

Synthesis of Bi-Te-Se-based Thermoelectric Powder by an Oxide-Reduction Process

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The present study focused on the synthesis of Bi-Te-Se-based thermoelectric powder by an oxide-reduction process. The phase structure and particle size of the synthesized powders were analyzed using XRD and FE-SEM. The synthesized powder was sintered by the spark plasma sintering method. The thermoelectric property of the sintered body was evaluated by measuring the Seebeck coefficient and specific electric resistivity. The $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ powder had been synthesized by a combination of mechanical milling, calcination and reduction processes using mixture of Bi_2O_3 , TeO_2 and SeO_2 powders. The sintered body of the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ powder synthesized by an oxide-reduction process showed n-type thermoelectric characteristics.

Keywords: thermoelectric, oxide, reduction, bismuth telluride, powder

1. INTRODUCTION

Thermoelectric materials (*TE*) for solid-state energy conversion have been widely used in cooling and generating for electronic devices. Recently, waste-heat recovery by using *TE* materials has attracted much attention regarding to a demand for reducing CO_2 .^[1-3] However, low *TE* performance reported during past decades has limited more wide practical application of *TE* materials. The energy conversion characteristics of *TE* materials can be expressed as figure-of-merit, $Z = \alpha^2/\rho\kappa$ (α : Seebeck coefficient, ρ : specific electric resistivity, κ : thermal conductivity).^[4] In order to obtain high-performance *TE* materials, high Seebeck coefficient and low specific electric resistivity and low thermal conductivity are required. Since these properties are materials constants depending on the behavior of carrier and phonon in the materials, appropriate combination among these properties is needed to improve *Z* values of *TE* materials.^[5,6]

Bismuth telluride-based alloys have been highly treated as important *TE* materials due to higher *TE* performance than those of other materials near ambient temperature. In particular, semiconducting behavior of bismuth telluride alloys can be changed by addition of alloying elements such as Sb for *p*-type and Se for *n*-type.^[2,3,7] The bismuth telluride-based alloys have been fabricated based on the melting and solidification process for single crystal growth technique. However, some researchers reported high *TE* performance caused by nanostructuring which results in "carrier filtering and

phonon blocking".^[8-10] For examples, Ma *et al.* introduced mechanical alloying process by pure metals,^[10] Poudel *et al.* reported nanostructured p-type bismuth telluride materials fabricated by mechanical milling process using alloyed powders^[9] and Xie *et al.* showed nanostructuring of the bismuth tellurides by the rapid solidification process.^[11] Furthermore, the wet-chemical methods^[12-17] and vapor condensation method^[18] have been vigorously studied to obtain bismuth telluride-based nanoparticles that can be used as raw materials. These processes are normally intended to produce p-type bismuth telluride-based *TE* powders and sometimes show unclear composition and phase due to low reaction among raw metal powders during the fabrication process.

In the present study, the focus is the synthesis of the n-type bismuth telluride-based *TE* powders by a reduction process using Bi-oxide, Te-oxide and Se-oxide powders as raw material. The thermoelectric properties of the sintered body of the synthesized n-type powders were characterized.

2. EXPERIMENTAL PROCEDURE

Bi_2O_3 (99.9% purity), TeO_2 (99.9% purity) and SeO_2 (99.9% purity) powders were used as raw material as shown in FE-SEM image of Fig. 1. In order to get designed composition of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, Bi_2O_3 , TeO_2 and SeO_2 powders were homogeneously mixed by the mechanical milling process using planetary ball mill. The oxide powder mixtures were calcined in air atmosphere to fabricate complex alloyed phase such as Bi-Te-Se-based oxide powders through reaction among the element oxides. The calcined powders were

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reduced into Bi-Te-Se-based n-type powders in hydrogen atmosphere. For comparison, only ball-milled powders without calcination heat-treatment were reduced in the same reduction condition. X-ray diffractions to powders in milling, calcination and reduction process were characterized to clarify the variation of phases. The microstructures of the powders in every processing step were observed by field emission scanning electron microscopy (FE-SEM).

The reduced powders were sintered by using the plasma enhanced sintering process at 300°C for 10 minutes under applied pressure of 45 MPa in vacuum atmosphere. The heating rate was 1.5°C/sec during sintering. The specific electric resistivity and Seebeck coefficient of fabricated sintered body were measured by using ZEM-3 equipment (Ulvac-Rico)^[9] at the temperature ranging from room temperature to 200°C. The oxygen content in sintered bodies was analyzed by using elemental analyzer (ON 900, Eltra).

