Constituent Element Addition to \(n\)-Type \(\text{Bi}_2\text{Te}_{2.67}\text{Se}_{0.33}\) Thermoelectric Semiconductor without Harmful Dopants by Mechanical Alloying

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\(N\)-type \(\text{Bi}_2\text{Te}_{2.67}\text{Se}_{0.33}\) thermoelectric materials with added constituent elements were prepared without the addition of harmful dopants using mechanical alloying (MA) followed by hot pressing (HP). All the prepared samples were identified from the \(\text{Bi}_2\text{Te}_3–\text{Bi}_2\text{Se}_3\) solid-solution diffraction peak. They were all single-phase \(n\)-type semiconductors. The maximum dimensionless figures of merit, \(ZT\), of \(\text{Bi}_2\text{Te}_{2.67}\text{Se}_{0.33}\), \(\text{Bi}_2\text{Te}_{2.67}\text{Se}_{0.34}\), and \(\text{Bi}_2\text{Te}_{2.67}\text{Se}_{0.35}\) were 0.93 at 440 K, 0.99 at 441 K, and 0.97 at 442 K, respectively. These results indicate that the figure of merit of \(\text{Bi}_2\text{Te}_{2.67}\text{Se}_{0.33}\) doped with constituent elements, prepared using the MA–HP process, is nearly the same as the highest value, i.e., 1.0, reported in the literature.

Keywords: eco-materials, bismuth telluride selenide, \(n\)-type, dopant, thermoelectrics

\(\text{Bi}_2\text{Te}_3\)-based \(p\)- and \(n\)-type materials have been widely used in thermoelectric cooling devices such as mini refrigerators and central processing unit (CPU) coolers for personal computers. They are also eco-materials because they can be used to recover exhaust heat below 500 K by thermoelectric conversion. These materials have a rhombohedral crystal structure with the \(R3m\) space group and anisotropic physical and thermoelectric properties. \(\text{Bi}_2\text{Te}_3\)-\(\text{Bi}_2\text{Se}_3\) solid solutions are \(n\)-type materials at room temperature. The efficiency of a thermoelectric material is defined by the dimensionless figure of merit \(ZT\):

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ZT = \alpha^2 \sigma / \kappa T
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where \(\alpha\), \(\sigma\), \(\kappa\), 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 highest reported dimensionless figures of merit for \(p\)-type materials are 1.0 at 1.8 K for \(\text{Bi}_2\text{Te}_3\) and 0.6 at 300 K for \(\text{Bi}_2\text{Te}_3\). The synthesis of \(n\)-type \(\text{Bi}_2\text{Te}_3\)-\(\text{Bi}_2\text{Se}_3\) thermoelectric materials generally involves addition of harmful halide dopants such as \(\text{CdI}_2\), \(\text{CdCl}_2\), \(\text{HgCl}_2\), \(\text{HgBr}_2\), and \(\text{SbBr}_3\). The addition of constituent elements (selenium, tellurium, and bismuth) without harmful dopants to control the donor properties of \(n\)-type \(\text{Bi}_2\text{Te}_3\)-\(\text{Bi}_2\text{Se}_3\) thermoelectric materials would enable the production of \(n\)-type \(\text{Bi}_2\text{Te}_3\)-based materials without hazardous substances. This would reduce the recycling energy needed for the recovery and refinement of elemental resources from discarded thermoelectric modules.

The present study, \(n\)-type \(\text{Bi}_2\text{Te}_{2.67}\text{Se}_{0.33}\) thermoelectric materials with added constituent elements and no harmful dopants were prepared using an MA–HP process. The thermoelectric properties of the products were investigated.

1. Introduction

2. Experimental Procedure

The MA powders, which contained no harmful dopants, were \(\text{Bi}_2\text{Te}_{2.67}\text{Se}_{0.33}\), \(\text{Bi}_2\text{Te}_{2.67}\text{Se}_{0.34}\), and \(\text{Bi}_2\text{Te}_{2.67}\text{Se}_{0.35}\) (\(x = 0.0–0.7\)) were prepared using the MA–HP process. All the prepared samples were identified from the \(\text{Bi}_2\text{Te}_3–\text{Bi}_2\text{Se}_3\) solid-solution diffraction peak. They were all single-phase \(n\)-type semiconductors. The maximum dimensionless figures of merit, \(ZT\), of \(\text{Bi}_2\text{Te}_{2.67}\text{Se}_{0.33}\) doped with constituent elements, prepared using the MA–HP process, is nearly the same as the highest value, i.e., 1.0, reported in the literature.

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disks were not used because HP affects the plastic deformation and anisotropic thermoelectric properties of these disks.

The disks were examined using X-ray diffraction (XRD) and the Seebeck coefficients and electrical and thermal conductivities were determined.

