Thermoelectric Properties of Alumina-Doped Bi$_{0.4}$Sb$_{1.6}$Te$_3$ Nanocomposites Prepared through Mechanical Alloying and Vacuum Hot Pressing

Chung-Kwei Lin $^1$, May-Show Chen $^{2,3}$, Rong-Tan Huang $^4$, Yu-Chun Cheng $^4$ and Pee-Yew Lee $^{4,*}$

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Abstract: In this study, γ-Al$_2$O$_3$ particles were dispersed in p-type Bi$_{0.4}$Sb$_{1.6}$Te$_3$ through mechanical alloying to form γ-Al$_2$O$_3$/Bi$_{0.4}$Sb$_{1.6}$Te$_3$ composite powders. The composite powders were consolidated using vacuum hot pressing to produce nano- and microstructured composites. Thermoelectric (TE) measurements indicated that adding an optimal amount of γ-Al$_2$O$_3$ nanoparticles improves the TE performance of the fabricated composites. High TE performances with figure of merit (ZT) values as high as 1.22 and 1.21 were achieved at 373 and 398 K for samples containing 1 and 3 wt % γ-Al$_2$O$_3$ nanoparticles, respectively. These ZT values are higher than those of monolithic Bi$_{0.4}$Sb$_{1.6}$Te$_3$ samples. The ZT values of the fabricated samples at 298–423 K are 1.0–1.22; these ZT characteristics make γ-Al$_2$O$_3$/Bi$_{0.4}$Sb$_{1.6}$Te$_3$ composites suitable for power generation applications because no other material with a similarly high ZT value has been reported at this temperature range. The achieved high ZT value may be attributable to the unique nano- and microstructures in which γ-Al$_2$O$_3$ nanoparticles are dispersed among the grain boundary or in the matrix grain, as revealed by high-resolution transmission electron microscopy. The dispersed γ-Al$_2$O$_3$ nanoparticles thus increase phonon scattering sites and reduce thermal conductivity. The results indicated that the nano- and microstructured γ-Al$_2$O$_3$/Bi$_{0.4}$Sb$_{1.6}$Te$_3$ alloy can serve as a high-performance material for application in TE devices.

Keywords: γ-Al$_2$O$_3$/Bi$_{0.4}$Sb$_{1.6}$Te$_3$; thermoelectric material; mechanical alloying; nano/microstructure; vacuum hot pressing

1. Introduction

Thermoelectric (TE) materials directly convert thermal energy into electrical energy and vice versa and are considered clean energy converters [1]. For practical applications, the conversion efficiency of TE materials is often characterized according to a TE figure of merit, ZT, which is a dimensionless parameter and is conventionally defined as [1]:

$$ZT = (\alpha^2\sigma/k)T$$ (1)

where \( Z, \alpha, \sigma, \kappa, \) and \( T \) are figure of merit, Seebeck coefficient, electrical conductivity, thermal conductivity and T absolute temperature, respectively. A high ZT indicates high energy conversion efficiency. Clearly, an efficient TE material with high ZT requires high \( \alpha \), high \( \sigma \), and low \( \kappa \). However, satisfying these criteria in a single crystalline bulk material is difficult because these three parameters are interrelated. An increase in \( \alpha \) normally implies a decrease in \( \sigma \) (because of carrier density) and an increase in \( \sigma \) implies an increase in the electronic contribution to \( \kappa \) (i.e., the Wiedemann-Franz law); hence, increasing ZT in typical TE materials is extremely difficult. Therefore, materials with ZT higher than that of conventional materials are necessary in industry, and TE conversion efficiency can and must be enhanced by increasing or maintaining the Seebeck coefficient and electrical conductivity and reducing thermal conductivity. However, material classes that contain effective TE properties are rare [2–6].

