) in a helium atmosphere from 300 K to 500 K. The thermal conductivity (κ) was calculated from the heat capacity (C_p), thermal diffusivity (λ) from LFA 427 laser flash apparatus, and density (d) using the relationship of $\kappa = \lambda C_p d$. The figure of merit ZT was calculated according to the equation: $ZT = \alpha^2 T/\rho\kappa$. The thermo-

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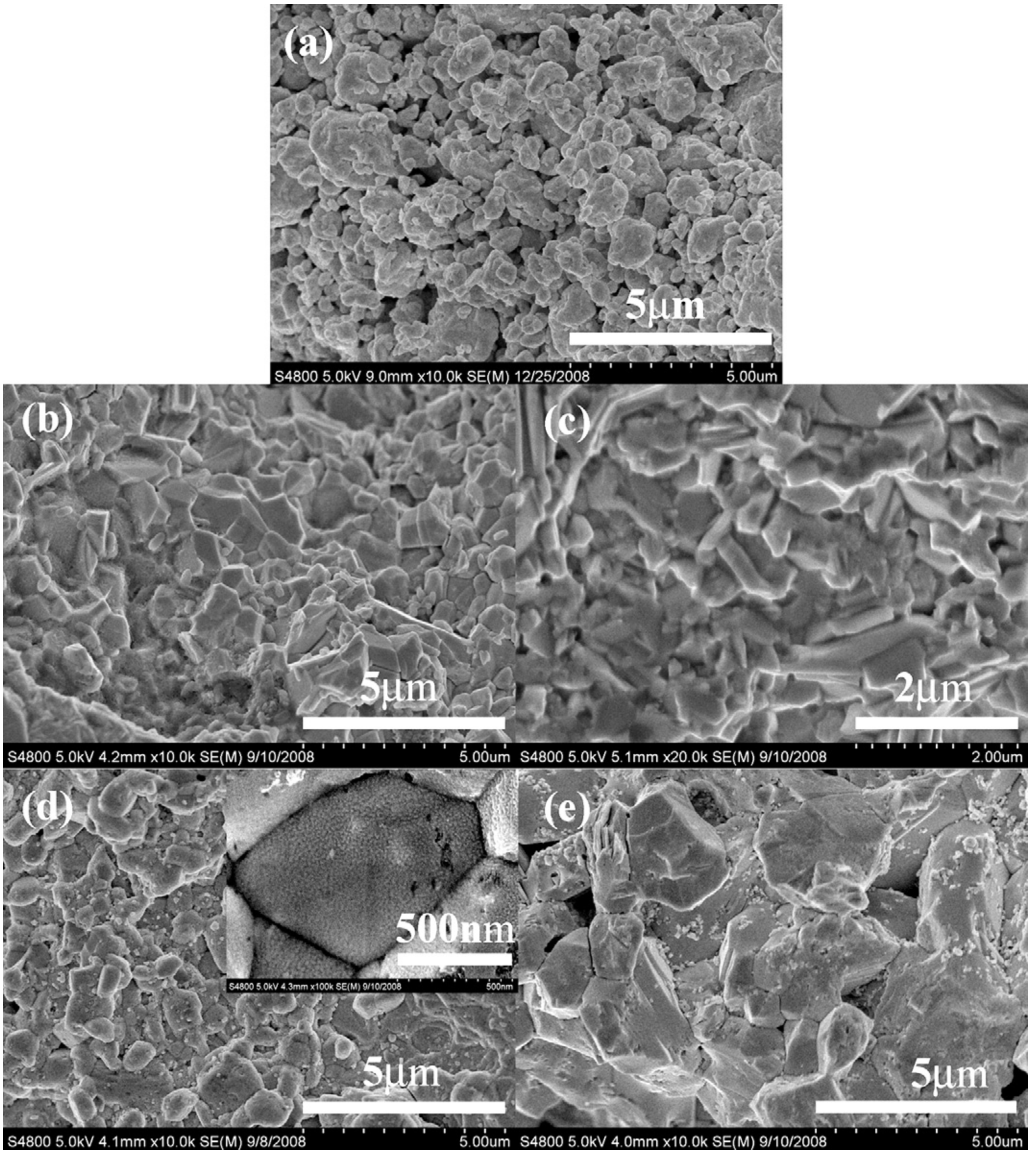

Fig. 1. SEM images of the as-milled powders (a) and the samples prepared by hot-pressing at (b) 643 K, (c) 673 K, (d) 703 K and (e) 733 K.

electric properties were measured perpendicular to the hot-pressing direction for the hot-pressed sample and along the crystal growth direction for the zone-melted crystal.

