Effect of Mechanical Alloying on Thermal Conductivity of Bi$_2$Te$_3$–Sb$_2$Te$_3$

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A Bi$_2$Te$_3$–Sb$_2$Te$_3$ solid solution was prepared by mechanical alloying (MA) followed by hot pressing (HP). X-ray diffraction indicated that all samples which were removed at a depth below the surface of approximately 1 mm were single-phase and isotropic Bi$_2$Te$_3$–Sb$_2$Te$_3$ solid solution. Reduction of the phonon thermal conductivity as a result of the fine-grains caused by MA predominated over the solid-solution effect caused by melt growth. The Seebeck coefficient and electrical and thermal conductivities fluctuated between those for (Bi$_2$Te$_3$)$_{0.15}$(Sb$_2$Te$_3$)$_{0.85}$ and (Bi$_2$Te$_3$)$_{0.1}(Sb$_2$Te$_3$)$_{0.8}$ at room temperature. A (Bi$_2$Te$_3$)$_{0.15}$(Sb$_2$Te$_3$)$_{0.85}$ solid solution with a dimensionless figure of merit $ZT = 1.16$ at 367 K was obtained by MA–HP. These results indicate that the maximum $ZT$ of the Bi$_2$Te$_3$–Sb$_2$Te$_3$ solid solution obtained by MA–HP was not restricted to a composition of (Bi$_2$Te$_3$)$_{0.25}$(Sb$_2$Te$_3$)$_{0.75}$, which has the minimum phonon thermal conductivity in the case of melt growth.

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1. Introduction

Bi$_2$Te$_3$–Sb$_2$Te$_3$ solid solutions are the best $p$-type thermoelectric semiconductors near room temperature, and are widely used for refrigerators and research generators.$^{1,2}$ They are eco-materials and recover exhaust waste heat well at near room temperature.$^3$ The performance of a thermoelectric semiconductor is defined by the dimensionless figure of merit $ZT$:

$$ZT = \alpha^2 \sigma / k T$$

where $\alpha$, $\sigma$, $k$, and $T$ are the Seebeck coefficient (V K$^{-1}$), electrical conductivity (S m$^{-1}$), thermal conductivity ($W m^{-1} K^{-1}$), and absolute temperature ($K$), respectively.

The thermal conductivity $k$ of a thermoelectric material is generally the sum of the phonon and carrier components, as shown in eq. (2)$^3$:

$$k_{total} = k_{phonon} + k_{carrier} = k_{phonon} + \sigma \kappa L T$$

where $k_{total}$, $k_{phonon}$, $k_{carrier}$, and $L$ are the total, phonon, and carrier thermal conductivities, and Lorenz number, respectively.

A Bi$_2$Te$_3$–Sb$_2$Te$_3$ solid solution has a rhombohedral crystal structure with the $R3m$ space group, and anisotropic physical and thermoelectric properties.$^4$ Bi$_2$Te$_3$–Sb$_2$Te$_3$ solid-solution materials are anisotropic. The anisotropies of the electrical and phonon thermal conductivities of Bi$_2$Te$_3$ are respectively estimated to be $\sigma_{//}/\sigma_{\perp} \approx 3$ and $k_{//}/k_{\perp} \approx 0.47$, for the values parallel and perpendicular to the $c$-basal plane, but the Seebeck coefficient is isotropic.$^5$

The total thermal conductivity is decreased by reductions in the phonon thermal conductivity caused by the solid-solution effect arising from mass difference scattering.$^4$ For example, the phonon thermal conductivity of a silicon-germanium solid-solution semiconductor produced by melt growth decreases with increasing mixing ratio.$^6$ The minimum phonon thermal conductivity of a Bi$_2$Te$_3$–Sb$_2$Te$_3$ solid solution formed by melt growth occurs at a composition of around (Bi$_2$Te$_3$)$_{0.25}$(Sb$_2$Te$_3$)$_{0.75}$.$^7$ The reduction in phonon thermal conductivity caused by the solid-solution effect determines the Bi$_2$Te$_3$–Sb$_2$Te$_3$ composition that gives the best thermoelectric figure of merit.$^7$ The best thermoelectric figure of merit for a Bi$_2$Te$_3$–Sb$_2$Te$_3$ solid solution formed by melt growth was achieved at a composition of (Bi$_2$Te$_3$)$_{0.25}$(Sb$_2$Te$_3$)$_{0.75}$.$^5$3.