Over the past 30 years, alloys based on Bi\(_2\)Te\(_3\) compounds have been extensively studied and optimized for their use as TE materials. Recently, numerous attempts have been made to increase the ZT of Bi\(_2\)Te\(_3\)-based TE materials [7–14]. An effective method is to increase the electrical conductivity and reduce the lattice thermal conductivity of TE materials by alloying, doping, or introducing complex crystal structures. Through such approaches, several Bi\(_2\)Te\(_3\)-based powders, such as CNTs/Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\), C\(_{60}\)/Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\), BN/Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\), WO\(_3\)/Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\), and PbTe/(Bi,Sb)\(_3\) [15–18], with various types of particles were consolidated into bulk shapes by using different consolidation methods. The results indicated that the thermal conductivity of Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) can be decreased by adding CNTs and C\(_{60}\) particles, which eventually increases ZT [15,16]. The thermal conductivity of BN/Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) and WO\(_3\)/Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) reduces slightly from 1.5 to 1.2 W m\(^{-1}\)K\(^{-1}\) when the volume fraction of BN and WO\(_3\) is increased from 0 to 7 vol %. However, ZT decreases because adding BN and WO\(_3\) considerably deteriorates the electrical conductivity [17]. Improving ZT of bulk PbTe/(Bi,Sb)\(_3\) samples was unsuccessful because adding PbTe particles drastically reduces the Seebeck coefficient [18]. From the aforementioned results, enhancing ZT clearly strongly depends on the optimal addition of second phase particles to Bi\(_2\)Te\(_3\)-based alloys.

Recently, Kim et al. reported the high ZT value of 1.5 was obtained at 323 K for p-type Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) alloy after doping 0.3 vol % \( \alpha \)-Al\(_2\)O\(_3\) nanoparticles [19]. Li et al. also found that with the introduction of the 1.0 vol % \( \gamma \)-Al\(_2\)O\(_3\) particles into n-type Bi\(_2\)Se\(_{0.3}\)Te\(_{2.7}\) thermoelectric alloy, Bi\(_2\)Se\(_{0.3}\)Te\(_{2.7}\) exhibits the highest ZT value of 0.99 at about 400 K, being 35% improvement compared to the monolithic Bi\(_2\)Se\(_{0.3}\)Te\(_{2.7}\) alloy [20]. These results indicated the thermoelectric properties of both p-type and n-type bismuth-antimony-tellurium alloys can be improved with addition of Al\(_2\)O\(_3\) particles. However, literature survey indicates the enhancement of p-type Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) alloy with the addition of \( \gamma \)-Al\(_2\)O\(_3\) particles has never been reported. Therefore, the \( \gamma \)-Al\(_2\)O\(_3\) and Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) were chosen in present study and the fabrication of \( \gamma \)-Al\(_2\)O\(_3\)/Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) composites were performed by mechanical alloying (MA) and vacuum hot pressing. The detailed microstructure and TE properties of samples with varying \( \gamma \)-Al\(_2\)O\(_3\) content were investigated. The results showed that the ZT values of the Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) alloy can be enhanced through the optimal addition of \( \gamma \)-Al\(_2\)O\(_3\) particles.

### 2. Experimental Procedure

Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) materials with varying contents of \( \gamma \)-Al\(_2\)O\(_3\) powder were prepared using a high-energy shaker ball mill installed inside an Ar-purified glove box in which the oxygen and moisture contents in an argon atmosphere were maintained at less than 1 ppm. To prepare Al\(_2\)O\(_3\)/Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) powders, a mixture of the elemental metallic powders Bi (99.999%), Sb (99.999%), Te (99.999%), and \( \gamma \)-Al\(_2\)O\(_3\) (approximately 99%, with particle size ranging from 0.2 to 7.5 \( \mu \)m with a mean particle size (\( d(0.5) \)) of approximately 1.39 \( \mu \)m) was mechanically alloyed using an SPEX 8016 shaker ball mill. The duration of the overall milling process was 2 h. The as-milled \( \gamma \)-Al\(_2\)O\(_3\)/Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) composite powders were consolidated in a vacuum hot pressing machine to prepare \( \gamma \)-Al\(_2\)O\(_3\)/Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) disks with diameter and thickness of 17 and 10 mm, respectively. Vacuum hot pressing was performed at 573 K under a pressure of 0.7 GPa for 30 min. The
as-milled powders and hot-pressed composite disks were examined using X-ray diffraction (XRD), differential scanning calorimetry, scanning electron microscope (SEM), and transmission electron microscopy (TEM). The TE properties were measured in the direction parallel to the hot-pressed direction. The hot-pressed bulk samples were then cut and polished into 8 × 6 × 6 mm bars. The thermoelectric properties of the hot-pressed samples were investigated using ALTEC-10001 (ITE, Ukraine). This equipment can simultaneously measure the Seebeck coefficient (α), electrical resistivity (σ), and thermal conductivity (κ) of thermoelectric materials from room temperature to 500 °C. The measurement is performed automatically, as well as the analysis of the measurements results, which excludes errors in operators work. ZT was calculated according to Equation (1).

