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EFFECTS OF MILLING DURATION ON THE THERMOELECTRIC PROPERTIES OF N-TYPE $Bi_2Te_{2.7}Se_{0.3}$

In this study, an oxide reduction process and a reduction-sintering process were employed to synthesize a thermoelectric alloy from three thermoelectric composite oxide powders, and the thermoelectric properties were investigated as a function of the milling duration. Fine grain sizes were analyzed by via X-ray diffraction and scanning electron microscopy, to investigate the influence of the milling duration on the synthesized samples. It was found that microstructural changes, the Seebeck coefficient, and the electrical resistivity of the compounds were highly dependent on the sample milling duration. Additionally, the carrier concentration considerably increased in the samples milled for 6 h; this was attributed to the formation of antisite defects introduced by the accumulated thermal energy. Moreover, the highest value of *ZT* (=1.05) was achieved at 373K by the 6-h milled samples. The temperature at which the *ZT* value maximized varied according to the milling duration, which implies that the milling duration of the three thermoelectric composite oxide powders should be carefully optimized for their effective application.

Keywords: Thermoelectric, bismuth telluride, powder, milling

1. Introduction

When temperature difference exists between two ends of a thermoelectric material, voltage is induced and electric power is generated. The resulting emission of heat at one end and its absorption at the opposite end induce a temperature difference between the two ends [1,2]. The energy-converting thermoelectric performance of thermoelectric materials is expressed as a dimensionless figure of merit ZT (= $(\alpha 2\sigma/\kappa)T$, where α, σ, κ, and T refer to the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. A high ZT means that the thermoelectric material has high energy conversion efficiency.

The thermoelectric material with the best figure of merit varies according to the temperature. Bi-Te-based materials are typically the material of choice, as they exhibit a high figure of merit near room temperature, which is applicable to a number of applications [3,4]. However, the figure of merit of n-type materials remains lower than those of p-type materials. Further study is needed to improve their performance [5].

The techniques to synthesize thermoelectric materials include single-crystal growth methods [6] and powder sintering. The representative powder sintering processes are melting/grinding [7] and oxide reduction. The single-crystal growth method is commonly used to fabricate commercial materials. Although the materials fabricated via this method exhibit high and stable thermoelectric characteristics, they are difficult to machine and experience increased material loss because of their low mechanical strength. In contrast, the melting/grinding method can yield stable material properties and less material loss, but grain refinement is restricted and composition control is difficult. In the oxide reduction process, composites are synthesized from oxides and metal-based powder for application in thermoelectric semiconductors, and they undergo heat treatment to compensate for the above-mentioned weaknesses [8-10].

Recent research aiming to improve the performance of thermoelectric materials has mainly focused on increasing the power factor ($\alpha^2\sigma$) or decreasing lattice thermal conductivity by inducing grain refinement and phonon scattering. Alternatively, oxide reduction processes can uniformly mix multiple components to form uniform composite compounds [11,12]. Furthermore, oxide base materials are used in milling, which helps enhance grain refinement.

In this study, thermoelectric composite oxide powder and other thermoelectric materials are synthesized via an oxide reduction process and a reduction-sintering process, respectively, in order to investigate the effects of these processes. Additionally, the effects of reaction time on the characteristics of the oxide powder were investigated, and the carrier concentration, electrical properties, thermal conductivity, and figure of merit of the thermoelectric materials were compared to determine their respective effects on base material dispersibility and grain size.

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2. Experimental

The n-type thermoelectric material was synthesized via an oxide reduction process. Mechanical milling was used to synthesize the thermoelectric composite oxide powders. The milling effects on the thermoelectric material properties were observed after reduction and sintering. The recognized composition of the thermoelectric powder is $Bi_2Te_{2.7}Se_{0.3}$. This composition is realized by doping Se in place of Te in Bi_2Te_3. Among the known thermoelectric materials, Se is recognized for its relatively stable material properties [13,14]. The base powders comprised 99.9% pure Te, Bi, and Se. The n-type $Bi_2Te_{2.7}Se_{0.3}$ thermoelectric material was synthesized via mechanical milling and after undergoing heat treatment (Fig. 1). An energy-dense horizontal rotating ball mill was used for the milling process. The oxides were weighed according to stoichiometric ratios, wet milled, mixed, and ground. The milling process resulted in the synthesis of Te, Bi, and Si oxide powders via mechanical mixing and grinding.

