Pre-oxidation effects on properties of bismuth telluride thermoelectric composites compacted by spark plasma sintering

Jinseo Kim*, Le Thai Duy, Byungmin Ahn, and Hyungtak Seo

*Department of Energy Systems Research, Ajou University, Suwon, Republic of Korea; ‡Department of Materials Science and Engineering, Ajou University, Suwon, Republic of Korea

ABSTRACT
Research on harvesting alternative energy sources is of interest to meet human demands for energy while reducing environmental pollution caused by the extensive use of fossil fuels. Thermoelectric materials are a promising technology for converting heat into electricity. Among thermoelectric materials, the binary bismuth telluride system (Bi-Te) is widely used. To produce high-quality Bi-Te systems with low materials consumption, spark plasma sintering (SPS) is commonly applied. Because SPS is a fast low-temperature process, controlling the ratio and crystallization of Bi-Te is critical for effective energy conversion. Here, we investigated the quality of Bi-Te systems formed by SPS compaction of raw powders with an in-depth examination of the oxidation effects on their thermoelectric performance. With increasing measurement temperature (300→420 K), the mechanically mixed sample and a commercial Bi$_2$Te$_3$ alloy (sintered at 533 K) showed differences in Seebeck coefficients (0.245→0.267 and 0.223→0.246 mV/K$^{-1}$, respectively). The alloy sample showed a decreased figure of merit (0.863→0.331) while that of the mechanically mixed sample (0.543→1.671) increased with temperature. This was related to the degree of oxygen impurity in each Bi-Te process based on XPS analysis. This study proposes that the integration of oxygen species to Bi-Te can be considered to maximize the thermoelectric efficiency at the specified temperature.

1. Introduction
Increasingly strict regulations on environmental pollution and the reduction of fossil fuel use are being implemented globally. Much research has been conducted on environmentally friendly and recyclable materials, as well as on energy-harvesting approaches [1,2]. Energy harvesting is among the most remarkable available technologies for collecting, reusing, and storing waste energy. Among various harvesting approaches, thermoelectricity is of interest because it allows the efficient conversion of abandoned thermal energy into electrical energy by using binary systems of p- and n-type semiconductors. Unlike conventional power generation devices, thermoelectric devices can convert heat and electricity without additional power requirements or noise generation. However, the low efficiency of energy conversion technologies using thermoelectric materials hinders their applicability in meeting increasing energy demands. In addition, there are many problems in maintaining the efficiency of a thermoelectric element after heat damage. Unless these problems are solved, widespread application of this technology will remain challenging. Therefore, it is urgent to solve these issues by studying thermoelectric materials for the improvement of efficiency.

In principle, high-efficiency thermoelectric materials play a key role in energy conversion applications, relying on three thermoelectric effects explored by Seebeck, Peltier, and Thomson [3]. This occurs when a current is applied to the thermoelectric material, yielding a temperature difference between the two ends of the material by the drift movement of charge carriers. In other words, when a bias voltage is applied to a binary system in a closed circuit, a temperature gradient is formed at the two ends of each semiconductor component. For an n-type component, charge excitation causes an endothermic phenomenon at one end, while charge recombination causes an exothermic phenomenon at rest. On the contrary, heating of the terminal of the p-type component arises from charge excitation, while the other terminal experiences an endothermic phenomenon via charge recombination. Generally, thermoelectric properties of a material are related to its electronic band structures near the Fermi level. The energy conversion efficiency of a thermoelectric device is determined by its electrical conductivity ($\sigma$), thermal conductivity ($k$), and Seebeck coefficient ($\alpha$). These values are used to define the thermoelectric performance index, characterized by the figure of merit $ZT = \sigma^2T/k$, in which $T$ is the absolute temperature [4]. To obtain a high $ZT$ value, a thermoelectric material
must have a high Seebeck coefficient and electrical conductivity values, but a low thermal conductivity. Besides, a low thermal conductivity is essential to maintain the temperature gradient between both ends of the material. However, the thermal conductivity of a material is a sum contribution of electronic \((k_e)\) and lattice vibrations \((k_l)\), in which electronic thermal conductivity \((k_e)\) is proportional to electrical conductivity by Wiedemann-Franz Law as \(k_e = L_0T\), in which \(L\) is the Lorentz number [5]. As a result, lowering the thermal conductivity of a material can be obtained more reasonably by optimizing its lattice thermal conductivity \((k_l)\). Because these values are dependent factors, optimizing the performance indices via controlling material crystallization with its carrier concentration and mobility is challenging. Thus, the choice of semiconductor components requires careful consideration.

