Influence of P on Microstructure and Thermoelectric Property of Sintered (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ Alloy

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A combination of mechanical alloying and pulse discharge sintering (MA-PDS) was employed to synthesize the bulk (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ alloys with the P addition up to 2.0 mass%. The effect of P on the microstructure and thermoelectric performance of the compacts were investigated. The added P exists in the alloyed powders and compacts in the form of second phase particles. The dispersed P particles were found to decrease the size of (Bi, Sb)$_2$Te$_3$ crystallites and inhibit the densification of the alloyed powders. When the P content $\geq$1.0 mass%, (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$/P nanocomposites were developed by the MA-PDS process. Inclusion of a small fraction of P (0.1 mass%) is harmless to the thermoelectric performance of the p-type (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ alloy. In the samples with high P contents, in particular, $\geq$1.0 mass%, however, the increase in the electrical resistivity is much greater than the decrease in the thermal conductivity, finally giving rise to degradation of the room-temperature figure of merit.

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1. Introduction

Significant efforts have been made in the past three decades to develop the high performance Bi$_3$Te$_3$-based thermoelectric (TE) materials for applications as heat pumps. Improvemont of TE performance of these materials requires a high figure of merit, defined by $Z = S^2/\kappa$ and $\sigma$, where $S$, $\sigma$, and $\kappa$ are respectively the Seebeck coefficient, electrical conductivity and thermal conductivity. The product $S^2/\kappa$ is usually referred to as thermoelectric power factor. Thus, the best TE material should have a good combination of high Seebeck coefficient, electrical conductivity and simultaneously low thermal conductivity. Since all the three quantities that enter the figure of merit are not independent of each other, the task of optimization appears to be difficult. Both Seebeck coefficient and electrical conductivity are a function of the density of the charge carriers. The thermal conductivity has two parts, the lattice thermal conductivity $\kappa_l$ and the electronic thermal conductivity $\kappa_e$. The lattice part is roughly independent of the carrier concentration while the electronic part is directly related to the electrical conductivity. So far, there are two general approaches to optimize the figure of merit by either maximizing the power factor via suitable doping or by minimizing the thermal conductivity through deliberately adding a controlled amount of inert phase particles.

As the (Bi, Sb)$_2$Te$_3$ crystal is intrinsically anisotropic in TE properties, say, the room-temperature figure of merit of the p-type (Bi, Sb)$_2$Te$_3$ alloy is much larger along the cleavage plane than in the perpendicular direction, a lot of previous researchers have focused on the fabrication of single crystals with a special well-defined crystallographic orientation in order to achieve the optimum TE properties. Alternatively, recent studies have indicated that the (Bi, Sb)$_2$Te$_3$ polycrystals synthesized by powder processing can also exhibit high values of room-temperature figure of merit that are close to or higher than 3 × 10$^{-3}$ K$^{-1}$. In a previous work, we introduced a new processing technique, mechanical alloying and pulse discharge sintering (MA-PDS), to fabricate the bulk (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ alloys with various Sb alloying contents. It was found that the room-temperature figure of merit of (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ alloys is optimized at $x = 0.8$. In the device application, a thin coating layer needs to be made on the surface of TE materials by electroless plating. The purpose is to prevent the diffusion of atoms from the solder into the p and n legs when the two legs are integrated with the electrode. In the commonly used plating solutions, say Ni–Co–P, Ni–Fe–P and Ni–Mn–P, P is an important constituting element so that the influence of P on the thermoelectric performance is a serious consideration. In this work, we selected (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ as the experimental material. The effect of P on the microstructure and thermoelectric performance of the (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ material is the subject of the current study. The experimental samples with various P additions were prepared by means of the MA-PDS process.

2. Experimental Procedures

5N elemental powders of Bi (–80 mesh), Te (–100 mesh) and Sb (–100 mesh) as well as the additive, P (–99% purity), were selected as the starting materials for mechanical alloying (MA). MA was carried out in a vibratory ball mill under the fixed vibration frequency of 25 Hz. The stainless steel vial with ZrO$_2$ lining and ZrO$_2$ balls of 15.5 mm diameter were utilized. The milling was conducted in argon atmosphere and at a ball-to-powder mass ratio of 75:1 for continuous 200 h. All the powder handling was done in an argon-filled glove box, in which the oxygen level is kept below 5 ppm, to prevent the powders from oxidation.

