Thermoelectric Properties of Nano/microstructured p -Type $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ Powders Fabricated by Mechanical Alloying and Vacuum Hot Pressing

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Two kinds of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ powder with different particle and grain sizes were fabricated by high-energy ball milling. Powder mixtures with varied weight ratios were consolidated by vacuum hot pressing (HP) to produce nano/microstructured composites of identical chemical composition. From measurements of the Seebeck coefficient, electrical resistivity, and thermal conductivity of these composites, a figure of merit (ZT) value of up to 1.19 was achieved at 373 K for the sample containing 40% nanograin powder. This ZT value is higher than that of monolithic nanostructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$. It is further noted that the ZT value of this sample in the temperature range of 450 K to 575 K is in the range of 0.7 to 1.1. Such ZT characteristics are suitable for power generation applications as no other material with a similar high ZT value in this temperature range has been observed until now. The achieved high ZT value can probably be attributed to the unique nano/microstructure, in which the dispersed nanograin powder increases the number of phonon scattering sites, which in turn results in a decrease of the thermal conductivity while simultaneously increasing the electrical conductivity, owing to the existence of the micro-sized powder that can provide a fast carrier transportation network. These results indicate that the nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ alloy can serve as a high-performance material for application in thermoelectric devices.

Key words: $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$, mechanical alloying, vacuum hot pressing, nano/microstructured materials, thermoelectrics

INTRODUCTION

Over the past 30 years, alloys based on Bi_2Te_3 have been extensively studied and optimized for use as thermoelectric (TE) materials. The efficiency of a TE material is often characterized by its corresponding figure of merit, ZT . ZT is a dimensionless parameter which is conventionally defined as¹

$$ZT = (\alpha^2 \sigma / \kappa) T,$$

where ZT is the figure of merit, T is the absolute temperature, α is the Seebeck coefficient, σ is the electrical conductivity, and κ is the total thermal conductivity with contributions from the lattice (κ_L) and the charge carriers (κ_e). The larger the ZT value, the higher the energy conversion efficiency of a TE material. Among bismuth-telluride-based materials, the ZT value of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ alloy in the high temperature region is larger than that of Bi_2Te_3 alloy. This implies that $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ alloy has great potential to serve as a high-performance material for power generation applications. Improving the ZT value of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ at high temperature is therefore of particular interest. Several groups have

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prepared nanocomposite $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk samples by using ball milling and the hot pressing or spark plasma sintering method.^{2–6} A peak ZT value of 0.9 at 450 K was obtained by combining ball milling and spark plasma sintering.³

An efficient TE material should have large Seebeck coefficient, high electrical conductivity, and low thermal conductivity. However, it is difficult to satisfy these criteria in single-crystalline bulk materials, as all three quantities (α , σ , and κ) that govern ZT are interrelated and modification of any of these quantities often adversely affects the others. Therefore, classes of good TE materials are relatively rare. Recently, there have been a number of attempts to increase the ZT value of TE materials.^{7–9} One of the effective ways is to reduce the lattice thermal conductivity by refining the grain size on the basis of incorporating extra phonon scattering sites inside grain-boundary regions. However, decrease in the lattice thermal conductivity based on a finer grain size structure also leads to a decrease in the electrical conductivity and, as a result, the enhancement of ZT is limited. Recently, several mechanically alloyed Bi_2Te_3 powders with various coarse/fine particle size ratios were consolidated into bulk form by spark plasma sintering.¹⁰ Significant enhancement of the ZT value at room temperature was observed in case of an optimized fine/coarse volume ratio of 6:4. Thus far, little work has been conducted on enhancement of the ZT value for Bi-Sb-Te materials by using powder mixtures with different particle and grain sizes. In the present work, we selected $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ as the base alloy. Nano/microstructured p -type $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ alloys were fabricated by combining mechanical alloying and hot pressing. The influence of the weight percentage of nanograin powder on the microstructures and thermoelectric properties of the sintered $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk specimens was investigated. The results reveal that it is possible to enhance the ZT value by optimal addition of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ nanograin powder.