Among the available thermoelectric materials, Bi$_2$Te$_3$ compound shows good figures of merit in the temperature range 250 ~ 500 K. Furthermore, both positive and negative Seebeck coefficients can be achieved depending on Bi and Te compositions [6,7]. Bi-rich composites are p-type with positive coefficients; n-type composites with negative coefficients are Te-rich. The hexagonal structure of Bi$_2$Te$_3$ contains stacked layers of Te and Bi. Thus, Bi$_2$Te$_3$ exhibits excellent thermoelectric properties in the plane perpendicular to the c-axis, despite its weak mechanical properties due to Te-Te van der Waals bonds [8,9]. To further understand the effects of structural engineering on the thermoelectric properties, nanostructured thermoelectric materials have received significant attention [10,11]. For this purpose, various approaches such as hot-pressing, hot-extrusion, mechanical alloying (MA), and spark plasma sintering (SPS) have been proposed [12,13]. Among these, the SPS process comprises sintering and hot-forging steps to produce high-quality and high-purity composites [14]. Therefore, we selected the SPS process to manufacture Bi-Te composites. However, oxidation of the materials can occur before, during, and immediately after fabrication [15,16]. The effects of oxygen impurities remain incompletely explored, but understanding and controlling impurities are essential to improve the quality and thermoelectric performance of nanostructured materials further.

In this study, we investigated the thermoelectric properties of Bi-Te composites formed from the SPS compaction of nanorized raw powders. Furthermore, we examined the effects of pre-oxidation by inserting oxygen impurities in the composites during the milling and SPS processes at ambient pressure (~101.3 kPa). The thermoelectric properties and performances of the mechanically mixed powders were measured and compared to those of a commercial Bi-Te alloy. This study demonstrates the ability to maximize the thermoelectric efficiency at a specified temperature by using O-associated dopants.

2. Experiment
2.1. Materials
All materials were obtained from Sigma Aldrich and used without further purification, including Bi powder (99.99%, <100 mesh), Te powder (99.99%, <30 mesh), and the Bi-Te alloy powder (99.99% Bi$_2$Te$_3$, <325 mesh).

2.2. Sample fabrication
The Bi and Te powders were mixed in ethanol to obtain the composition ratio of Bi$_2$Te$_3$. The Bi-Te mixed powder (10 g in 200mL of ethanol) was ball-milled in air for 15 h at a rotation speed of 400 rpm using ZrO$_2$ balls of 3 mm in diameter. Here, ethanol also has a role to limit surface oxidation occurred during the long milling process. After that, the nanorized powders were dried in a vacuum oven at 60°C for 4 h. The mixed powder and commercial alloy were both processed by SPS using carbon mold dies. The SPS system is SPS 332Lx from Fuji Electronic Industrial Co., Ltd., Japan. The SPS chamber was purged twice with argon gas before performing SPS at the respective temperatures of 483 and 533 K (in-situ measured by a thermocouple) under argon (Ar) gas at 40 MPa [17]. The time periods of temperature raising, retention, and cooling are 3, 10, and about 30 min, respectively, which are the same for both samples at 488K and 533K. The water cooling was applied to accelerate the cooling to room temperature. The cylindrical specimens (coin-shape, 15 mm in diameter and 2 mm in height) were then subjected to characterization.