3. Results and Discussion

Figure 1 shows the XRD patterns of the Bi_{0.4}Sb_{1.6}Te_{3} composite samples with 1 and 3 wt % γ-Al_{2}O_{3} additions after 2 h of milling. The diffraction peaks cited from the database of the (Bi_{0.2}Sb_{0.8})_{2}Te_{3} (JCPDS 072-1836) were also plotted with vertical lines in Figure 1 for comparison. All diffraction peak positions and (hkl) values were highly consistent with the standard diffraction data of the pure (Bi_{0.2}Sb_{0.8})_{2}Te_{3} phase (JCPDS 072-1836), implying that the (Bi_{0.2}Sb_{0.8})_{2}Te_{3} phase can be successfully prepared through high-energy ball milling of γ-Al_{2}O_{3}/Bi_{0.4}Sb_{1.6}Te_{3} composite powders. However, as seen in Figure 1, the Bragg peaks of γ-Al_{2}O_{3} are barely detectable in the XRD patterns of the composite powders of the alloy mixed with γ-Al_{2}O_{3} particles after 2 h of milling, which may be attributable to the low volume fraction of γ-Al_{2}O_{3} particles and their small crystalline size. Similar to the observations regarding the preparation of Al_{2}O_{3}/NiAl intermetallic–matrix composite in this study, Lin et al. [21] reported that for 5 vol % Al_{2}O_{3} additions in mechanically alloyed NiAl alloys, no Al_{2}O_{3} phase could be detected using XRD after 10 h of milling.

![XRD patterns](https://example.com/xrd_patterns.png)

**Figure 1.** XRD patterns of as-milled Bi_{0.4}Sb_{1.6}Te_{3} and γ-Al_{2}O_{3}-doped Bi_{0.4}Sb_{1.6}Te_{3} powders. (a) 1 wt % Al_{2}O_{3}; (b) 3 wt % Al_{2}O_{3}.
The Bi$_{0.4}$Sb$_{1.6}$Te$_3$ composite powders were subsequently consolidated into disks using vacuum hot pressing process; the corresponding XRD patterns are shown in Figure 2. All reflection peaks are attributable to the (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ phase. Compared with the as-milled composite powders, the peaks of the consolidated samples are narrow because of strain relaxation and grain growth in the Bi$_{0.4}$Sb$_{1.6}$Te$_3$ nanograin powders. SEM was used to examine the cross-sectional view of γ-Al$_2$O$_3$/Bi$_{0.4}$Sb$_{1.6}$Te$_3$ disks after vacuum hot pressing (Figure 3). Although several γ-Al$_2$O$_3$ nanoparticles tend to agglomerate each other, most fine γ-Al$_2$O$_3$ particles were distributed uniformly within the Bi$_{0.4}$Sb$_{1.6}$Te$_3$ matrix. The size distribution ranged from 0.3 µm to less than 50 nm, which is the resolution limit of the microscope. The composition of the particles was determined to be that of pure γ-Al$_2$O$_3$ through energy-dispersion X-ray spectrometry analysis. Significant pores were not observed in the cross-sectional view (Figure 3) at 20,000× magnification, indicating that highly dense Bi$_{0.4}$Sb$_{1.6}$Te$_3$ bulk samples can be successfully fabricated using vacuum hot pressing. The densities of the Bi$_{0.4}$Sb$_{1.6}$Te$_3$ bulk sample measured using the Archimedean method were 6.70 and 6.71 g/cm$^3$ for 1 and 3 wt % γ-Al$_2$O$_3$/Bi$_{0.4}$Sb$_{1.6}$Te$_3$ samples, respectively, yielding corresponding relative densities of 93.2% and 93.6%. To observe the microstructure within the γ-Al$_2$O$_3$/Bi$_{0.4}$Sb$_{1.6}$Te$_3$ composites, Bi$_{0.4}$Sb$_{1.6}$Te$_3$ with 1 wt % γ-Al$_2$O$_3$ additions (Figure 3) was examined using TEM; a TEM bright-field image is shown in Figure 4. Two types of γ-Al$_2$O$_3$ distributions were observed in the composites; most γ-Al$_2$O$_3$ nanoparticles smaller than 10 nm in size were homogeneously dispersed along the grain boundary. A small quantity of the γ-Al$_2$O$_3$ nanoparticles with irregular shapes and sizes ranging from 60 to 400 nm were embedded within the Bi$_{0.4}$Sb$_{1.6}$Te$_3$ matrix. A similar microstructure was reported for the nanocomposites of CoSb$_3$/TiO$_2$ [13] and ZrNiSn/ZrO$_2$ [14].