3. Results and discussion

The SEM images of the as-milled $Bi_{0.4}Sb_{1.6}Te_3$ powders and the samples prepared by hot-pressing at different temperatures were shown in Fig. 1. It was observed that the grain sizes varied with the hot-pressing temperatures for the hot-pressed samples. With increasing the hot-pressing temperature from 643 K to 673 K, the sizes of grains decreased. And a special micro/nanostructure of as-prepared sample was obtained at 703 K, as shown in Fig. 1(d), where the nanoparticles dispersed on the micrograins and the sizes of micrograin were about 1 μm. When the hot-pressing temperature increased from 703 K to 733 K, the grain sizes increased to a few micrometers as shown in Fig. 1(e). The XRD patterns of the as-milled powders and the hot-pressed samples were presented in Fig. 2. All of peaks in these spectra can be indexed to the diffraction peaks of $Bi_{0.4}Sb_{1.6}Te_3$ (JCPDS 65-3674).

The temperature dependence of Seebeck coefficient (α) was shown in Fig. 3(a) for the hot-pressed samples and zone-melted

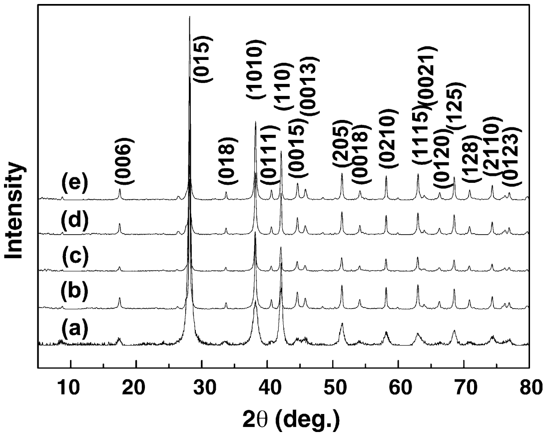

Fig. 2. XRD patterns of the as-milled powders (a) and the samples prepared by hot-pressing at (b) 643 K, (c) 673 K, (d) 703 K and (e) 733 K.