2.3. Characterization
The surface area was measured by the Brunauer-Emmett-Teller (BET) method. The sample morphology was checked via field emission scanning electron microscope (FESEM, S-4800, Hitachi). Energy dispersive X-ray spectrometry (EDX) analysis was performed with transmission electron microscopy (TEM, JEM-2100F, with spherical aberration (Cs) corrector) to analyze the microstructures and compositions of the bulk samples [18]. The crystal phases were confirmed by X-ray diffraction (XRD) using the Cu Kα line at room temperature, ~300 K (Rigaku MiniFlex-II, Japan) [19,20]. Chemical compositions were examined by X-ray photoelectron spectroscopy (XPS, Theta Probe base system, Thermo Fisher Scientific Co., USA) [21,22]. The electrical conductivity, carrier concentration, carrier mobility, and Seebeck coefficient were measured at 300 ~ 420 K in the ambient atmosphere using a parameter analyzer (Keithley S4200SCS, USA) and Hall measurement system (Ecopia HMS-3000). The thermal diffusivity coefficient (D) was determined using the laser flash method (NETZSCH, LFA427, Germany) [23].
The specific heat \((C_p)\) was measured using a simultaneous thermal analyzer-mass spectrometer (STA-MS, NETZSCH, STA 409 PC + QMS 403 C, Germany). The densities \((d)\) of the samples were measured with the Archimedes method. The thermal conductivities were calculated by \(k = D \cdot C_p \cdot d\) [24,25].

3. Results and discussion

Figure 1(a) illustrates our synthesis process for the nanopowders and the samples of Bi-Te. Here, the ball-milling step was used to achieve nanorized Bi and Te powders (i.e., mixed nanopowder or M-Bi-Te) and commercial Bi-Te alloy (i.e., alloy nanopowder or A-Bi-Te). After that, SPS was performed at various temperatures to build testing samples from the mixed nanopowders (i.e., SM-Bi-Te) and the nanorized alloy (i.e., SA-Bi-Te).

In Figure 1(b,c), FESEM images of compacted samples made of the commercial Bi-Te alloy and the Bi-Te mixed powder, respectively. As seen here, both nanopowders consist of many nanoparticles and submicron-sized grains, of which the mean size is about 1 μm less. Especially, these particles and grains assembled together as clusters with a flake-like shape shown in the inset figures. Besides, A-Bi-Te has a more uniform size distribution while there are more aggregations of M-Bi-Te particles. In Figure 1(d,e), the SA-Bi-Te and SM-Bi-Te samples display a partially laminated and polycrystal structure. Figure 1(f,g) show an enlargement of laminated layer stacks of Figure 1(d,e), respectively. Through FESEM-EDX analysis in Supporting Tables S1 and S2, we also found that SM-Bi-Te has a higher Te/Bi ratio, but its Te/Bi distribution is not uniform compared to those of SA-Bi-Te. As known, the semiconductor type of bismuth telluride is dependent on the chemical stoichiometry; Bi-rich shows p-type whereas Te-rich shows n-type [26]. Consequently, our SA-Bi-Te owned a uniform Te-rich stoichiometry as well as n-type behavior. While that, the SM-Bi-Te sample with non-uniform Te/Bi ratio had both p-type and n-type semiconducting domains.

Figure 2(a) presents the specific surface area data of the nanopowders obtained by BET method with Ar gas. Through the linear fitting of these data, the average surface areas of the A-Bi-Te and M-Bi-Te nanopowders are 1.0747 ± 0.1049 and 0.9698 ± 0.0947 m²/g, respectively. Although these average values are not significantly different, they indicate a bit larger size of A-Bi-Te particles. Figure 2(b) shows XRD patterns of the nanopowders. In general, the patterns of these nanorized powders contain many diffraction peaks, indicating their polycrystallinity. Here, the characteristic peaks such as (0 1 5), (1 0 10), (2 0 5), and (1 1 0) are indexed according to the standard JCPDS cards of rhombohedral Bi₂Te₃ with a hexagonal crystal structure (015–0863). Furthermore, the XRD pattern of A-Bi-Te shows fewer
satellite peaks than that of M-Bi-Te. This implies that the M-Bi-Te nanopowder could have lower crystallization or more defects including impurities. Figure 2(b) shows the XRD patterns of the commercial Bi-Te alloy and the Bi-Te mixed powder. After ball-milling, M-Bi-Te has more oxides peaks (Bi$_2$O$_3$ and TeO$_2$) than A-Bi-Te does. It is because Bi and Te elements are more reactive than Bi$_2$Te$_3$. Additionally, the major orientations of A-Bi-Te and M-Bi-Te particles are similar, (0 1 5) and (1 0 10). Here, the characteristic peaks are indexed according to the standard JCPDS cards of Bi$_2$O$_3$ (041–1149) and TeO$_2$ (011–0693). However, due to the higher oxidation, the particle size distribution of M-Bi-Te was less uniform as shown in FESEM images of Figure 1(b,c). As a result, the SPS processing temperature made a slightly different impact on the crystallization of the compacted samples.