XRD measurements were performed with a Rigaku MultiFlex diffractometer using Cu Kα radiation at a step size of 0.1° and step speed of 1.0 s/step in the Bragg angle range 2θ = 20–90°.

The Seebeck coefficients α were estimated at room temperature from α = ΔV/ΔT, where ΔV and ΔT are the thermoelectric motive force and temperature differences, respectively. A thermal contact system was used to measure ΔV at a ΔT value of about 4 K. The thermal contact system was constructed using a copper heating chip, copper base plate, and constantan block type-T (copper–constantan) thermocouple. The thermal contact system was calibrated using a standard Seebeck coefficient material (SRM 3451)10,14,15). The accuracy of Seebeck coefficient with this thermal contact system has been less than ±2%.

The electrical conductivity σ was measured at room temperature by the four-point probe method using an electrical resistance system based on a 2182A/6220 instrument (Keithley Instruments, Inc.). The probe material and spacing were WC and 1.00 mm, respectively. The accuracy of electrical conductivity with the four-point probe method has been less than ±1%. The electrical conductivity measurement system confirmed ohmic contact for each measurement.

The thermal conductivity was measured at room temperature using a static comparison method. The equipment of a static comparison method consisted of a film heater, sample and quartz disks, and water-cooled sink. A film heater of thickness 0.8 mm was used as a heat source in order to prevent the heat radiation toward the side wall. A quartz disk 1.0 mm thick and 10 mm in diameter was used as the reference material (κ = 1.411 W m⁻¹ K⁻¹). The water-cooled sink was used for the low temperature side. The chamber of the equipment was evacuated to less than 0.1 Pa using a vacuum pump. The thermal conductivity was evaluated from the temperature drops of sample and quartz disks between the heater and water-cooled sink. The accuracy of thermal conductivity with this static comparison method has been less than ±1%.

The room-temperature performance of the thermoelectric material was estimated using the power factor, P = σα^2κT.

The temperature dependences of the Seebeck coefficients and electrical conductivities of the compositions that had high power factors at room temperature were determined. Sintered compacts were obtained by HP at 623 K under an axial compressive pressure of 147 MPa in an argon atmosphere, i.e., the same conditions as for production of the sintered cylinders. The dimensions of the sintered compacts were 10 mm × 10 mm × 7 mm. The sintered compacts were cut into samples of dimensions 4 mm × 6 mm × 4 mm. The centers of the rectangular samples were cut out and used to investigate the thermoelectric properties, as in the case of the cylinder central disks. The temperature dependences of the Seebeck coefficient and electrical conductivity were measured using a ZEM-3 instrument (Advance-Riko) in the temperature range 298–523 K. The accuracy of Seebeck coefficient and electrical conductivity with ZEM-3 has been less than ±7%, respectively. The dimensionless figures of merit (ZT = α^2σκT) were measured in the range 298–523 K, with the thermal conductivity fixed at room temperature.

3. Results and Discussion

All the samples of Bi2(Te2.67Se033)x+x, Bi2(Te2.67)1+xSe033, and Bi2(Te2.67Se033)1+x showed negative Seebeck coefficients. This shows that Bi2(Te2.67)1+xSe033 and Bi2(Te2.67Se033)1+x have n-type conduction. The Seebeck coefficient was constant at −300 μV K⁻¹ at room temperature for all the samples prepared without harmful dopants. Figure 1 shows the XRD patterns of disks of Bi2(Te2.67Se033), Bi2(Te2.67Se033)1+0.07, Bi2(Te2.67)1+0.06Se033, and Bi2(Te2.67Se033)1+0.07. The compositions of all the disks were identified from the Bi2(Te2–Bi2Se3) solid-solution diffraction peaks; all the samples were single phase. No peaks were observed for elemental bismuth, tellurium, and selenium, or other compositions.

Figure 2 shows the relationships between the Seebeck coefficient and temperature for all the samples prepared without harmful dopants. The Seebeck coefficient was constant at −300 μV K⁻¹ at room temperature for all the samples prepared without harmful dopants. The added selenium and tellurium act as negative carriers. The Seebeck coefficient of the materials double-doped with selenium and tellurium remained constant at −180 μV K⁻¹. The selenium-tellurium combination acts as negative carriers.

The relationships between the electrical conductivity and temperature for all the samples prepared without harmful dopants are shown in Fig. 3. For selenium addition, the electrical conduc-

![Fig. 1 XRD patterns of Bi2(Te2.67Se033), Bi2(Te2.67)1+xSe033, Bi2(Te2.67Se033)1+0.07, Bi2(Te2.67)1+0.06Se033, and Bi2(Te2.67Se033)1+0.07](image-url)
activity was constant at $2 \times 10^4$ S m$^{-1}$ up to $x = 0.03$ and rose to $7 \times 10^4$ S m$^{-1}$ at $x = 0.04$. In contrast, the electrical conductivity increased from $3 \times 10^4$ to $8 \times 10^4$ S m$^{-1}$ with increasing tellurium addition. The electrical conductivity of the material double doped with selenium and tellurium fluctuated and then remained constant at $8 \times 10^4$ S m$^{-1}$ with increasing element addition. If the carrier concentration increases as a result of element addition, the absolute Seebeck coefficient decreases and the electrical conductivity increases simultaneously. The Seebeck coefficient behaviors in Fig. 2 and electrical conductivity behaviors in Fig. 3 are consistent with the thermoelectric properties. Doping with selenium, tellurium, and a combination of these provides donor carriers.