EXPERIMENTAL PROCEDURES

Two kinds of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ powder were prepared in this study by using a high-energy shaker ball mill located inside an Ar-purified and Ar-filled glovebox, in which the oxygen and moisture contents were

maintained at less than 1 ppm. To produce $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ nanograin powder, a mixture of elemental metallic powders of Bi (99.999%), Sb (99.999%), and Te (99.999%) was mechanically alloyed using a SPEX 8016 shaker ball mill. The duration of the overall milling process for preparation of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ nanograin powder was 2 h. The source material for micrometer-sized $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ powder was a $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bar made by the zone-melting method, which was crushed into a granular powder, and sieved into particles of size of about 106 μm to 250 μm with a 60 to 140 mesh nylon sieve. Then, the micrometer-sized powder was further mixed with $x = 10$ wt.% or $x = 40$ wt.% $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ nanograin powder and mechanically milled for 15 min in the SPEX ball mill to prepare nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ composite powders. For brevity, the nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ samples with 10 wt.% and 40 wt.% nanograin powder are denoted $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -10N and $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N, respectively. The as-milled $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ composite powders were then consolidated in a vacuum hot-pressing machine to prepare $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ discs with diameter of 17 mm and thickness of 10 mm. Vacuum hot pressing was performed at 573 K under pressure of 0.7 GPa for 60 min. Table I summarizes the sample compositions and vacuum hot-pressing parameters of the $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ composite powders. The crystal structure of as-milled and hot-pressed samples were examined by x-ray diffraction (XRD) using a Siemens D-5000 XRD diffractometer with monochromatic Cu K_α radiation. Fractographs of hot-pressed samples were observed by scanning electron microscopy (SEM, S-4700; Hitachi).

The thermoelectric properties were measured along the hot-pressing direction. The Seebeck coefficient and electrical resistivity of the hot-pressed samples were investigated using a ZEM-3 instrument (Ulvac-Riko, Japan). The thermal conductivity was calculated from the thermal diffusivity measured by the laser flash method (LFA 447, Netzsch), the specific heat, and the density of the hot-pressed body.

RESULTS AND DISCUSSION

XRD experiments were carried out to determine the structure of the $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ powders prepared from different starting materials, and the results

Table I. Sample designations and vacuum hot-pressing parameters for composite $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ thermoelectric powders

Sample Designation	$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ Micropowder (%)	$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ Nanopowder (%)	Hot-Pressing Pressure (GPa)	Hot-Pressing Temperature ($^{\circ}\text{C}$)	Hot-Pressing Time (h)
$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -10N	90	10	0.7	300	1
$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N	60	40	0.7	300	1
Monolithic $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$	—	100	0.7	300	1

are shown in Fig. 1. As evident from this figure, all diffraction peaks can be indexed to the $(\text{Bi,Sb})_2\text{Te}_3$ phase, implying that this $(\text{Bi,Sb})_2\text{Te}_3$ phase can be successfully prepared by high-energy ball milling, irrespective of differences in the starting material. The mechanically alloyed $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ powders have a characteristic nanostructure with grain size

Fig. 1. XRD patterns of as-milled $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ powder fabricated from (a) crushed powders from $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bar, and (b) a mixture of Bi, Sb, and Te elemental powders.

Fig. 2. XRD patterns of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ specimens before and after consolidation.

of around 17 nm, as calculated by employing the Scherrer formula. Figure 2 presents the XRD patterns obtained from nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ composite powders in which the nanograin and micro-sized powders are mixed in weight ratio of 4:6 (designated as $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N) and 1:9 (designated as $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -10N). Although the weight ratios are different, all diffraction peak positions and (hkl) values of the nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ composites match very well with the standard diffraction data of the pure $(\text{Bi,Sb})_2\text{Te}_3$ phase (JCPDS 072-1835). This is not surprising since the crystalline phases of the two original micro- and nanograin $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ powders correspond to this $(\text{Bi,Sb})_2\text{Te}_3$ phase. These $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ composite powders were then consolidated in the form of discs with diameter of 17 mm and thickness of 10 mm under vacuum hot-pressing conditions, as listed in Table I, and the corresponding XRD patterns are included in Fig. 2. It is noticed that all reflections can be attributed to the $(\text{Bi,Sb})_2\text{Te}_3$ phase. However, compared with the as-milled composite powders, the peaks of the samples after consolidation are narrower due to strain relaxation and grain growth occurring in the nanostructured powders.

Figure 3 shows the outer morphology and a cross-sectional view of a $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N disc after vacuum hot pressing at 573 K and pressure of 0.7 GPa for 1 h. No significant pores were observed in the cross-sectional view (Fig. 3b) taken at magnification of 5000 times, which reveals that relatively dense nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk composite samples can be successfully fabricated by using vacuum hot pressing. The relative density value of the monolithic $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk sample as measured by the Archimedes method was 96.1%, while those for the $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N and $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -10N samples were 94.8% and 95.1%. However, it is hard to identify the micro-sized or nanograin $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ powders. In order to observe the microstructure of the composite material, the fracture surface of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N and $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -10N bulk samples was examined by SEM. As shown in Fig. 4, the SEM micrographs indicate the coexistence of two types of particles, namely larger ones with size of over $50\text{ }\mu\text{m}$ with a flaky surface and