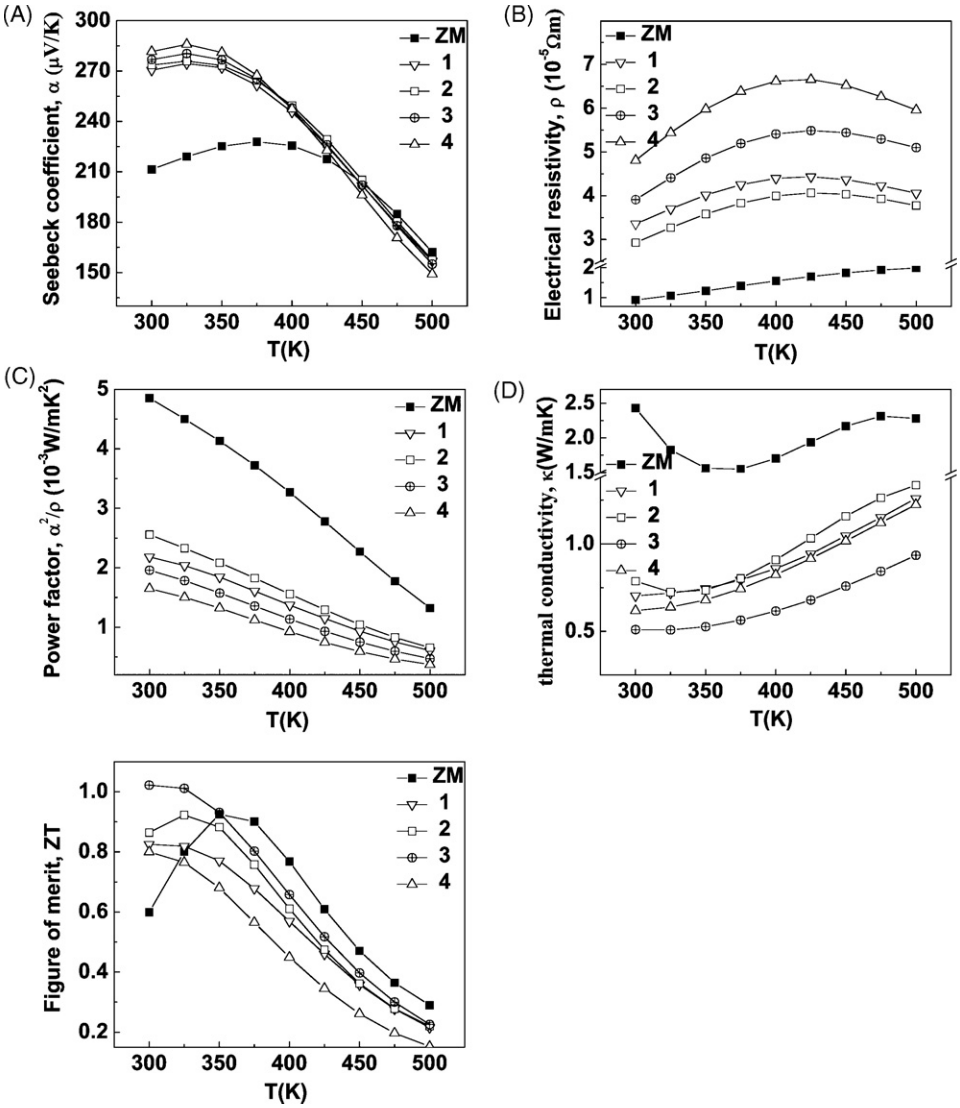

Fig. 3. Temperature dependence of the thermoelectric properties for the sample as-prepared at (1) 643 K (2) 673 K (3) 703 K (4) 733 K and ZM (zone-melted crystal).

crystal. Seebeck coefficient of p-type thermoelectric materials can be derived from $\alpha = k_B/e[\gamma + C - \ln n]$ at a constant temperature in the extrinsic conduction region (where k_B is Boltzmann constant, e is electrical charge of electron, γ is scattering parameter, C is a constant and n is carrier concentration) [19]. When the measurement temperature was below 400 K, α increased slightly with the increase of hot-pressing temperature, which was in consistent with the report of Fan et al. [20]. While compared with that of zone-melted crystal, α of hot-pressed samples increased drastically in the same range of the measurement temperature, which maybe originate from the larger scattering factor γ due to the fine grains boundaries and the variation in carrier concentration caused by the inherently higher donor-like defects [21,22].

The electrical resistivities (ρ) of the hot-pressed samples and zone-melted crystal were shown in Fig. 3(b). It could be observed that ρ of the hot-pressed sample was increased while compared to that of zone-melted crystal, which could be attributed to the introduction of grain boundaries and interfaces into hot-pressed sample. Due to the lower electrical resistivity, the power factor (α^2/ρ) of the zone-melted crystal was larger than that of hot-pressed sample, as shown in Fig. 3(c). The thermal conductivities (κ) of hot-pressed samples as shown in Fig. 3(d) were significant lower than that of zone-melted crystal in the whole range of the measurement temperature. Meanwhile, it can be seen that the sample prepared by hot-pressing at 703 K possessed the lowest κ (0.5 W/mK). Compared with other hot-pressed materials, the achieved lowest κ maybe originate from the unique micro/nanostructures shown in Fig. 1(d). From the above-mentioned analysis, although such structures made no contribution to the decrease of electrical resistivity, the thermal conductivity was decreased effectively, suggesting that the grain boundaries and interfaces in the hot-pressed sample prepared at 703 K could result in an effective scattering of the long wave phonons, thus the lowest thermal conductivity was obtained [23].

The temperature dependence of the figure of merit ZT was shown in Fig. 3(e) for the hot-pressed samples and zone-melted crystal, which was calculated with the obtained values of Seebeck coefficient, electrical resistivity and thermal conductivity. Improvements of ZT value were achieved for the hot-pressed samples at room temperature and the maximum ZT value up to 1.15 was achieved for the sample hot-pressed at 703 K. Taking into account the lower merit of power factor (α^2/ρ) in Fig. 3(c), the maximum ZT value was resulted from the reduced thermal conductivity which mainly due to the unique micro/nanostructures shown in Fig. 1(d).

4. Conclusions

Micro/nanostructured p-type $Bi_{0.4}Sb_{1.6}Te_3$ was prepared by hot-pressing at 703 K. It was found that such structure could reduce the thermal conductivity effectively by increasing the density of grain boundaries and interfaces. Resulted from the enhanced blocking of heat flow by grain boundaries and interfaces, the ZT value up to 1.15 was obtained in micro/nanostructured sample at room temperature. It indicated that the micro/nanostructured $Bi_{0.4}Sb_{1.6}Te_3$ alloy could be served as a high-performance material for the application on thermoelectric devices.

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