Figure 2. XRD patterns of γ-Al$_2$O$_3$-doped Bi$_{0.4}$Sb$_{1.6}$Te$_3$ bulk specimens. (a) 1 wt % Al$_2$O$_3$; (b) 3 wt % Al$_2$O$_3$.
TEM images of the consolidated 1 wt % Bi$_{0.4}$Sb$_{1.6}$Te$_3$ matrix. A similar microstructure was reported for the nanocomposites of CoSb$_3$/TiO$_2$ [13] nanoparticles with irregular shapes and sizes ranging from 60 to 400 nm were embedded within the γ and ZrNiSn/ZrO$_2$ [14].

At 373 K for 0, 1 and 3 wt % after peaking, it starts decreasing with rising temperatures because of the thermal excitation of extrinsic charge carriers at high temperatures. The maximum value of the Seebeck coefficient initially increases rapidly at 300–375 K, which is consistent with the Mott formula [22], but after peaking, it starts decreasing with rising temperatures because of the thermal excitation of extrinsic charge carriers at high temperatures. The maximum value of the Seebeck coefficient is 242, 234 and 229 μV/K at 373 K for 0, 1 and 3 wt % γ-Al$_2$O$_3$/Bi$_{0.4}$Sb$_{1.6}$Te$_3$ samples, respectively. Figure 5b shows the temperature dependence of electrical conductivity. The samples exhibited a metallic dependence: conductivity gradually decreased as temperature increased from 300 to 473 K. Electrical conductivity of γ-Al$_2$O$_3$/Bi$_{0.4}$Sb$_{1.6}$Te$_3$ composite decreases as γ-Al$_2$O$_3$ particles increases. The highest electrical conductivities at 300 K were observed for 1 and 3 wt % γ-Al$_2$O$_3$/Bi$_{0.4}$Sb$_{1.6}$Te$_3$ samples, with values of 1080 and 895 Ω$^{-1}$ cm$^{-1}$, respectively. The power factor (PF) of TE materials is usually calculated as PF = α$^2$σ; Figure 5c is a graph of the PF of Bi$_{0.4}$Sb$_{1.6}$Te$_3$ bulk composite samples versus the temperature. All samples showed positive values in the whole temperature range of measurement, indicating p-type semiconducting behavior. The 1 wt %
\(\gamma\)-Al\(_2\)O\(_3\)/Bi\(_{1.6}\)Sb\(_{1.6}\)Te\(_3\) samples exhibited the highest PF (5.4 mWm\(^{-1}\)·K\(^{-2}\) at 298 K). The temperature dependence of thermal conductivity is shown in Figure 5d. The 3 wt % \(\gamma\)-Al\(_2\)O\(_3\)/Bi\(_{1.6}\)Sb\(_{1.6}\)Te\(_3\) samples have significantly lower thermal conductivity than the 1 wt % \(\gamma\)-Al\(_2\)O\(_3\)/Bi\(_{1.6}\)Sb\(_{1.6}\)Te\(_3\) samples in the whole temperature range. The lowest value of thermal conductivity for this sample was 1.12 W/mK, which was obtained at 373 K.