The relationships between thermal conductivity $x$ in Bi$_2$Te$_2.67$(Se$_{0.33}$)$_{1+x}$, Bi$_2$(Te$_{2.67}$)$_{1+x}$Se$_{0.33}$, and Bi$_2$(Te$_{2.67}$Se$_{0.33}$)$_{1+x}$ ($x = 0$ to 0.07) at room temperature are shown in Fig. 4. The thermal conductivities of the doped disks were stable at 1 W m$^{-1}$ K$^{-1}$ and slightly higher than that of Bi$_2$Te$_2.67$Se$_{0.33}$, i.e., without dopant addition. The thermal conductivity of a thermoelectric material is generally the sum of the phonon and carrier components. These measured values are lower than 1.45 W m$^{-1}$ K$^{-1}$, which is the minimum reported value, obtained using the crystal growth method with a traveling heater. This is because the conductivity of the phonon component was reduced as a result of the fine grain size obtained by MA. Furthermore, the thermal conductivity of the carrier component is proportional to the electrical conductivity, and follows the Wiedemann–Franz law, so the slightly higher thermal conductivities of materials with additional dopants compared with that of Bi$_2$Te$_2.67$Se$_{0.33}$ is consistent with the electrical conductivity results in Fig. 2.

Figure 5 shows the plots of power factor versus $x$ for Bi$_2$Te$_2.67$(Se$_{0.33}$)$_{1+x}$, Bi$_2$(Te$_{2.67}$)$_{1+x}$Se$_{0.33}$, and Bi$_2$(Te$_{2.67}$Se$_{0.33}$)$_{1+x}$ ($x = 0$ to 0.07) at room temperature. For selenium and tellurium additions, the maximum power factors were $2.7 \times 10^{-3}$ and $2.5 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$, respectively, at $x = 0.06$. In contrast, the maximum power factor of the material double doped with selenium and tellurium was $2.7 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$ at $x = 0.03$. The maximum of the power factor with added elements for Bi$_2$(Te$_{2.67}$Se$_{0.33}$)$_{1+0.03}$ corresponds to the half of sum with that for Bi$_2$Te$_2.67$Se$_{0.33}$$_{1+0.06}$ and Bi$_2$(Te$_{2.67}$Se$_{0.33}$)$_{1+0.05}$. The power factor has the maximum at a carrier concentrations of around $10^{25}$ m$^{-3}$ 3). If added elements are proportional to the carrier concentrations, the behavior of the power factor with added elements is consistent.

The temperature dependences of the Seebeck coefficients and electrical conductivities of rectangular samples of Bi$_2$Te$_2.67$(Se$_{0.33}$)$_{1+0.06}$, Bi$_2$(Te$_{2.67}$)$_{1+0.06}$Se$_{0.33}$, and Bi$_2$(Te$_{2.67}$Se$_{0.33}$)$_{1+0.05}$, which had higher room-temperature power factors, were measured. Figure 6 shows the Seebeck coefficient versus temperature plots for Bi$_2$Te$_2.67$(Se$_{0.33}$)$_{1+0.06}$, Bi$_2$(Te$_{2.67}$)$_{1+0.06}$Se$_{0.33}$, and Bi$_2$(Te$_{2.67}$Se$_{0.33}$)$_{1+0.05}$, the Seebeck coefficients at 300 K of all the samples, determined using a thermal contact method,
were almost the same. The Seebeck coefficients of the all samples were maximum at around 420 K. All the samples showed the same Seebeck coefficient behavior.

The plots of electrical conductivity versus temperature for Bi\(_2\)Te\(_{2.67}\)(Se\(_{0.33}\))\(_{1+0.06}\), Bi\(_2\)(Te\(_{2.67}\))\(_{1+0.06}\)Se\(_{0.33}\), and Bi\(_2\)(Te\(_{2.67}\)Se\(_{0.33}\))\(_{1+0.03}\) are shown in Fig. 7. The electrical conductivities of the all samples at 300 K, measured using a four-point probe method, were almost the same. The values for all the samples decreased with temperature.