In Figure 2(c), no significant changes occurred in the XRD patterns of the SA-Bi-Te samples obtained through SPS at 483 and 533 K. In contrast, SM-Bi-Te has some changes in the intensities of the major peaks, especially (0 1 5), as shown in Figure 2(d). In this figure, we saw that the SM-Bi-Te had an improvement of Bi$_2$Te$_3$ characteristic peaks and a decrease of Bi$_2$O$_3$ oxide peaks with high processing temperatures. At the processing temperature of 533 K, the XRD peaks of the SM-Bi-Te sample are not as sharp as those of SA-Bi-Te, particularly from the planes (0 1 5), (1 0 10), (1 0 15), (2 0 5), and (0 2 10). That indicates the higher crystallinity of SA-Bi-Te formed at 533 K. Additionally, while oxide peaks of Bi$_2$O$_3$ in SM-Bi-Te slightly decreased, characteristic peaks of TeO$_2$ remained significantly. Overall, the oxidation of our samples could be happened during the long ball-milling process (perhaps when ethanol was mostly evaporated) and remain after SPS. Furthermore, it is evidence of the pre-oxidation of our Bi-Te nanocomposites and the stability of TeO$_2$ impurity

Figure 3(a,b) display high-resolution TEM images of the compacted samples at 533 K. Many boundaries appear between randomly oriented grains, as manifested by the high angles between adjacent lattice planes. That further demonstrates the polycrystallinity of the compacted samples. By using fast Fourier transformation (FFT) processing of selected areas in these TEM images, we found the rhombohedral crystal structure of the samples. The EDX results in Figure 3(c,d) show the atomic
ratios of bismuth/tellurium in the SA-Bi-Te and SM-Bi-Te samples which are approximately 40.7/59.3 and 40.2/59.8, respectively. Although these values are slightly different from EDX data in Supporting Tables S2, they confirmed that compacted samples had mainly the stoichiometry of Bi$_2$Te$_3$.

To further understand the chemical compositions of the SA-Bi-Te and SM-Bi-Te samples, XPS using Ar-etching was performed and shown in Figure 4. Here, the observed peaks in the typical wide-scan XPS spectra in Figure 4(a) are assigned to the elements Te, Bi, C, and O. Figure 4(b) shows the calculated elemental contents of the compacted samples before and after Ar-etching. Here, the amounts of C and O were reduced drastically after Ar bombardment. As a result, the C peaks probably arise from the air or contamination by the carbon mold for SPS. Besides, the reduction of the O peaks confirmed the natural oxidation of the powders or samples occurring mainly on their surfaces.