Mechanical alloying (MA) is also used for the preparation of thermoelectric materials.$^{1,4,8,9}$ MA has a refining effect because of boundary scattering.$^{10}$ To maintain a low phonon thermal conductivity, fine-grained materials are normally prepared using a powder metallurgy method such as MA.$^5$ MA followed by hot pressing (HP) can be used to synthesize materials that remain as solid solutions. Sintered compact MA powders have random crystal orientations and refined structures, which decrease the phonon thermal conductivity.

In MA–HP processes, reduction of the phonon thermal conductivity is simultaneously caused by solid-solution and fine-grain effect.$^{10–12}$ It is not clear whether the main cause of the reduced phonon thermal conductivity is the solid-solution or the fine-grain effect.$^{13}$

The preferred orientation also affects the electrical and phonon thermal conductivities on the surface of a Bi$_2$Te$_3$–Sb$_2$Te$_3$ solid solution, as a result of thermal stress at the heterojunction between the HP mold and sintered compact in Bi$_2$Te$_3$–Sb$_2$Te$_3$ solid-solution formation using a hot deformation process.$^{14–17}$

In the present study, a Bi$_2$Te$_3$–Sb$_2$Te$_3$ solid solution was prepared by MA–HP without the influence of a preferred orientation, because a preferred orientation causes anisotropies of the electrical and thermal conductivities. The reduced phonon thermal conductivity caused by the solid-solution effect was investigated based on the effect of the Bi$_2$Te$_3$–Sb$_2$Te$_3$ composition ratio.

2. Experimental Procedure

Bismuth (99.999%), antimony (99.999%), and tellurium (99.99999%) were weighed to give stoichiometries of...

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(Bi₂Te₃)ₓ(Sb₂Te₃)₁₋ₓ (x = 0.05–0.5). Only millimeter-scale grains of the raw materials were used, to suppress contamination by a surface oxide layer. The raw materials were placed in a stainless-steel vessel with a milling ball made of a silicon nitride ceramic in a glove box filled with argon. MA was performed in a Fritsch P-5 planetary ball mill at a maximum speed of 180 rpm for 30 h. The mechanically alloyed powder was passed through a 150-μm diameter sieve and it was confirmed that no raw materials remained. The mechanically alloyed powder was sintered by HP at 623 K under a uniaxial pressure of 147 MPa in an argon atmosphere. The sintered compacts were cylinders of diameter 10 mm and height 9 mm. These compacts were cut into disks approximately 1 mm and 10 mm in diameter to obtain isotropic disks. Approximately 1 mm of material was removed from the top and bottom of the sintered compact surface, because it has been reported that this promotes formation of the (00l) texture.

The out-of-plane direction of the disks was examined by X-ray diffraction (XRD; Rigaku Multiflex) using Cu Kα radiation at the Bragg angle range 2θ = 20–80° with a step size of 0.1° and a step speed of 1.0 s per step. The orientation factor F for evaluating the isotropy was determined using the Lotgering method:

$$ F = \frac{(D - D_0)}{1 - D_0} \quad (3) $$

$$ D = \frac{\Sigma I_{00l}}{\Sigma I_{hkl}} \quad (4) $$

where $$\Sigma I_{00l}$$ and $$\Sigma I_{hkl}$$ are the sums of the 00l and hkl reflection intensities, respectively, and D is the observed degree of orientation for the disk. According to eq. (3), F = 0 for a random orientation and $$F = 1$$ for $$D = 1$$ and $$\Sigma I_{00l} = \Sigma I_{hkl}$$ at the complete 00l orientation. $$D_0$$ = 0.0111 was calculated in the 2θ range 20–80° from the diffraction intensities for a randomly oriented powder, (Bi₂Te₃)₀.₅(Sb₂Te₃)₀.₅ [19].

The Seebeck coefficients, electrical conductivities, and thermal conductivities at room temperature of all the disks were measured, and their power factors were measured using the constructed thermal contact method [20], and the thermal conductivity was determined using the constructed static comparison method [2, 21]. The electrical conductivity was measured by the four-point probe method using an electrical resistance system based on a Keithley 2182A/6220 instrument (Keithley Instrument, Inc.). The probe size was 1.0 mm and it was made of tungsten carbide. All measurements made using the electrical conductivity system were confirmed by ohmic contact [21]. The accuracies of the Seebeck coefficient was less than ±2% and electrical conductivity and thermal conductivity were less than ±1%, respectively [20, 22]. The figures of merit of the (Bi₂Te₃)ₓ(Sb₂Te₃)₁₋ₓ materials were determined at room temperature, based on the temperature dependences of the Seebeck coefficient and electrical conductivity from 300 to 573 K, determined using a ZEM-3 instrument (Advance-Riko). (Bi₂Te₃)ₓ(Sb₂Te₃)₁₋ₓ specimens of dimensions 10 mm × 10 mm × 9 mm were sintered using MA–HP. A piece with the dimensions 3.0 mm × 3.0 mm × 8.0 mm was removed from the center of the sintered specimen to eliminate the influence of anisotropy. The ZEM-3 instrument had an accuracy of less than ±7%; the dimensionless figure of merit ZT was estimated from the temperature dependences of the Seebeck coefficients and electrical conductivities obtained using the ZEM-3 instrument, and the thermal conductivity at room temperature.