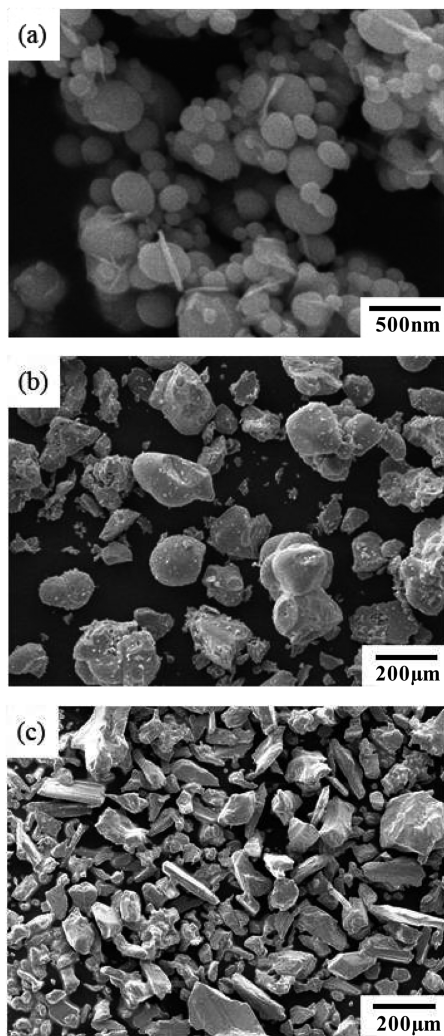


Fig. 1. FE-SEM micrographs of the (a) Bi_2O_3 , (b) TeO_2 and (c) SeO_2 powders.

3. RESULTS AND DISCUSSION

XRD patterns of mixtures of oxide powders with ball-milling time of 30 minutes, 3 hours and 12 hours were displayed in Fig. 2. In case of 30 minutes of ball milling, XRD pattern show the peaks revealing Bi_2O_3 , TeO_2 and SeO_2 oxides without a big change. The diffraction peak to 3 hours-milled powder shows that peak intensity decreases and only main peaks are observed while there are no peaks with weak intensity. As milling time increases to 12 hours, XRD peak intensity severely decreases and peak width is significantly broadened. It is described that this transformation into amorphous-like peak behavior results from change of powder particle size and grain refinement by effect of mechanical milling with increasing milling time.

XRD patterns on reduction treatment to both oxide mixture mixed by mechanical milling and simply mixed oxide mixture without mechanical milling were shown in Fig. 3, respectively. The reduction treatment carried out at 330°C for 3 hours in the hydrogen atmosphere. The simply mixed and reduced powder shows Bi_2O_3 , TeO_2 as main peaks and small amount of Bi_2Te_3 as additional peaks. On the contrary, the oxide mixture by 12 hours mechanical milling and followed by reduction shows $\text{Bi}_{3.2}\text{Te}_{0.8}\text{O}_{6.4}$, Te and $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ that is designed phase. That is, it is considered that the mechanical milling treatment provides high reduction reactivity to the oxide mixtures. Furthermore, individual oxide materials are alloyed into metal phases of Bi_2Te_3 and $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ by solid state diffusion during reduction process. In general, mechano-chemical (MC) effect is well known that powder-reactivity is increased by collisions among the milling balls during the mechanical milling treatment.^[20] Thus, it is described that the increased reactivity observed in this study is originated from the MC effect.

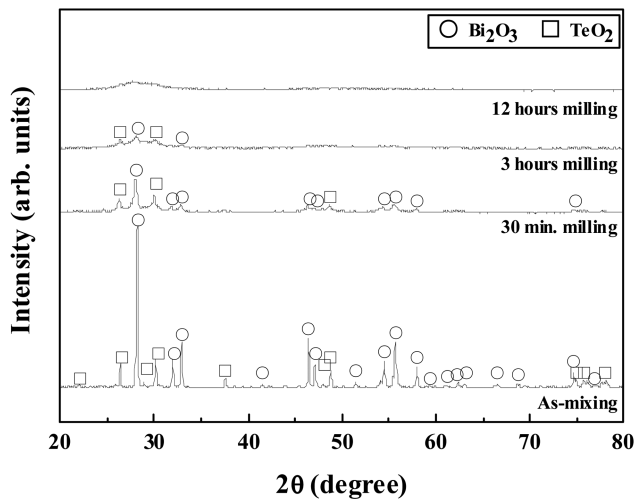


Fig. 2. X-ray diffraction patterns of the oxide mixtures under various mechanical milling times.