Figure 8 shows the power factor versus temperature plots for Bi\(_2\)Te\(_{2.67}\)(Se\(_{0.33}\))\(_{1+0.06}\), Bi\(_2\)(Te\(_{2.67}\))\(_{1+0.06}\)Se\(_{0.33}\), and Bi\(_2\)(Te\(_{2.67}\)Se\(_{0.33}\))\(_{1+0.03}\). The maximum power factor for Bi\(_2\)Te\(_{2.67}\)(Se\(_{0.33}\))\(_{1+0.06}\) was 2.8 × 10\(^{-3}\) W m\(^{-1}\) K\(^{-2}\) at 319 K, that for Bi\(_2\)(Te\(_{2.67}\))\(_{1+0.06}\)Se\(_{0.33}\) was 2.8 × 10\(^{-3}\) W m\(^{-1}\) K\(^{-2}\) at 367 K, and that for Bi\(_2\)(Te\(_{2.67}\)Se\(_{0.33}\))\(_{1+0.03}\) was 2.3 × 10\(^{-3}\) W m\(^{-1}\) K\(^{-2}\) at 300 K.

Figure 9 shows plots of the dimensionless figures of merit (\(ZT = \alpha^2\sigma T / k\)) in the range 298–523 K with the thermal conductivity fixed at room temperature. It was presumed due to Wiedemann-Franz law and high temperature Umklapp processes that the thermal conductivities of these materials are approximately constant in these temperature ranges\(^{19}\). The effects of doping with selenium, tellurium, and a combination of these were nearly identical. The maximum dimensionless figures of merit of Bi\(_2\)Te\(_{2.67}\)(Se\(_{0.33}\))\(_{1+0.06}\), Bi\(_2\)(Te\(_{2.67}\))\(_{1+0.06}\)Se\(_{0.33}\), and Bi\(_2\)(Te\(_{2.67}\)Se\(_{0.33}\))\(_{1+0.03}\) were 0.93 at 440 K, 0.99 at 441 K, and 0.97 at 442 K, respectively. The maximum dimensionless figures of merit of Bi\(_2\)Te\(_{2.67}\)(Se\(_{0.33}\))\(_{1+0.06}\), Bi\(_2\)(Te\(_{2.67}\))\(_{1+0.06}\)Se\(_{0.33}\), and Bi\(_2\)(Te\(_{2.67}\)Se\(_{0.33}\))\(_{1+0.03}\) were nearly the same as the highest value reported in the literature\(^{2,3}\).

These results show that the maximum figures of merit of \(n\)-type Bi\(_2\)Te\(_{2.67}\)Se\(_{0.33}\) with added constituent elements, produced by MA, were nearly the same. It is not necessary to dope \(n\)-type Bi\(_2\)Te\(_{2.67}\)Se\(_{0.33}\) prepared by MA with harmful elements.

4. Conclusion

In the present study, \(n\)-type Bi\(_2\)Te\(_{2.67}\)Se\(_{0.33}\) thermoelectric materials containing additional constituent elements, without harmful dopants, were prepared using an MA–HP process. The thermoelectric properties of the materials were investigated. The results are as follows.

(1) All the prepared samples of Bi\(_2\)Te\(_{2.67}\)(Se\(_{0.33}\))\(_{1+x}\), Bi\(_2\)(Te\(_{2.67}\))\(_{1+x}\)Se\(_{0.33}\), and Bi\(_2\)(Te\(_{2.67}\)Se\(_{0.33}\))\(_{1+x}\) (\(x = 0.0–0.7\)) were identified from the Bi\(_2\)Te\(_3\)–Bi\(_2\)Se\(_3\) solid-solution diffraction peak. They all consisted of a single phase.

(2) The absolute Seebeck coefficient decreased and the electrical conductivity increased simultaneously on addition of selenium, tellurium, or a combination of these. The
selenium, tellurium, and selenium–tellurium combination acted as donor carriers.

(3) The maximum power factors achieved with selenium and tellurium additions at room temperature were $2.7 \times 10^{-3}$ and $2.5 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$ at $x = 0.06$. The maximum power factor of the material doped with both selenium and tellurium was $2.7 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$ at $x = 0.03$.

(4) The maximum dimensionless figures of merit $ZT$ of $\text{Bi}_2\text{Te}_{2.67}\text{Se}_{0.33}^{1+0.06}$, $\text{Bi}_2(\text{Te}_{2.67})^{1+0.06}\text{Se}_{0.33}$, and $\text{Bi}_2(\text{Te}_{2.67}\text{Se}_{0.33})^{1+0.03}$ were 0.93 at 440 K, 0.99 at 441 K, and 0.97 at 442 K, respectively.

These results indicate that the dimensional figure of merit of $\text{Bi}_2\text{Te}_{2.67}\text{Se}_{0.33}$ doped with constituent elements, prepared using MA, is nearly the same as the highest dimensionless figure of merit, i.e., 1.0, reported in the literature.

REFERENCES