Fig. 3. (a) Outer morphology and (b) cross-sectional view of a $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N disc after vacuum hot pressing at 573 K and pressure of 0.7 GPa for 1 h.

smaller ones of less than 200 nm diameter with spherical shape. Figure 5 shows the fracture surface of micro-sized $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ particles formed by crushing the zone-melted $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ ingot, where the typical flaky surface can be observed. Comparing with Fig. 5, it is clear that the larger particles shown in Fig. 4 correspond to the micro-sized $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ powder whereas the smaller particles correspond to the nanograin $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ powder. Figure 4 also reveals that both the larger and smaller powders are tightly bonded, which further proves that vacuum hot pressing is suitable to fabricate highly dense nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk composite samples.

Figure 6 shows the thermoelectric properties of the nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk composite samples. The variation of the Seebeck coefficient as a function of temperature is shown in Fig. 6a. All samples have a positive Seebeck coefficient, suggesting that they are p -type conductors. The Seebeck coefficient values of the nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk composite samples are found to increase with temperature in

the range from 300 K to 500 K. The maximum value of the Seebeck coefficient of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -10N is $203 \mu\text{V/K}$ at around 518 K, compared with $210 \mu\text{V/K}$ at around 459 K for $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N.

Fig. 5. SEM image of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ particles obtained by crushing the zone-melted $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bar.

Fig. 4. SEM fractographs of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk specimens consolidated by vacuum hot pressing at 573 K and 0.7 GPa for 1 h: (a) $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -10N, (b) $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N.

Figure 6b shows the temperature dependence of the electrical conductivity. The samples show metallic behavior in which the conductivity decreases as the temperature increases from 300 K to 575 K. It is noticed that the electrical conductivity of nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ is twice that of monolithic nanostructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ in the temperature range from 300 K to 460 K. This is mainly attributed to the introduction of micro-sized $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ powder, which is believed to provide a fast carrier transportation network and improved electrical performance. The highest electrical conductivities at 308 K are for the $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N and $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -10N samples with values of $802 \Omega^{-1} \text{cm}^{-1}$ and $538 \Omega^{-1} \text{cm}^{-1}$, respectively.

The power factor of a TE material is usually calculated by the formula $\text{PF} = \alpha^2 \sigma$. The power factor of the $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk composite samples is plotted

against temperature in Fig. 6c. All samples show positive values in the whole temperature range, and $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N has the highest calculated power factor of all samples. The enhancement of the power factor of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N is driven by the enhancement of the electrical conductivity, which in turn is driven by the large ratio of micro-sized $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ particles. With the largest Seebeck coefficient and the highest electrical conductivity observed among all investigated samples, it has the highest power factor of $0.0027 \text{ W m}^{-1} \text{ K}^{-2}$ at 308 K. The temperature dependence of the thermal conductivity is presented in Fig. 6d. As evident from Fig. 6d, $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N samples have a significantly lower thermal conductivity than $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -10N and monolithic nanostructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ specimens in the entire measured temperature range. The lowest value of the thermal conductivity of this sample is 0.76 W/m-K , obtained at 339 K. The

Fig. 6. Temperature dependence of thermoelectric properties for nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk samples with different nanograin powder ratios.

Fig. 7. Variation of ZT as a function of temperature for nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk samples with different nanograin powder ratios.

achievement of such a low thermal conductivity may originate from the unique nano/microstructure shown in Fig. 4. The introduction of 40 wt.% nanograin powder can significantly contribute to the formation of additional grain boundaries and interfaces, thereby resulting in effective scattering of long-wave phonons. Based on this mechanism, the lowest thermal conductivity was obtained.

The variation of ZT as a function of temperature for the nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk specimens is shown in Fig. 7. For $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N, the highest ZT value in the entire temperature range is obtained, benefiting from the high power factor and low thermal conductivity. The ZT value is 1.07 at 308 K and increases with increasing temperature, reaching its maximum value of 1.19 at 400 K, and then decreases to 0.7 with further increase of the temperature up to 575 K. Compared with the $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -10N and monolithic nanostructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ samples, the ZT value of the $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N sample in the temperature range of 300 K to 450 K is enhanced by a factor of two to three by the introduction of 40 wt.% nanograin powder.