The size and shape of the grains synthesized after wet milling were examined by scanning electron microscopy (SEM). X-ray diffraction (XRD) phase analysis was used to identify the phase change during the milling process. The milled oxide powders were then dried and heat-treated to form a thermoelectric phase. The heat treatment was performed at 430°C under a reducing atmosphere. The reduced thermoelectric powder was synthesized, underwent spark plasma sintering (SPS), and was fabricated into a bulk-type thermoelectric material. The thermoelectric and electrical properties of the resulting thermoelectric material were then evaluated by density and phase analysis methods and a four-probe method, respectively. A laser flash method was used to measure the thermal conductivity. The specific heat of the material, defined as the average of the specific heat of the sample measured by a differential scanning calorimeter, was found to be 0.16 J/(gK).

3. Results and discussion

The compound Bi2Te2.7Se0.3 was synthesized from milled Bi-Te-Se oxide powder after reduction. This synthesized n-type thermoelectric powder was then fabricated into a bulk material by pressure sintering. The microstructure of the milled oxide base powder and its energy-dispersive X-ray spectrometry (EDS)-mapped dispersibility after mixing the three-element base materials can be observed in Fig. 2(a) and (b), respectively, for different milling durations. The EDS results show the milled powder was nonuniform and comprised local clusters following 2-h milling of the Bi and Te base powders. However, the three-element base powders were uniformly distributed after milling for 6 h. The EDS mapping results were consistent with the XRD phase analysis results presented in Fig. 3, which also indicate poor dispersibility with locally clustered Bi and Te. The nonuniform dispersion of the base materials that have undergone less than 6 h of milling may impede the stable formation of the composite and affect the properties of the sintered body, leading to nonuniformity of the material.

Fig. 2(c) shows the finite element (FE)-SEM images of the alloy powder obtained after the milled powder was reduced in a hydrogen atmosphere at 430°C. The resulting grain-size distribution was similar to that of the oxide powder. It can be seen that the grains became finer as the milling duration increased. The highest degree of uniformity of the grain-size distribution of the reduced powder was observed after 12 h of milling. However, compared to the 6-h milled sample, there was no significant increase in the effects of grinding. Furthermore, it seems that the grain-refining grinding effect becomes less critical after a certain level of refinement.

Fig. 3 shows the XRD phase analysis results of the sintered body for each milling duration. It is important to note that milling not only served to grind the powders, but also resulted in the partial bonding of the phases, and, ultimately, the formation of a Bi-Te-Se compound phase. Two hours of milling resulted in a compound phase for two-element oxide compounds. Conversely, a milling duration of at least 6 h resulted in nearly all of the powder being formed into the target composition for the Bi-Te-Se compound, with very few two-element phases.

The milled and reduced Bi-Te-Se thermoelectric compound powders were then sintered via an SPS process at 450°C. The microstructure and properties of the resulting sintered material were subsequently evaluated. Fig. 2(d) shows the FE-SEM images of the fracture surfaces of the Bi-Te-Se thermoelectric sintered body. The sintered Bi-Te-Se thermoelectric compound had layered structures, and the average grain size was approximately 2-3 μm. Grain refinement was observed as the milling process progressed. Coarse Bi-Te-Se grains were observed in the 2-h