To examine the bonding types of the samples, the peaks of C 1s, O 1s, Te 3d, and Bi 4f were fitted by the Lorentzian-Gaussian optimization, as presented in Figure 4(c–f), respectively. The fitting and analysis results are collected and summarized in Table 1. In Figure 4(c), the C 1s peak appears in all samples, in which C-C and C-O bonds (at 284.5 and 285.2 eV, respectively) are significantly dominant. Additionally, it indicates that bonding between C and Bi or Te is negligible. Figure 4(d) shows the O 1s spectra of all compacted samples. Here, three bonding types are observed at 529.0, 530.3, and 531.8 eV. The major peak located at 529.0 eV may be associated with lattice oxygen from metal-oxide bonds in the Bi-Te samples. Two minor peaks located at 530.3 and 531.8 eV correspond to dangling bonds (O$^-$, O$_2^-$) and surface-adsorbed oxygen (O$_2^-$), respectively [27]. These minor bonds in the XPS spectra are attributed to the formation of surficial oxygen vacancies in Bi$_2$O$_3$ and
TeO₂. According to the relative intensity ratio (RIR) of O 1s (lattice O)/O 1s (dangling bonds and adsorbed O), the relative concentration of surficial oxygen vacancies can be estimated. The calculated RIR values before and after Ar-etching are 1.13 → 1.11 and 1.13 → 1.43 for the SA-Bi-Te and SM-Bi-Te samples, respectively. That is a clear difference in the oxygen vacancy concentration between SA-Bi-Te and SM-Bi-Te formed under the same processes. Therefore, the results suggest that such chemical differences arise from the initial state of the powder mixture and alloy. In Figure 4(e), the Te 3d orbitals of all samples contain four characteristic peaks. Two of them are Te 3d₃/₂ and Te 3d₅/₂ (at about 571.5 and 581.8 eV, respectively) which represent metallic bonds. Other peaks at 576 and 586.5 eV are assigned to the oxide bonds of Te. Actually, the analysis of the Te 3d peaks shows the presence of various oxidation states of Te, such as Te²⁻ in Bi₂Te₃ (571.3 and 581.6 eV), Te⁰ in Bi₂Te₃ (572.0 and 582.3 eV), Te⁴⁺ in TeO₂ (573.7 and 584.0 eV), and TeO₃ (or Bi-Te-O at 575.2 and 585.5 eV). From our observation, the changes in peak intensities before and after Ar-etching proved that the Te component got heavily oxidized and TeO₂ was the dominant oxide impurity. More interestingly, a similar oxidation phenomenon is observed in the Bi component as in Figure 4(f). The Bi 4f spectra of SA-Bi-Te and SM-Bi-Te before Ar-etching have four characteristic peaks. Two peaks at about 157.5 and 163.5 eV in the spectra are assigned to the Bi 4f₅/₂ and Bi 4f₇/₂ orbitals, respectively. They represent metallic bonds between Bi and Bi or Bi and Te in Bi₂Te₃. Two other peaks at about 159 and 164.5 eV are Bi 4f₇/₂ and Bi 4f₅/₂, respectively, indicating Bi-O bonds. Through the analysis of Bi 4f, we also observed the presence of various oxidation states of Bi, such as Bi⁰ in Bi₂Te₃ (155.6 and 160.9 eV), Bi³⁺ in Bi₂Te₃ (156.1 and 161.4 eV), Bi⁵⁺ in Bi₂O₃ (157.2 and 162.5 eV), and BiO₃ (157.8 and 163.1 eV). Generally, the XPS survey shows
Table 1. The binding energy and areal percentage of each components in XPS peaks extracted from the high-resolution XPS spectra of SA-Bi-Te and SM-Bi-Te samples (533 K).