![Figure 5](image-url)  
**Figure 5.** Temperature dependence of the TE properties for the \(\gamma\)-Al\(_2\)O\(_3\)/Bi\(_{1.6}\)Sb\(_{1.6}\)Te\(_3\) specimens: (a) Seebeck coefficient; (b) electrical resistivity; (c) PF; and (d) thermal conductivity.

The variation of ZT as a function of temperature for the \(\gamma\)-Al\(_2\)O\(_3\)/Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) bulk specimens is shown in Figure 6.

![Figure 6](image-url)  
**Figure 6.** Variation of ZT as a function of temperature for \(\gamma\)-Al\(_2\)O\(_3\)/Bi\(_{0.4}\)Sb\(_{1.6}\)Te\(_3\) bulk samples.
For the 1 wt % $\gamma$-Al$_2$O$_3$/Bi$_{0.4}$Sb$_{1.6}$Te$_3$ sample, a high ZT value can be obtained within the entire temperature range because of high PFs and low thermal conductivity; ZT at 300 K is 1.17 and increases with increasing temperature, peaking at 1.22 at 323 and 348 K, before subsequently decreasing to 0.86 at 473 K. For the 3 wt % $\gamma$-Al$_2$O$_3$/Bi$_{0.4}$Sb$_{1.6}$Te$_3$ composite sample (Figure 6), ZT at 300 K is 1.0 and increases with increasing temperature, peaking at 1.21 at 373 and 398 K, before subsequently decreasing to 0.93 when the temperature increases to 473 K.

Several studies have reported the preparation of nanocomposite Bi$_{0.4}$Sb$_{1.6}$Te$_3$ bulk samples [15–17,22–26] through BM and hot pressing or spark plasma sintering (SPS). TE properties and preparation methods are listed in Table 1. The ZT values of the consolidated Bi$_{0.4}$Sb$_{1.6}$Te$_3$ alloys as a function of temperature are plotted in Figure 7, and the results of this study are included for comparison.

![Figure 7. Temperature dependence of ZT of the Bi$_{0.4}$Sb$_{1.6}$Te$_3$-based bulk specimens prepared through various methods.](image)

In this study, ZT of the $\gamma$-Al$_2$O$_3$/Bi$_{0.4}$Sb$_{1.6}$Te$_3$ sample at 298–473 K were 0.86–1.22 (1 wt % $\gamma$-Al$_2$O$_3$) and 0.93–1.21 (3 wt % $\gamma$-Al$_2$O$_3$), with an average value of 1.10 for both samples. Compared with other studies, the ZT obtained in this study at high temperatures are higher. Advances in ZT can be achieved through considerable reductions in thermal conductivities through phonon scattering. Incorporating nanoparticles into TE materials to act as additional phonon scattering sites inside the grain boundary or matrix regions has recently been demonstrated effectively increase ZT [27–29]. According to this approach, for nano- and microstructured TE composite materials shown in Figure 4, the dispersed $\gamma$-Al$_2$O$_3$ nanoparticles are expected to create an additional grain boundary and interfacial area, which increases phonon scattering and decreases thermal conductivity. To further verify this argument, the temperature dependence of lattice thermal conductivity ($\kappa_l$) and electronic thermal conductivity ($\kappa_e$) of present $\gamma$-Al$_2$O$_3$/Bi$_{0.4}$Sb$_{1.6}$Te$_3$ samples are shown in Figure 8. $\kappa_l$ was calculated by subtracting the electronic thermal conductivity $\kappa_e$ from $\kappa$, and $\kappa_e$ is calculated by the Wiedemann–Franz relation, $\kappa_e = L\sigma T$ (where $L = 2.0 \times 10^{-8} \text{ V}^2/\text{K}^2$ is Lorenz number, $\sigma$ is electrical conductivity, and $T$ is absolute temperature) [30].
Table 1. TE properties and preparation methods of typical Bi$_{0.4}$Sb$_{1.6}$Te$_3$-based nanocomposites.