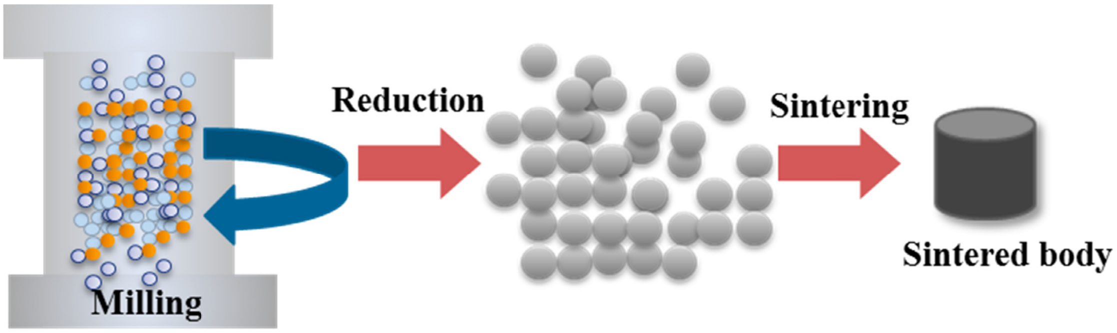

Fig. 1. Oxide reduction process used to synthesize the thermoelectric material

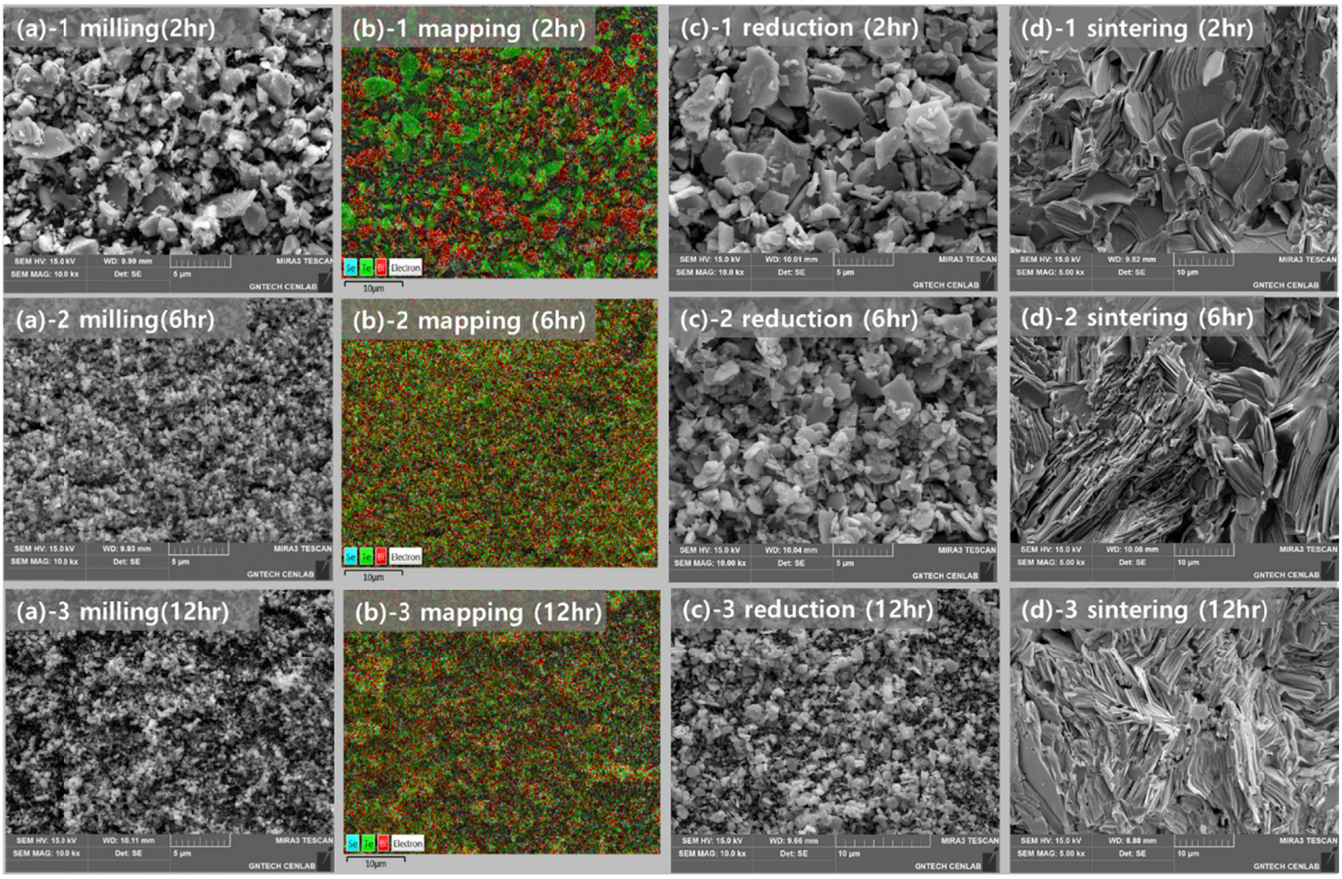

Fig. 2. FE-SEM images of Bi-Te-Se thermoelectric material: (a) microstructure of the milled powder, (b) EDS mapping of the milled powder, (c) reduced powder, and (d) fracture surface of the sintered body

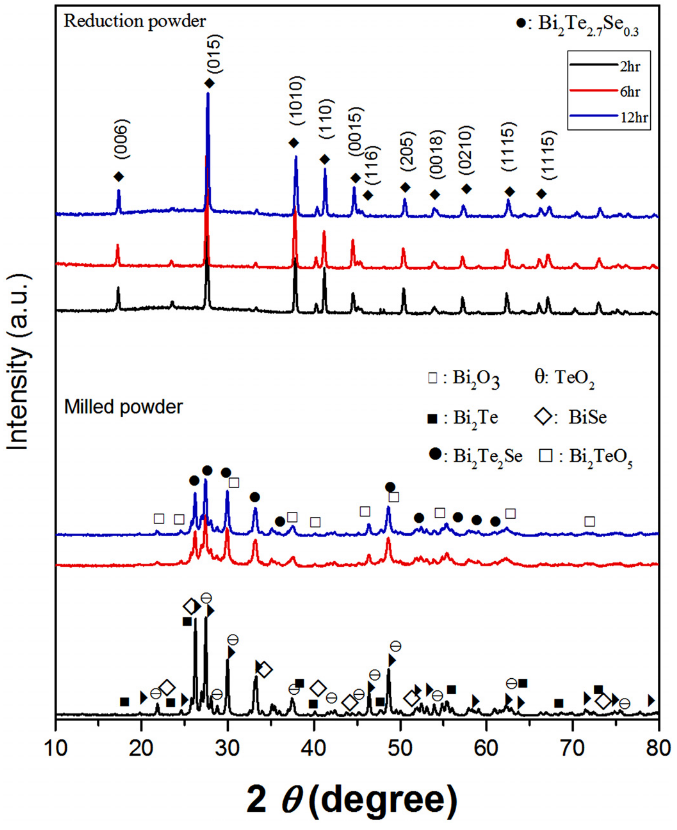

Fig. 3. XRD patterns of Bi-Te-Se compounds fabricated via oxide reduction

milled powders even after sintering, probably because the size of the milled grains was larger than that of the reduced grains. It is difficult to clearly determine the effects of milling on sintered powders because factors such as grain growth induce changes in the microstructure after sintering. However, it is evident that performing the reduction process after milling the alloy powder for a longer period of time (for 6 and 12 h) resulted in reduced grain sizes, and that subsequent sintering only slightly reduced the grain size.

To quantify the grain size results discussed above, the full width at half maximum (FWHM) was calculated by solving the Scherrer equation [15]. The average grain size of the reduced Bi-Ti-Se powder and Bi-Te-Se thermoelectric sintered body are illustrated in Fig. 4 as a function of the milling duration. It can be seen that the reduced thermoelectric powder exhibited the smallest average grain size (between 25 and 30 nm) after 6-8 h of milling. Although the grain size observed in the microstructure of the sintered thermoelectric material was also minimized between 6 and 8 h of milling, the grains observed during this period reached a size of 40 nm.