3. Results and Discussion

The obtained disks were p-type conductors and optical microscopy showed that they were dense materials.

Figure 1 shows the XRD patterns of (Bi₂Te₃)ₓ(Sb₂Te₃)₁₋ₓ (x = 0.05, 0.125, 0.15, and 0.5) prepared using MA–HP. The main hkl and 00l reflections showed that the material was a Bi₂Te₃–Sb₂Te₃ solid solution. All the diffraction peaks indicated a single-phase of Bi₂Te₃–Sb₂Te₃ solid solution. No peaks were observed other than those from bismuth, antimony, and tellurium, and other compounds. The D and F values for (Bi₂Te₃)₀.₅(Sb₂Te₃)₀.₅ were estimated, using eqs. (3) and (4), to be 0.0192 and 0.0081, respectively, in the 2θ range 20–80°. A preferred orientation in the (00l) direction was not observed for the obtained disks. These results show that all the disks were single-phase, isotropically oriented Bi₂Te₃–Sb₂Te₃ solid solutions; isotropic disks had been obtained from MA–HP sintered compacts from which 1 mm of material had been eliminated from the top and bottom surfaces.

Figure 2 shows the relationship between the electrical conductivity σ and x for (Bi₂Te₃)ₓ(Sb₂Te₃)₁₋ₓ at room temperature. The electrical conductivity σ gradually decreased with increasing Bi₂Te₃ content. This trend is similar to that of the electrical conductivity of a material synthesized using the melt-growth method [23, 24]. However, fluctuations in the electrical conductivity were observed at around x = 0.2; such fluctuations have not been reported in the literature.

Figure 3 shows the relationships among the total, phonon, and carrier thermal conductivities and x for (Bi₂Te₃)ₓ(Sb₂Te₃)₁₋ₓ (x = 0.05–0.5). The phonon and carrier...
Thermoelectric materials with compositions around (Bi$_2$Te$_3$)$_{0.25}$(Sb$_2$Te$_3$)$_{0.75}$ have been developed for many applications because they have the advantage of low phonon thermal conductivity because of melt growth. The predicted maximum thermoelectric figure of merit was not close to that of (Bi$_2$Te$_3$)$_{0.25}$(Sb$_2$Te$_3$)$_{0.75}$ produced by MA–HP.

The relationship between the Seebeck coefficient $\alpha$ and $x$ for (Bi$_2$Te$_3$)$_{0.15}$(Sb$_2$Te$_3$)$_{0.85}$ and (Bi$_2$Te$_3$)$_{0.125}$(Sb$_2$Te$_3$)$_{0.875}$, which had higher power factor at room temperature, were determined.

Figure 7 shows the Seebeck coefficient versus temperature plots for (Bi$_2$Te$_3$)$_{0.15}$(Sb$_2$Te$_3$)$_{0.85}$ and (Bi$_2$Te$_3$)$_{0.125}$(Sb$_2$Te$_3$)$_{0.875}$. The Seebeck coefficients were constant up to 450 K and decrease above that temperature. The predicted maximum thermoelectric figure of merit was not close to that of (Bi$_2$Te$_3$)$_{0.25}$(Sb$_2$Te$_3$)$_{0.75}$ produced by MA–HP.

Fluctuations in the total thermal conductivity $\kappa_{\text{total}}$ were observed at around $x = 0.2$, consistent with the behavior of the electrical conductivity (Fig. 2). The total thermal conductivity seemed to be decreased because of a reduction in the phonon thermal conductivity caused by the solid-solution effect. The carrier thermal conductivity $\kappa_{\text{carrier}}$ decreased with increasing Bi$_2$Te$_3$ content. The trend in the carrier thermal conductivity corresponded to that in the electrical conductivity (Fig. 2), based on eq. (2). The phonon thermal conductivity $\kappa_{\text{phonon}}$ increased with increasing Bi$_2$Te$_3$ content and did not correspond to the reduction in the thermal conductivity caused by the solid-solution effect in melt growth. In the case of the melt-growth method, the phonon thermal conductivity decreased with increasing Bi$_2$Te$_3$ content because of the solid-solution effect. There is clearly a minimum composition close to (Bi$_2$Te$_3$)$_{0.25}$(Sb$_2$Te$_3$)$_{0.75}$. In the case of the MA–HP method, a composition of (Bi$_2$Te$_3$)$_{0.25}$(Sb$_2$Te$_3$)$_{0.75}$ was not the minimum for phonon thermal conductivity.