The mechanically alloyed powders were sieved and the powders under 28 μm were consolidated into bulk in graphite dies by pulse discharge sintering (PDS). The compaction was...
carried out in a DR. SINTER SPS-1020 system at 50 MPa, 618 K and for 10 min in vacuum (10^{-3} Pa). The resulting compact is a column, measuring 5–10 mm height and 20 mm diameter.

Both the as-milled powders and the as-sintered compacts were followed by X-ray diffraction (XRD) in a Philips X’Pert-MPD system (Cu Kα) over the 2θ span of 25–65°. Scanning electron microscope (SEM) observations were made on the fracture surfaces of the compacts along the pressing direction using a Philips XL-30S system. Transmission electron microscope (TEM) observations on the compacts were performed on a JEM 3010 system with an EDX attachment. The system was operated at an accelerating voltage of 300 kV. The thin foils for TEM observations were prepared by the ion thinning technique. Prior to ion milling, the sample pre-treatment followed the conventional cutting, polishing and dimpling. Samples in the forms of pillar and disk were cut from the columnar compacts by electro-discharge machine (EDM) for Seebeck coefficient, electrical resistivity, and thermal diffusivity measurements. All the measurements were made with the heat/current flow perpendicular to the pressing direction. Both the Seebeck coefficient (S) and the electrical resistivity (ρ = 1/σ) were determined from room temperature to 433 K on an ULVAC ZEM-1 apparatus in He gas. The temperature gradients applied on the two ends of the pillar sample for Seebeck coefficient measurements were 10–30 K. The estimated error for both the Seebeck coefficient and the resistivity data was no more than 3%. Specific heat capacity (c_p) was determined using a differential scanning calorimeter (DSC, Seiko EXSTAR DSC6200). A pure sapphire disk (about 10 mg) was used as the standard sample. The thermal diffusivity (κd) was determined at room temperature using a Laser Flash TC-7000 Thermal Constant Analyzer in vacuum. The thermal conductivity (κ) was calculated from the experimental density (d), heat capacity (c_p) and thermal diffusivity (κd) values by

\[ \kappa = d \times c_p \times \kappa_d. \]

3. Results and Discussion

3.1 Microstructures of the bulk (Bi_{0.2}Sb_{0.8})_2Te_3 samples with various P additions synthesized by MA-PDS

As the first step, the alloyed powders were prepared by mechanical alloying from the elemental powders. After milling for 200 h, the XRD patterns contain only the peaks of a trigonal (Bi, Sb)_2Te_3 phase in the mechanically alloyed powders which contain the P content up to 2.0 mass% (Fig. 1). The diffraction lines were broadened because of the fine crystallites and the introduction of microstrain during MA. Also, it was noted that the diffraction peaks were not obviously shifted by P addition.

The MA powders were subsequently compacted into bulk by PDS. Upon sintering, the Z-axis displacement along the pressing direction was recorded in Fig. 2, by which the sinterability of the alloyed powders may be evaluated. Note that the load was kept at 16 MPa below 473 K. At 473 K, the pressure was raised to 50 MPa and the load was kept at 50 MPa until the whole sintering finished. It is seen that the recorded displacement data for the unadded sample is almost saturated after 550 K, while for the P-added sample the data keeps going up with temperature, especially as T > 500 K. No saturation was observed up to 618 K. This suggests that the P addition hinders densification of the alloyed powders, resulting in a loose compact under the current sintering conditions.

The sintered compacts were followed by XRD in Fig. 3. All the samples keep the single-phase state. There is no evident peak position shift as the P content changes. The average lattice parameters of the (Bi, Sb)_2Te_3 phase, quantified from the peak positions of 205 and 1019 lines, were 0.429 nm for a and 3.043 nm for c. It is noteworthy that when the P content \geq 1.0 mass%, the diffraction lines were remarkably broadened relative to those of the mother alloy, indicating the grain size refinement in the compacts. Due to the data scattering, the
separation of the average grain size and the microstrain using the well-known Cauchy method failed to result in any convincing result. Neglecting the contribution of microstrain to the 1010 peak broadening, the Scherrer equation yields a lower limit of 68 nm on the average grain size of the sample with 1.0 mass% P.