As shown in Fig. 5(a), extending the milling duration decreased the electrical conductivity of the material; this means that a longer milling duration corresponds to increased electrical resistivity. More specifically, the electrical resistivity of the 12-h milled sample increased to nearly twice that of the 2-h milled sample. Additionally, in Fig. 5(b), the Seebeck coefficient tended

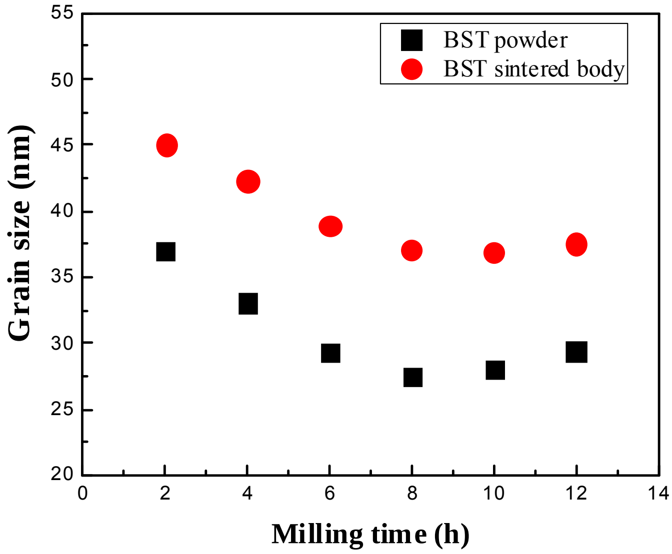

Fig. 4. Grain size of Bi-Te-Se thermoelectric material

to be larger when the carrier concentration was low, and the electrical resistivity was found to be dependent on the charge concentration and charge mobility. Defects were observed to form within the grains because of the directly proportional relationship between milling duration and grain refinement, and these defects increased the carrier concentration within the material. In Fig. 5(b), it can be seen that the charge concentration and milling duration have an inversely proportional relationship, which is exaggerated after 6 h of milling. Conversely, a significant increase in the carrier mobility was observed after 6 h of milling. These results imply that a substantial decrease in the carrier concentration after 6 h of milling corresponds to increased electrical resistivity. In addition, the carrier mobility of the 12-h sample drastically increased, probably owing to the accumulated thermal energy that led to the formation of antisite defects. This phenomenon was also evident from the Seebeck coefficient results. As shown in Fig. 5(c), lattice thermal conductivity of the micro-sized composite material was lower at 298K [13]; this phenomenon is presumed to be a consequence of the nanostructure, which affects lattice phonon scattering. The inversely proportional relationship between the thermal conductivity of the lattice and the milling duration has been identified as the reason that the total thermal conductivity tended to decrease as the milling duration was extended. Additionally, it is believed that the finer grains that result from a longer milling duration deteriorate the electrical properties of the alloy, but improve the thermal properties. Fig. 5(d) shows the effects of milling duration on the figure of merit (*ZT*). Although extending the milling duration initially increases the figure of merit, once the maximum is