The reduction in the phonon thermal conductivity caused by the fine-grain effect caused by MA was more important than that caused by the solid-solution effect in melt growth.
increased above 450 K. The Seebeck coefficient of \((\text{Bi}_2\text{Te}_3)_{0.15}(\text{Sb}_2\text{Te}_3)_{0.85}\) was slightly higher than that of \((\text{Bi}_2\text{Te}_3)_{0.125}(\text{Sb}_2\text{Te}_3)_{0.875}\) up to 475 K. Above 475 K, the Seebeck coefficient of \((\text{Bi}_2\text{Te}_3)_{0.15}(\text{Sb}_2\text{Te}_3)_{0.85}\) was slightly lower than that of \((\text{Bi}_2\text{Te}_3)_{0.125}(\text{Sb}_2\text{Te}_3)_{0.875}\). This could be because of band gap differences, because the band gaps of \(\text{Bi}_2\text{Te}_3\) and \(\text{Sb}_2\text{Te}_3\) are 0.13 and 0.28 eV, respectively.26 The band gap of \((\text{Bi}_2\text{Te}_3)_{0.125}(\text{Sb}_2\text{Te}_3)_{0.875}\) is wider than that of \((\text{Bi}_2\text{Te}_3)_{0.15}(\text{Sb}_2\text{Te}_3)_{0.85}\). The maximum Seebeck coefficient of a wide band gap semiconductor shifts to a higher temperature24.

Figure 8 shows plots of the electrical conductivities of \((\text{Bi}_2\text{Te}_3)_{0.15}(\text{Sb}_2\text{Te}_3)_{0.85}\) and \((\text{Bi}_2\text{Te}_3)_{0.125}(\text{Sb}_2\text{Te}_3)_{0.875}\) versus temperature. The electrical conductivity decreased with increasing temperature. These \((\text{Bi}_2\text{Te}_3)_{x}(\text{Sb}_2\text{Te}_3)_{1-x}\) \((x = 0.05–0.5)\) solid-solution materials synthesized using MA–HP had the conductive properties of a degenerate semiconductor.

Figure 9 shows plots of the power factors of \((\text{Bi}_2\text{Te}_3)_{0.15}(\text{Sb}_2\text{Te}_3)_{0.85}\) and \((\text{Bi}_2\text{Te}_3)_{0.125}(\text{Sb}_2\text{Te}_3)_{0.875}\) versus temperature. The power factor of \((\text{Bi}_2\text{Te}_3)_{0.15}(\text{Sb}_2\text{Te}_3)_{0.85}\) was slightly higher than that of \((\text{Bi}_2\text{Te}_3)_{0.125}(\text{Sb}_2\text{Te}_3)_{0.875}\) up to 475 K. Above 475 K, the power factor of \((\text{Bi}_2\text{Te}_3)_{0.15}(\text{Sb}_2\text{Te}_3)_{0.85}\) was lower than that of \((\text{Bi}_2\text{Te}_3)_{0.125}(\text{Sb}_2\text{Te}_3)_{0.875}\). These behaviors are consistent with the temperature dependence of the Seebeck coefficient. The power factors decreased with increasing temperature. The maximum power factor for \((\text{Bi}_2\text{Te}_3)_{0.15}(\text{Sb}_2\text{Te}_3)_{0.85}\) was 3.41 \(\times 10^{-3}\) W m\(^{-1}\) K\(^{-2}\) at 343 K, and for \((\text{Bi}_2\text{Te}_3)_{0.125}(\text{Sb}_2\text{Te}_3)_{0.875}\) was 3.08 \(\times 10^{-3}\) W m\(^{-1}\) K\(^{-2}\) at 300 K.

Figure 10 shows plots of the dimensionless figures of merit \(Z^T\) for \((\text{Bi}_2\text{Te}_3)_{0.15}(\text{Sb}_2\text{Te}_3)_{0.85}\) and \((\text{Bi}_2\text{Te}_3)_{0.125}(\text{Sb}_2\text{Te}_3)_{0.875}\) versus temperature at a fixed total thermal conductivity \(\kappa_{\text{total}}\) at room temperature. It was presumed that because of the
of a material produced by melt growth.

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