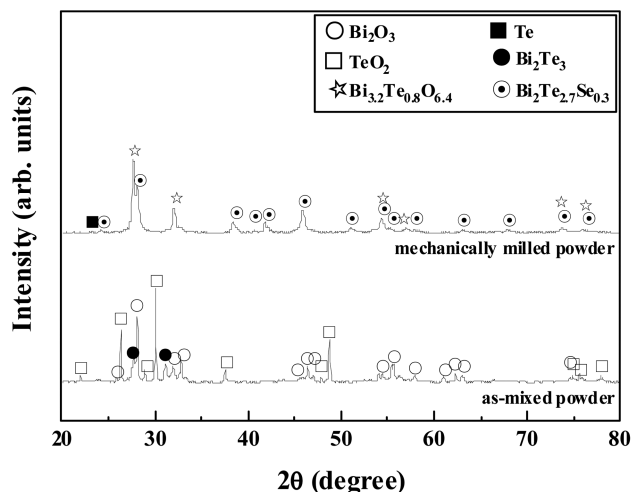


Fig. 3. X-ray diffraction patterns of the reduced powders of as-mixed and mechanically milled powders.

Although ternary phase of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ is observed in the powders which are 12 hours milled and reduced as shown in Fig. 3, high temperature and long time reduction are required to obtain designed n-type powders because there are still remained many oxide peaks. However, it is possible that reduction at high-temperature and for long time might cause inhomogeneous powder size distribution by agglomeration among the reduced powders. Thus, the reduction at low-temperature and for a short time is needed to synthesize homogeneous alloyed powders. To solve this issue, homogeneous mixing in atomic-scale of constituents such as Bi, Te and Se is preferred. In this study, solid solution and alloying through heat-treatment of the oxide mixtures are induced for homogeneous mixing of the constituent elements.

Figure 4 shows the XRD pattern of the heat treated oxide

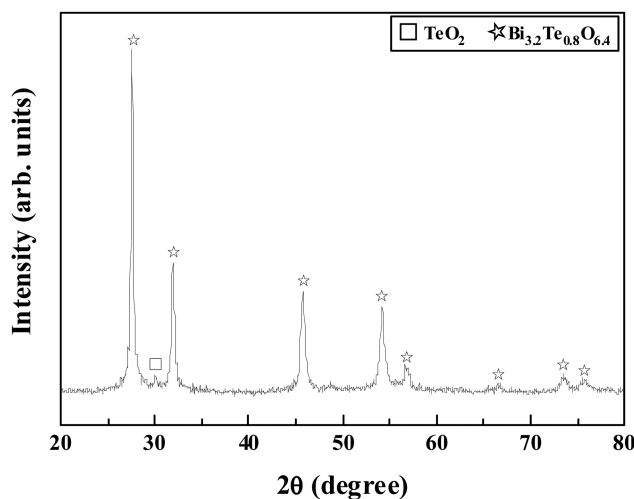


Fig. 4. X-ray diffraction of the calcined powder after mechanical milling.

mixture fabricated by 12 hours mechanical milling and followed by calcination at 300°C for 12 hours in an air atmosphere. The peaks of $\text{Bi}_{3.2}\text{Te}_{0.8}\text{O}_{6.4}$ and small amount of TeO_2 are observed in calcined powders. This peak indicates that mechanically milled oxide mixture consisting of Bi_2O_3 , Sb_2O_3 and TeO_2 is alloyed into complex oxide phase by the solid state reaction among the constituent oxides during calcination heat-treatment. Therefore, the calcination heat-treatment of mechanically milled oxide mixture leads to formation of complex oxide which is homogeneous mixing state of the Bi, Te and Se.

Figure 5 displays XRD patterns of reduced powders at 330°C for 3 hours to both only mechanically milled oxide mixture, and mechanically milled and followed by calcined oxide mixture, respectively. Only mechanically milled oxide mixture shows $\text{Bi}_{3.2}\text{Te}_{0.8}\text{O}_{6.4}$, $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ and additional Te diffraction peaks. While, calcined oxide mixture shows only $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ diffraction peaks which is designed phase in this study. Hence, it is analyzed that Bi-Te-Se alloy phase with the designed composition is obtained when mechanical milling process is combined with calcination heat-treatment. This phase formation might be due to increased homogeneity in mixing status during calcination process at the elevated temperature among Bi-oxide, Te-oxide and Se-oxide powders. However, it is considered that the phase transformation with reduction should be further investigated for clear description on increasing formability of the Bi-Te-Se ternary alloy phase.

FE-SEM image as shown in Fig. 6 displays the surface morphology of the synthesized $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ powders which is approximately below $1\ \mu\text{m}$ in size and irregular shapes in some parts.