<table>
<thead>
<tr>
<th>Nanocomposite</th>
<th>Highest ZT</th>
<th>ZT (&gt;400 K)</th>
<th>Method$^{a,b}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$<em>{0.4}$Sb$</em>{1.6}$Te$_3$</td>
<td>1.15 at 350 K</td>
<td>0.2-0.4</td>
<td>BM + HP (200 MPa/430 C/2 h)</td>
<td>[24]</td>
</tr>
<tr>
<td>Bi$<em>{0.4}$Sb$</em>{1.6}$Te$_3$</td>
<td>1.14 at 323 K</td>
<td>0.2-0.74</td>
<td>BM (300 rpm/10 h) + SPS (50 MPa/420 C/10 min)</td>
<td>[25]</td>
</tr>
<tr>
<td>Bi$<em>{0.4}$Sb$</em>{1.6}$Te$_3$</td>
<td>1.15 at 350 K</td>
<td>0.63-0.9</td>
<td>BM (1200 rpm/5 h) + SPS (60 MPa/420 C/5 min)</td>
<td>[23]</td>
</tr>
<tr>
<td>Bi$<em>{0.4}$Sb$</em>{1.6}$Te$_3$</td>
<td>1.0 at 300 K</td>
<td>-</td>
<td>BM (400 rpm/2 h) + SPS (50 MPa/450 C/5 min)</td>
<td>[26]</td>
</tr>
<tr>
<td>Bi$<em>{0.4}$Sb$</em>{1.6}$Te$_3$ + 4 wt % Te</td>
<td>0.98 at 343 K</td>
<td>0.55-0.68</td>
<td>BM (400 rpm/12 h) + HP (60 MPa/290 C/1 h) + ECAE (753 K)</td>
<td>[22]</td>
</tr>
<tr>
<td>Bi$<em>{0.4}$Sb$</em>{1.6}$Te$_3$ + 1 wt % CNT</td>
<td>1.08 at 323 K</td>
<td>0.52-0.92</td>
<td>ZM + BM + HP (27.6 MPa/440 C/10 min)</td>
<td>[15]</td>
</tr>
<tr>
<td>Bi$<em>{0.4}$Sb$</em>{1.6}$Te$<em>3$ + 1.5 wt % C$</em>{60}$</td>
<td>1.15 at 375 K</td>
<td>0.79-1.08</td>
<td>BM (500-2220 rpm/30 min) + sinter (5 kbar/400 C) + annealing (300 C/2 h)</td>
<td>[16]</td>
</tr>
<tr>
<td>Bi$<em>{0.4}$Sb$</em>{1.6}$Te$_3$ + 7 wt % BN</td>
<td>0.54 at 300 K</td>
<td>-</td>
<td>BM (1200 rpm/5 h) + HP (425 MPa/550 C/30 min)</td>
<td>[17]</td>
</tr>
<tr>
<td>Bi$<em>{0.4}$Sb$</em>{1.6}$Te$_3$ + 7 wt % WO$_3$</td>
<td>0.75 at 300 K</td>
<td>-</td>
<td>BM (1200 rpm/5 h) + HP (425 MPa/550 C/30 min)</td>
<td>[17]</td>
</tr>
<tr>
<td>Bi$<em>{0.4}$Sb$</em>{1.6}$Te$_3$ + 1 wt % Al$_2$O$_3$</td>
<td>1.22 at 340 K</td>
<td>0.86-1.12</td>
<td>BM + HP (700 MPa/300 C/1 h)</td>
<td>This work</td>
</tr>
<tr>
<td>Bi$<em>{0.4}$Sb$</em>{1.6}$Te$_3$ + 3 wt % Al$_2$O$_3$</td>
<td>1.21 at 398 K</td>
<td>0.93-1.21</td>
<td>BM + HP (700 MPa/300 C/1 h)</td>
<td>This work</td>
</tr>
</tbody>
</table>