SEM observations were performed on the fracture surfaces of the compacts in Fig. 4. From the cleavage plane of the SEM image, the average crystal size of the unadded sample was estimated to be about 300 nm. A small fraction of P addition (≤0.1 mass%) does not affect much the morphology of the fracture surfaces. In the samples with the P content ≥0.2 mass%, SEM cannot yield useful information about the crystal morphology and size. Moreover, a number of open pores were observed in the compacts with high P contents, which make the compacts porous and mechanically weak.
A bright field TEM image of the (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ sample was shown in Fig. 5. In addition to the large equiaxed crystallites with the average size of about 400 nm, many small particles, less than 100 nm in diameter, were identified. These small particles are preferably present at the boundaries of large crystallites. The cause for this structural inhomogeneity is unknown at the present time. A further EDX analysis failed to reveal large difference in the chemical composition between the large crystallites and small particles. Nor did we detect oxygen in the small particles, thus excluding the possibility of oxides. The microstructural inhomogeneity is still kept when 0.5 mass% of P was added (Fig. 6). However, as shown in Fig. 7, with 1.0 mass% P addition, the grains become fine and homogeneous. The average grain diameter is about 65 nm, which is consistent with the result (68 nm) estimated from 1010 line by the well-known Scherrer formula. The existence of P was not detected by electron diffraction. As illustrated in Fig. 8, when the P content was increased to 3.0 mass%, the grain size was further decreased. The average size is only about 20 nm. In this sample, the P particles were clearly identified by EDX as indicated by the arrows in the image. In this way, it is concluded that dispersion of P did occur in the compacts. A large amount of P addition (≥1.0 mass%) can hinder the grain growth, giving rise to (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$/P nanocomposites. Theoretically, the maximum grain size $D_{\text{max}}$ of the alloy with dispersion of second phase particles is limited to $4r/3f$, $r$ and $f$ are respectively the average radius and the volume fraction of the dispersed second phase.\(^{11}\)

### 3.2 Transport properties of the bulk (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ samples with various P additions made by MA-PDS

The Seebeck coefficient of the bulk (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ samples with or without phosphorous additions was studied from room temperature to 433 K in Fig. 9. In the temperature range studied, all the samples exhibit p-type semiconduction. It seems that the P addition has a little influence on the Seebeck coefficient values.

The temperature dependence of electrical resistivity of the bulk (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ samples with or without P additions was presented in Fig. 10. It is seen that addition of P with the content ≤0.1 mass% has little influence on the resistivity and its
Table 1  Room-temperature properties of the bulk (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ samples with various P additions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d$ ($10^3$ Mg/m$^3$)</th>
<th>$\kappa_a$ ($10^{-6}$ m$^2$/s)</th>
<th>$\kappa$ ($=d\cdot c_p\cdot \kappa_a$) W/Km$^2$</th>
<th>$S^2\sigma$ ($10^{-3}$ W/K$^2$m)</th>
<th>$Z$ ($=S^2\sigma/\kappa$) 10$^{-3}$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>unadded</td>
<td>6.67</td>
<td>0.701</td>
<td>0.92</td>
<td>3.01</td>
<td>3.27</td>
</tr>
<tr>
<td>0.05 mass%P</td>
<td>6.64</td>
<td>0.675</td>
<td>0.89</td>
<td>2.89</td>
<td>3.25</td>
</tr>
<tr>
<td>0.1 mass%P</td>
<td>6.63</td>
<td>0.663</td>
<td>0.87</td>
<td>3.02</td>
<td>3.47</td>
</tr>
<tr>
<td>0.2 mass%P</td>
<td>6.59</td>
<td>0.640</td>
<td>0.85</td>
<td>1.72</td>
<td>2.02</td>
</tr>
<tr>
<td>0.5 mass%P</td>
<td>6.54</td>
<td>0.605</td>
<td>0.83</td>
<td>1.68</td>
<td>2.02</td>
</tr>
<tr>
<td>1.0 mass%P</td>
<td>6.34</td>
<td>0.510</td>
<td>0.70</td>
<td>0.88</td>
<td>1.26</td>
</tr>
<tr>
<td>1.5 mass%P</td>
<td>6.22</td>
<td>0.420</td>
<td>0.58</td>
<td>0.73</td>
<td>1.26</td>
</tr>
<tr>
<td>2.0 mass%P</td>
<td>6.09</td>
<td>0.397</td>
<td>0.56</td>
<td>0.56</td>
<td>1.0</td>
</tr>
</tbody>
</table>