| Chemical components | (Binding energy, eV) | SA-Bi-Te | Etched SA-Bi-Te | SM-Bi-Te | Etched SM-Bi-Te |
|---------------------|----------------------|----------|----------------|----------|----------------|
| **Carbon (C 1s)**   | C-C (284.5)          | 17.87    | 13.44          | 14.22    | 6.09           |
|                     | C-O (285.2)          | 49.41    | 43.86          | 46.68    | 31.60          |
|                     | O-C-O (286.4)        | 22.22    | 32.09          | 29.09    | 49.76          |
|                     | O = C-O (288.0)      | 10.50    | 10.61          | 10.01    | 12.55          |
| **Oxygen (O 1s)**   | O-metal (529.0)      | 42.62    | 52.77          | 53.2     | 59.04          |
|                     | Dangling Bond O (530.3) | 33.52   | 16.02          | 37.44    | 23.27          |
|                     | ABS O (531.8)        | 23.86    | 31.21          | 9.36     | 17.69          |
| **Tellurium (Te 3d)** | Te$^{2+}$ in Bi$_2$Te$_3$ (571.3, 581.6) | 11.54    | 9.81           | 11.63    | 22.73          |
|                     | Te$^{4+}$ in Bi$_2$Te$_3$ (572.0, 582.3) | 7.34     | 84.27          | 46.13    | 73.54          |
|                     | Te$^{2+}$ in TeO$_2$ (573.7, 584.0) | 7.32     | 4.11           | 5.06     | 2.54           |
|                     | Te$^{4+}$ in TeO$_2$ (575.2, 585.5) | 73.80    | 2.71           | 37.18    | 1.19           |
| **Bismuth (Bi 4f)** | Bi$^{3+}$ in Bi$_2$Te$_3$ (155.6, 160.9) | 9.61     | 19.42          | 14.13    | 8.95           |
|                     | Bi$^{4+}$ in Bi$_2$Te$_3$ (156.1, 161.4) | 19.02    | 52.72          | 15.23    | 69.50          |
|                     | Bi$^{3+}$ in Bi$_2$O$_3$ (157.2, 162.5) | 58.41    | 22.55          | 16.32    | 8.81           |
|                     | Bi$^{5+}$ in Bi$_2$O$_3$ (157.8, 163.1) | 12.96    | 5.31           | 54.32    | 12.74          |

that oxides of both Bi and Te are remained after SPS processing. This is in agreement with the XRD results in Figure 2. The changes in the intensity ratios of oxide/metallic bonds after Ar-etching reveal that the surficial Te component of SA-Bi-Te in Figure 4(e) was oxidized more easily while Bi oxidation is more prominent in the SM-Bi-Te surface in Figure 4(f). In addition to the mentioned dissimilar oxidation degrees, the thermoelectric properties of the compacted samples are clearly different between the alloyed and mixed samples.

As in Figure 5(a), the electrical conductivities ($\sigma$) of the SA- and SM-Bi-Te samples showed opposing changes upon heating. At 300 K, the conductivity of the SA-Bi-Te sample (about $1 \times 10^{-2}$ Sm$^{-1}$) was higher than that of SM-Bi-Te (about $0.6 \times 10^{-2}$ Sm$^{-1}$). When the measurement temperature was increased from 300 to 420 K, the electrical conductivity of SA-Bi-Te decreased gradually while that of SM-Bi-Te increased. As a result, SA-Bi-Te acts like a metallic conductor while SM-Bi-Te is a semiconductor with higher oxidation. When Regarding the effect of SPS processing temperature it was increased from 483 to 533 K, the electrical conductivity of the SA-Bi-Te samples was lowered. In contrast, the SM-Bi-Te sample formed at 533 K (i.e., "SM-Bi-Te (533 K)") showed a higher conductivity compared to that at 483 K (i.e., "SM-Bi-Te (483 K)"). For detail, the electrical conductivity of SM-Bi-Te (483 and 533 K) is $0.558 \times 10^{-2}$ and $0.639 \times 10^{-2}$ Sm$^{-1}$, respectively, while that of SA-Bi-Te (483 and 533 K) is $1.024 \times 10^{-2}$ and $0.875 \times 10^{-2}$ Sm$^{-1}$, respectively (measured at 300 K). Here, we assume that the powder mixture (M-Bi-Te) underwent more structure reconstruction than the alloy (A-Bi-Te) did during SPS, as revealed by their changes in the XRD patterns in Figure 2(c,d). The improvement of the crystallization during SPS at 533 K led to the reduction of grain boundaries (increased grain size) and then the enhancement of the electrically conductive pathways of Bi-Bi and Te-Bi interfaces (metallic conducting) as well as Bi-O and Te-O interfaces (semi-conducting). As reported previously, TeO$_2$ and Bi$_2$O$_3$ can act as p-type semiconductors at $<500$ K, while Bi$_2$Te$_3$ grains are topological insulators [28,29]. Additionally, the semiconducting SM-Bi-Te has higher oxidation than the metallic SA-Bi-Te did, as is Supporting Table S2. From the viewpoint of metal–semiconductor junctions, SA-Bi-Te (533 K) would have more p-type conduction due to oxidation. Here, the electrical characteristics of the SA-Bi-Te and SM-Bi-Te samples (coin-shaped) were checked with horizontal and vertical electrode configurations as shown in Supporting Figure S3; the differences between their parallel and perpendicular conductivities is negligible because of their polycrystal structures (Figure 1f,g) and (2c,d) [30].