Measured the Seebeck coefficient and specific electric resistivity with temperature to sintered body of the synthe-

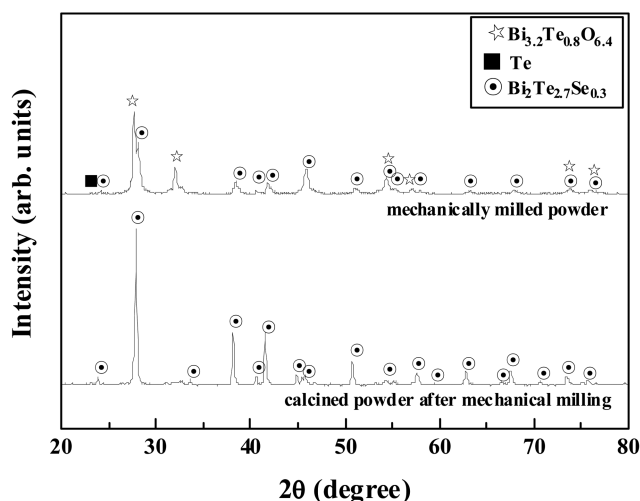


Fig. 5. X-ray diffraction patterns of the reduced powders of the mechanically milled powder and calcined powder after mechanical milling.

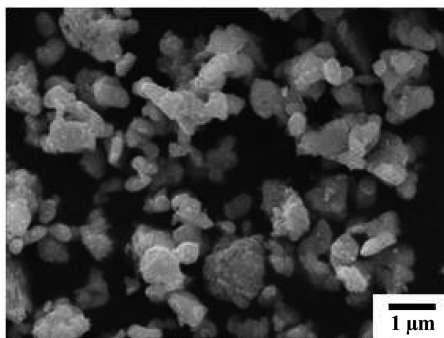


Fig. 6. FE-SEM micrograph of the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ powder synthesized by an oxide-reduction process.

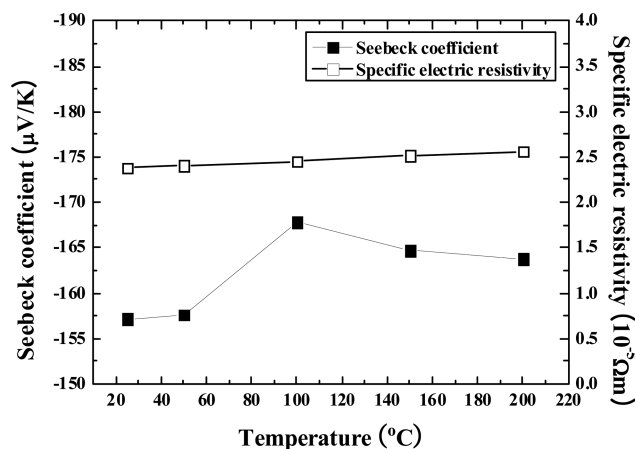


Fig. 7. Changes in the Seebeck coefficient and specific electric resistivity of the sintered body of the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ powder synthesized by an oxide-reduction process versus temperature.

sized $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ powder are shown in Fig. 7. The sintered body exhibits negative Seebeck coefficient that is reflected to characteristics of the n-type thermoelectric materials. The Seebeck coefficients show about $-157 \mu\text{V}/\text{K}$ at room temperature, about $-167 \mu\text{V}/\text{K}$ at 100°C . The specific electric resistivities show about $2.5 \times 10^{-5} \Omega\text{m}$ at the temperature ranging from room temperature to 200°C . The oxygen content of about 1.8 wt% in the sintered body was characterized. The n-type Bi-Te-Se based thermoelectric materials fabricated by the single crystal growth method show typically about $-160 \mu\text{V}/\text{K}$ to $-230 \mu\text{V}/\text{K}$ of Seebeck coefficient and about 0.6 – $1.5 \times 10^{-5} \Omega\text{m}$ of specific electric resistivity.^[7] In addition, it has been reported that the n-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ bulk fabricated by the melting and crushing method shows about $200 \mu\text{V}/\text{K}$ of Seebeck coefficient and about $2 \times 10^{-5} \Omega\text{m}$ of specific electric resistivity at room temperature.^[21] The n-type bismuth telluride bulk materials fabricated in this study shows lower Seebeck coefficient and higher specific electric resistivity than those of conventional materials. It is expected that low thermoelectric properties might come from high remnant oxygen content of 1.8 wt% not fully removed from reduction

process of complex oxides. Therefore, to control the oxygen content of the n-type Bi-Te-Se based alloys as key factor to enhance the thermoelectric properties and even commercialize the materials should be further investigated.

4. CONCLUSION

The present study focused on the synthesis of the Bi-Te-Se-based thermoelectric powder to investigate the possibility of synthesizing n-type Bi-Te-based alloy thermoelectric powder by an oxide-reduction process. The $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ alloyed powder was fabricated by a reduction of the mixture of Bi-oxide, Te-oxide and Se-oxide powders accompanying with the mechanical milling and calcination processes. The combination of the mechanical milling and calcination processes to oxide mixture leads to high reactivity to form Bi-Te-Se-based ternary alloy phase with designed composition. The sintered body of the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ powder synthesized by an oxide-reduction process showed n-type thermoelectric characteristics, even though it had lower electric properties than the conventional materials.

ACKNOWLEDGMENT

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