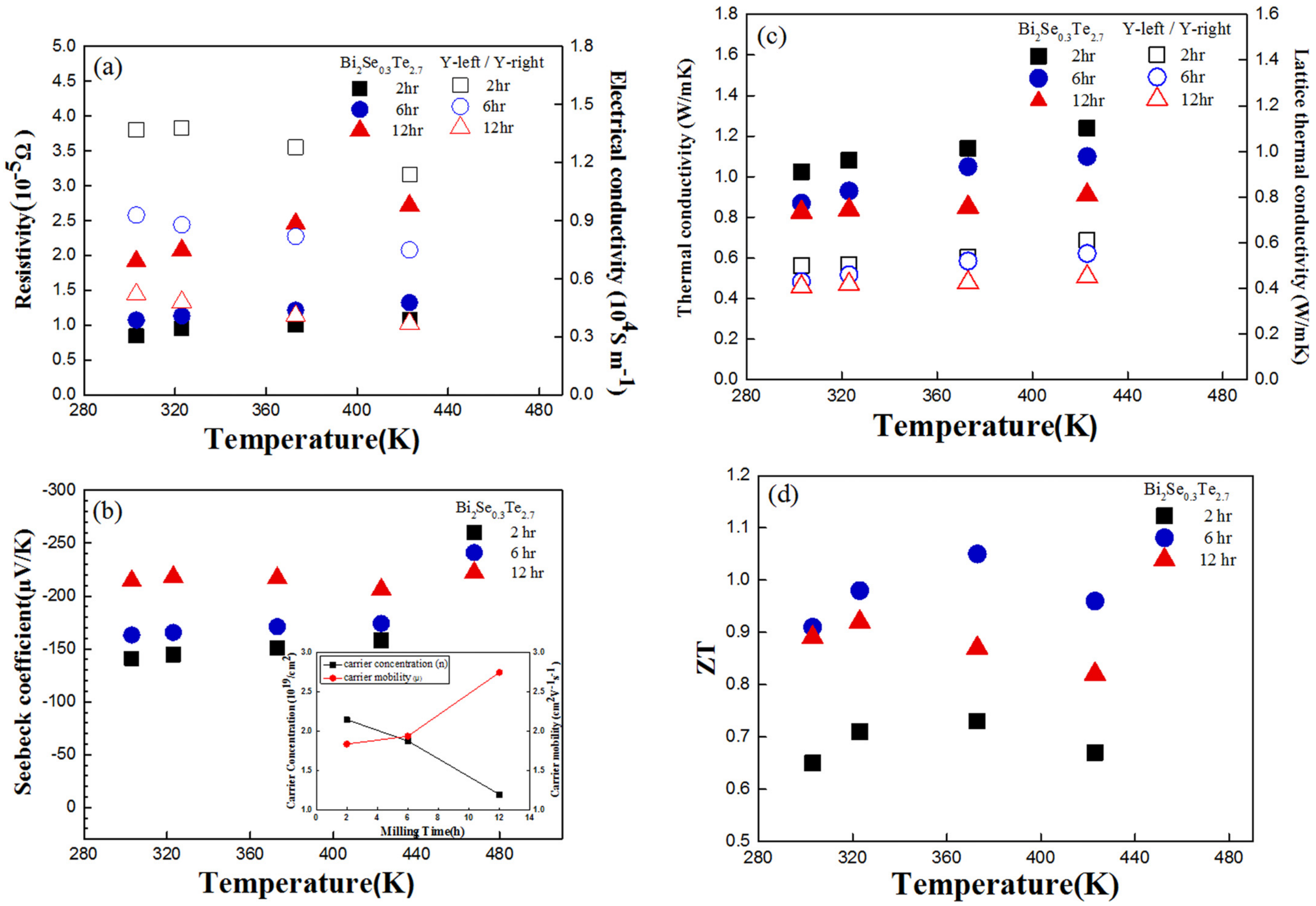

Fig. 5. Thermoelectric and electrical properties as a function of temperature (298-423K): (a) resistivity and electrical conductivity , (b) Seebeck coefficient, (c) thermal conductivity, lattice thermal conductivity and (d) Figure of merit (*ZT*) of $Bi_2Te_{2.7}$-$Se_{0.3}$ alloys

reached, a decreasing trend seems to emerge. The maximum *ZT* value was 1.05, which corresponded to the material synthesized from powders milled for 6 h at 373 K.

4. Conclusions

This study investigated the effects of milling duration on the properties of an n-type thermoelectric compound fabricated via an oxide reduction process that uses milling, and is distinct from conventional Bi-Te-based powder fabrication processes. Changes in grain dispersibility and grain size reductions were identified and quantified via microstructure analysis, EDS, and XRD. Moreover, we were able to enhance the thermoelectric material characteristics by controlling the characteristics of the base powders. Additionally, the maximum *ZT* value of 1.05 was achieved by the sample milled for 6 h at 373K. Grain refinement caused by extended milling was found to deteriorate the electrical properties of the thermoelectric alloy, while simultaneously improving its thermal properties.

Acknowledgements

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