Figure 5(b,c) show the carrier concentration and carrier mobility of the compacted samples as a function of the measurement temperature, respectively. As the temperature increased from 300 to 420 K, the carrier concentration of the SA-Bi-Te and SM- Bi-Te (533K) samples raised rapidly (about 4 folds). However, the carrier mobility of SM-Bi-Te tended to increase while that of SA-Bi-Te decreased. Overview, similar
Figure 5. Thermoelectric properties of SA-Bi-Te and SM-Bi-Te samples obtained under different SPS temperatures. Their changes in (a) electrical conductivity ($\sigma$), (b) carrier concentration, (c) carrier mobility, (d) Seebeck coefficient ($\alpha$), (e) total thermal conductivity ($k_T$), (f) electronic thermal conductivity ($k_e$), (g) lattice thermal conductivity ($k_l$), and (h) figures of merit ($ZT$), respectively.
trends in Figure 5(a,c) indicate that the contribution of the carrier mobility to their electrical conductivity is predominant.

Figure 5(d) shows the Seebeck coefficients (a) of the compacted samples. When the measurement temperature increased, the maximum a values of SA-Bi-Te (483 K) and (533 K) were slightly increased from 0.218 and 0.223 mV/K (measured at 300 K) to 0.242 and 0.246 mV/K (measured at 420 K), respectively. Similarly, those of SM-Bi-Te (483 K) and (533 K) grew from 0.242 and 0.245 mV/K (at 300 K) to 0.264 and 0.267 mV/K (at 420 K), respectively. So, the Seebeck coefficients of both SA- and SM-Bi-Te are positive. According to the Ioffe theory, because the grain size increases, the carrier concentration at the grain boundary is also improved, leading to the increased Seebeck coefficient [31]. The temperature dependence of the carrier concentration of our SA-Bi-Te and SM-Bi-Te samples (Figure 5b) correlated well with the behaviors of their a. However, the a value of SA-Bi-Te is smaller than that of SM-Bi-Te. It can be because the behavior expected from a metallically doped material [32]. Generally, the data indicates that higher Seebeck coefficients are obtained for the SM-Bi-Te samples due to better electrical conductivity, particularly the improved charge mobility and increased carrier concentration, at high temperatures.