The dispersed nanograin powder in the nano/microstructured thermoelectric composite materials is designed to create extra grain-boundary areas which can increase phonon scattering and result in a decrease of the thermal conductivity. On the other hand, the existence of the micro-sized powder can provide a fast carrier transportation network which can increase the electrical conductivity.¹⁰ Therefore, the strongest enhancement of the ZT value is expected in the case of an optimal nano/microstructured powder ratio in the TE composite material. Figures 6 and 7 also display the TE properties of a nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk specimen, reported by Li et al.¹¹ The sample was likewise obtained by hot pressing of powders prepared

Table II. Thermoelectric properties and preparation methods of some typical nanocomposites

Nanocomposite	Highest ZT	ZT (>450 K)	Method	Ref.
$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$	1.15 at 350 K	0.2–0.4	BM + HP (200 MPa/430°C/2 h)	[11]
$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$	1.14 at 323 K	0.2–0.74	BM (300 rpm/10 h) + SPS (50 MPa/420°C/10 min)	[2]
$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$	1.15 at 350 K	0.63–0.9	BM (1200 rpm/5 h) + SPS (60 MPa/420°C/5 min)	[3]
$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$	1.0 at 300 K		BM (400 rpm/2 h) + SPS (50 MPa/450°C/5 min)	[4]
$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ + 4 wt.% Te	0.98 at 343 K	0.55–0.68	BM (400 rpm/12 h) + HP (60 MPa/290°C/1 h) + ECAE (753 K)	[5]
$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ + 7 wt.% BN	0.54 at 300 K		BM (1200 rpm/5 h) + HP (425 MPa/550°C/30 min)	[6]
$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ + 7 wt.% WO_3	0.75 at 300 K		BM (1200 rpm/5 h) + HP (425 MPa/550°C/30 min)	[6]
$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$	1.19 at 373 K	0.7–1.1	BM + HP (700 MPa/300°C/1 h)	This work

Experimental details are listed in parentheses. BM, ball-milling; SPS, spark plasma sintering; ECAE, equal channel angular extrusion; HP, hot pressing.

Fig. 8. Temperature dependence of ZT for $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk specimens prepared by different methods.

beforehand by milling of granular powders crushed from a zone-melted $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bar. The microstructure of this nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk specimen was composed of nanoparticles dispersed on top of micrograins with size of about $1\ \mu\text{m}$. Compared with the thermoelectric data of Ref. 11, our $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N sample has a significantly higher electrical conductivity (Fig. 6b) along with a lower thermal conductivity (Fig. 6d), probably due to an optimal distribution of micro-sized and nanostructured particles. Therefore, the measured ZT value of our $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N sample in the temperature range of 300 K to 500 K is higher than that of the samples reported in Ref. 11. It is also noticed that the difference of the ZT values increases with temperature in this temperature range, with the maximum difference reaching a factor of three at high temperatures.

Using ball milling and the hot pressing or spark plasma sintering method, several groups have prepared nanocomposite $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk samples.²⁻⁶ The thermoelectric properties and the preparation methods are summarized in Table II. The ZT values of consolidated $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ alloys are shown in Fig. 8 as a function of temperature, including the results of our present work for comparison. It is worth noting that the ZT values of our $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ -40N sample in the temperature range of 450 K to 575 K are 0.7 to 1.1 with an average value of 0.89. Compared with other works, our ZT values in the high-temperature region are higher than those of most other samples. The Bi-Sb-Te alloys are categorized as low-temperature TE materials whose utilization at temperatures higher than 450 K is limited due to their low TE performance. A good ZT value at high temperature is very important for power generation applications. Considering that there are no alternative Bi-Sb-Te materials with a similar high ZT value in this temperature range, the presently obtained ZT

characteristics indicate that nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk samples containing 40 wt.% nanograin particles have great potential to serve as a high-performance material for application in thermoelectric devices in the temperature range of 450 K to 575 K.

CONCLUSIONS

In this study, two kinds of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ powder with different particle and grain sizes were fabricated by a high-energy ball milling process. Powder mixtures at different weight ratios were consolidated by vacuum hot pressing to produce nano/microstructured bulk composite samples of identical chemical composition. No significant pores were observed in hot-pressed samples, which indicates that dense nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ bulk composite samples can be successfully fabricated by the combination of high-energy ball milling and vacuum hot pressing. A substantial difference in TE performance was observed for nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ with different nanograin powder ratios. From the measurements of the Seebeck coefficient, electrical resistivity, and thermal conductivity, a ZT value of up to 1.19 was achieved at 373 K for the sample containing 40% nanograin powder. The achieved high ZT value is attributed to the unique nano/microstructure, which can simultaneously improve the electrical performance and suppress the thermal conductivity effectively. As a result, this nano/microstructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ alloy holds great promise for use as a high-performance material for application in thermoelectric devices. The results also demonstrate the possibility of enhancing the ZT value of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ by introducing nonuniform microstructures, even without changing the chemical composition.

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