variation with temperature. In the temperature range studied, the mother sample and the added samples with the P content $\leq$0.5 mass% show a linear increase in resistivity with temperature. In the case of composites with higher P contents ($\geq$1.0 mass%), however, a contrary tendency was observed, i.e., the electrical resistivity decreases linearly with temperature. At a given temperature, the samples with the P content $\leq$0.1 mass% exhibit almost the same values of resistivity. When the P content $\geq$0.5 mass%, the resistivity was markedly enhanced and the higher the P content the larger the resistivity. The observed high resistivity at the P content $\geq$0.2 mass% is probably caused by the refined grain size, the pores and the dispersed fine P particles in the compacts.

Figure 11 illustrated the specific heat capacity $c_p$ of the (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ samples with or without P additions. From 273 to 373 K, all the samples showed an increased $c_p$ with temperature. One can see that addition of P up to 0.1 mass% yields almost the same $c_p$ values as the mother alloy. For the composites with the P content $\geq$0.5 mass%, $c_p$ was increased. The enhanced $c_p$ is presumably caused by the grain size refinement in the compact as a result of P addition.$^{12,13}$

Table 1 lists the room-temperature properties of the (Bi$_{0.2}$Sb$_{0.8}$)$_2$Te$_3$ samples with or without P additions. Obviously, addition of P decreases the density and thermal diffusivity of the compacts. The calculated thermal conductivity shows a monotonic decrease with the P content. At 2.0 mass%P, the thermal conductivity is as low as 0.56 W/Km, which is 39% smaller than that of the unadded. It is considered that the grain size refinement in the compacts contributes to the reduced thermal conductivity.

The figure of merit estimated from the experimental power factor and thermal conductivity values was also summarized in Table 1. It is seen that as the P content $\leq$0.1 mass% the samples show the figure of merit, which is in the same magnitude as that of the mother alloy. In other words, addition
of P with the level ≤0.1 mass% does no harm to the thermoelectric performance. A large amount of P addition, however, remarkably deteriorates the figure of merit because in the heavily added samples the increase in the electrical resistivity is much greater than the decrease in the thermal conductivity. This study is of practical significance because the P-containing plating solution is usually used in the device applications of the current Bi$_2$Te$_3$-based thermoelectric materials. Diffusion of a small fraction of P (≤0.1 mass%) into the p-type material has been shown to have no adverse effect on the thermoelectric performance of the material.

4. Conclusion

Bulk (Bi$_{1.2}$Sb$_{0.8}$)$_2$Te$_3$ samples with various P additions were synthesized by mechanical alloying followed by pulse discharge sintering. The effect of P on the microstructure and thermoelectric performance of the sintered samples were systematically investigated. It was shown that the added P existed in the compacts as second phase particles. The dispersed P particles hinder the growth of (Bi, Sb)$_2$Te$_3$ crystallites and inhibit densification of the alloyed powders during sintering. As the P content ≥1.0 mass%, (Bi$_{1.2}$Sb$_{0.8}$)$_2$Te$_3$/P nanocomposites were developed by the current MA-PDS process. A high thermoelectric performance was obtained as the P content ≤0.1 mass%. A further increase in the P content, however, gives rise to a degraded room-temperature figure of merit because in the case of the samples with the P content ≥0.2 mass% the increase in the electrical resistivity is much greater than the decrease in the thermal conductivity.

REFERENCES