Figure 5(e-g) show the total thermal conductivity (k or kL), which is contributed by the electronic thermal conductivity (kE) and lattice thermal conductivity (kL), of the compacted samples as a function of the measurement temperatures. As observed in Figure 5(e), both of our samples had small changes in the total thermal conductivity even when the measurement temperature raised from 300 to 420 K. This is in agreement with the literature where thermal conductivity of Bi2Te3 has a small temperature dependence [33]. For confirmation, we checked the electronic and lattice thermal conductivities of these samples. Figure 5(f) shows that kE is proportional directly to the electrical conductivity (Figure 5(a)) but inversely to kL (Figure 5(g)). The different temperature dependence of kL in SA-Bi-Te and SM-Bi-Te relates to their anharmonicity in bonding [34]. As aforementioned, the FESEM-EDX results (Supporting Tables S1 and S2) revealed that SM-Bi-Te has a higher Te/Bi ratio, but its Te/Bi distribution is not uniform compared to those of SA-Bi-Te. That suggests weak interatomic bonding and possible strong anharmonicity in SM-Bi-Te. Thereby, the kL values of SM-Bi-Te decreased while that of SA-Bi-Te slightly increased with an increase in measurement temperature. Due to the contrasting behaviors of the electronic and lattice contributions, the total thermal conductivity of SA-Bi-Te and SM-Bi-Te was seemingly independent with measurement temperatures (300 ~ 420 K). Particularly, the SA-Bi-Te samples owned smaller kL values (about 1.55 Wm⁻¹K⁻¹) than that of SM-Bi-Te (about 2.1 Wm⁻¹K⁻¹), probably because of non-uniformly mixing by ball-milling as revealed in FESEM and TEM analysis. The figures of merit ZT = a²σT/k for these samples are presented in Figure 5(h). Here, we observed a similar measurement-temperature dependence between the electrical conductivity (Figure 5(a)) and the ZT values of the compacted samples. Along these lines, the ZT value of the heated SA-Bi-Te samples was decreased while that of the heated SM-Bi-Te samples was increased. In comparison, the ZT value of SA-Bi-Te (483 K) is 1.67 times higher than that of SM-Bi-Te (483 K) when measured at 300 K (0.922 and 0.469, respectively). The ZT value of SM-Bi-Te (533 K) is 5.05 times higher than that of SA-Bi-Te (533 K) when measured at 420 K (1.671 and 0.331, respectively). The obtained data in Figure 5(e) confirms that the k values of the compacted samples are not significantly different when measured at 300 ~ 420 K. Consequently, the behavior of ZT values of the samples upon on heating could be caused by their electrical conductivity as well as carrier mobility. Indirectly, this phenomenon indicates the positive effects of pre-oxidation on the thermoelectric performances of the semiconducting Bi-Te samples. Indeed, Bi2Te3Ox, Bi2O3, and Te2O3 are formed on the Bi-Te surfaces by reaction with surrounding oxygen, permitting surface stabilization as the temperature is increased. Regarding SA-Bi-Te, the oxides decrease its metallic conductive behavior, thus decreasing its electrical conductivity and thereby figure of merit. For semiconducting SM-Bi-Te, the oxygen concentration is higher than that of the SA-Bi-Te sample as revealed by XPS surveys (Figure 4). When the measurement temperature is increased, p-doping oxidation occurs more frequently on the dangling-bond O sites, thereby decreasing defects and increasing the electrical conductivity. The intersection of ZT of the SA-Bi-Te and SM-Bi-Te samples (Figure 5(h)) is considered indicating the highest device efficiency of this meta-metal and p-type semiconductor system at approximately 330 K.

4. Conclusion

In summary, we synthesized Bi-Te samples using a two-step process of ball-milling and SPS that introduced oxide impurities to the samples. The pre-oxidation (mainly formed during the ball-milling process) seemingly did not affect the total thermal conductivity of the Bi-Te samples. However, due to the hole-doping behavior of oxides, the electrical conductivity of the thermoelectric Bi-Te samples changed in two opposing tendencies. That is because SA-Bi-Te is electron-rich (like meta-metal), SM-Bi-Te easily turns into a hole-rich semiconductor. More interestingly, while the figure of merit values of SA-Bi-Te with the electron-rich behavior were
suppressed, those of p-type semiconducting SM-Bi-Te were improved due to more oxidation at higher measurement temperatures (300 ~ 420 K). These results provided evidence of the positive effects of pre-oxidation on the performance of p-type semiconducting Bi-Te samples (Te/Bi ratio < 1.5). The highest efficiency of the thermoelectric system of a meta-metal (SA-Bi-Te) and a p-type semiconductor (SM-Bi-Te) was determined at approximately 330 K. Overall, our proposed method is promising for the fabrication and doping of Bi-Te nanostructures as well as other thermoelectric materials in other to obtain a higher efficiency at targeted operation temperatures.

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ORCID

Le Thai Duy http://orcid.org/0000-0003-0070-8984
Byungmin Ahn http://orcid.org/0000-0002-0866-6398
Hyungtak Seo http://orcid.org/0000-0001-9485-6405

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