$a$: BM: ball milling; SPS: spark plasma sintering; ECAE: equal channel angular extrusion; $b$: Experimental details are listed in parentheses.
Accordingly, the lattice thermal conductivity $\kappa_l$ decreased with the addition of $\gamma$-Al$_2$O$_3$ particles, while the electronic thermal conductivity $\kappa_e$ decreased less drastically than did the lattice thermal conductivity. It is thus concluded that the decrease in thermal conductivity with increasing the amount of $\gamma$-Al$_2$O$_3$ particles was mainly due to the reduction in lattice thermal conductivity. Bi-Sb-Te alloys are categorized as low-temperature TE materials, and their use at temperatures higher than 400 K is limited because of low TE performance. A satisfactory ZT value at high temperatures is vital for power generation. Because no other Bi-Sb-Te material with a similarly high ZT in this temperature range has been reported, Bi$_{0.4}$Sb$_{1.6}$Te$_3$ bulk samples containing $\gamma$-Al$_2$O$_3$ nanoparticles were dispersed along the grain boundary or inside the matrix grain, as revealed through high-resolution TEM. The dispersed $\gamma$-Al$_2$O$_3$ nanoparticles thus increase phonon scattering sites and reduce thermal conductivity. The ZT values of these samples at 373 and 398 K for samples containing 1 and 3 wt % were achieved at 1.22 and 1.21.

4. Conclusions

Through MA and vacuum hot pressing, $p$-type $\gamma$-Al$_2$O$_3$/Bi$_{0.4}$Sb$_{1.6}$Te$_3$ composites were fabricated. No significant pores were observed in the hot-pressed samples, indicating that highly dense Bi$_{0.4}$Sb$_{1.6}$Te$_3$ bulk samples can be successfully prepared using the proposed approach. The influence of the alumina content on TE properties was measured in the temperature range 300–473 K. The measured Seebeck coefficient, electrical resistivity, and thermal conductivity indicate that adding an optimal amount of $\gamma$-Al$_2$O$_3$ particles improves the TE performance of the $\gamma$-Al$_2$O$_3$/Bi$_{0.4}$Sb$_{1.6}$Te$_3$ composites. High TE performance with ZT as high as 1.22 and 1.21 were achieved at 373 and 398 K for samples containing 1 and 3 wt % $\gamma$-Al$_2$O$_3$ particles. These ZT values are higher than those of several reported monolithic Bi$_{0.4}$Sb$_{1.6}$Te$_3$ samples prepared through BM and hot pressing or SPS. The achieved high ZT value may be attributable to the unique nano- and microstructures in which $\gamma$-Al$_2$O$_3$ nanoparticles were dispersed along the grain boundary or inside the matrix grain, as revealed through high-resolution TEM. The dispersed $\gamma$-Al$_2$O$_3$ nanoparticles thus increase phonon scattering sites and reduce thermal conductivity. The ZT values of these samples at 298–423 K are 1.0–1.22. Such ZT characteristics render $\gamma$-Al$_2$O$_3$/Bi$_{0.4}$Sb$_{1.6}$Te$_3$ suitable for power generation applications because other materials with similarly high ZT are yet to be reported in this temperature range.
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Author Contributions: Chung-kwei Lin and May-Show Chen carried out the sample preparation and data analysis work. Rong-Tan Huang conducted the SEM and TEM study. The measurement of thermoelectric properties was performed by Yu-Chun Cheng. Pee-Yew Lee designs the experimental procedure and prepared the manuscript of the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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