

Investigation of Low-Cost, Simple Recycling Process of Waste Thermoelectric Modules Using Chemical Reduction

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Received March 22, 2013, Accepted May 10, 2013

A low-cost and simple recycling process of waste thermoelectric modules has been investigated using chemical reduction methods. The recycling is separated by two processes, such as dissolving and reduction. When the waste thermoelectric chips are immersed into a high concentration of HNO₃ aqueous solution at 100 °C, oxide powders, *e.g.*, TeO₂ and Sb₂O₃, are precipitated in the Bi³⁺ and HTeO₂⁺ ions contained solution. By employing a reduction process with the ions contained solutions, Bi₂Te₃ nanoparticles are successfully synthesized. Due to high reduction potential of HTeO₂⁺ to Te, Te elements are initially formed and subsequently Bi₂Te₃ nanoparticles are formed. The average particle size of Bi₂Te₃ was calculated to be 25 nm with homogeneous size distribution. On the other hand, when the precipitated powders reduced by hydrazine, Sb₂O₃ and Te nanoparticles are synthesized because of higher reduction potentials of TeO₂ to Te. After the washing step, the Sb₂O₃ are clearly removed, results in Te nanoparticles.

Key Words : Thermoelectric materials, Bi₂Te₃ nanoparticles, Te nanoparticles, Chemical reduction, Recycling

Introduction

Alloy materials based on bismuth-telluride (Bi₂Te₃) have attracted much attention in academic researches and industrial applications because of its easy processing and stable performance.¹⁻⁴ The Bi₂Te₃ based alloys are known as the most readily available thermoelectric (TE) materials for power generation and refrigeration at temperatures relatively near room temperature.⁵ The performance of TE is determined by the figure of merit ($ZT = S^2\sigma T/k$), where S is the TE power, *i.e.*, Seebeck coefficient, σ is the electrical conductivity and k is the thermal conductivity, respectively. In comparison with bulk structured TE materials, the factors of nanostructured TE materials are independent of each other.⁶ According to previous studies, TE devices with nanostructure have potential for greatly improving the value of ZT by controlling each factor.^{7,8} This significant enhancement of ZT values of nanostructured TE materials is due to phonon scattering effects and the increasing density of states (DOS) around the Fermi level.⁹

Phonon scattering depends on the average size and shape of the nanoparticles, the control of which is essential for achieving enhanced ZT values.¹⁰ Generally, TE powders are synthesized by ball-milling and metallurgical melt processes. However, these processes are not suitable for preparing high-performance of TE materials, because it is difficult to control the size and shape of nano-sized Bi₂Te₃, and they require relatively high temperature, complex processing and expensive and/or toxic precursors. In contrast, using chemical methods, (such as polyol, solvothermal reduction, electrodeposition methods, and *etc.*), various sizes and shapes of nanoparticles are easily synthesized and the resulting ZT values have been higher than those of the bulk structures.¹¹⁻¹³ Despite these achievements, however, cost-issues have not

yet been solved.

We report a low production cost process for the Bi₂Te₃ nanopowders using a recycling method. The recycling of wasted materials seems to be one of the best alternatives to reduce the production cost, and which is important for the TE materials, since they consist of rare metals such as bismuth (Bi), tellurium (Te), antimony (Sb), and *etc.* Moreover, a recycling study of used TE materials has not yet been reported. Furthermore, waste has to be recycled to address environmental issues. For this reason, we have synthesized nano-sized Bi₂Te₃ and Te powders by hydrazine reduction processes using the waste TE modules of discarded vehicles as source materials. Our approach is simple, cost effective, and has potential for application to other materials.

Experimental

Used n-type and p-type chips were collected by a thermal separation process from the TE modules of waste vehicles. The separated TE chips were washed in acetone and an acidic solution. Then, 3 g of the cleaned TE chips were immersed into a 68 wt % nitric acid (HNO₃, 100 mL) solution, and the temperature was elevated to 100 °C for dissolving. After the dissolving process, the ion-containing solution and precipitated white powders were separated by a centrifuge at 10,000 rpm for 5 min, resulting in the separation of solutions containing Bi and Te ions and the white powders (0.12 g).

To synthesize the nanopowders by the chemical reduction process, hydrazine hydrate (55 %, N₂H₄·H₂O) solutions were used as a reduction agent. In order to synthesize Bi₂Te₃ nanoparticles, 20 mL of the hydrazine hydrate solution was carefully dropped into the HNO₃ solutions containing Bi and Te ions with magnetic stirring for 10 min. For Te nano-

particles, the hydrazine solutions were directly dropped onto the surface of the precipitated white powders. These reduction processes were performed until the color of the solution changed to dark blue. In order to confirm the crystalline phase, X-ray diffraction (XRD) patterns were obtained with Cu K α radiation at an operation voltage of 40 kV. The particle size and morphology were examined using field emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2100F).

Results and Discussion

Figure 1 (a) shows the XRD pattern of the alloy powders synthesized by the hydrazine reduction process. It was clearly confirmed that the synthesized powders consist of a Bi₂Te₃ phase (JCPDS No. 15-0863) without any crystalline phases. The average crystal size of the synthesized Bi₂Te₃ was calculated to be 25 nm by Scherrer's formula. On the other hand, when the crystalline phase of the precipitated

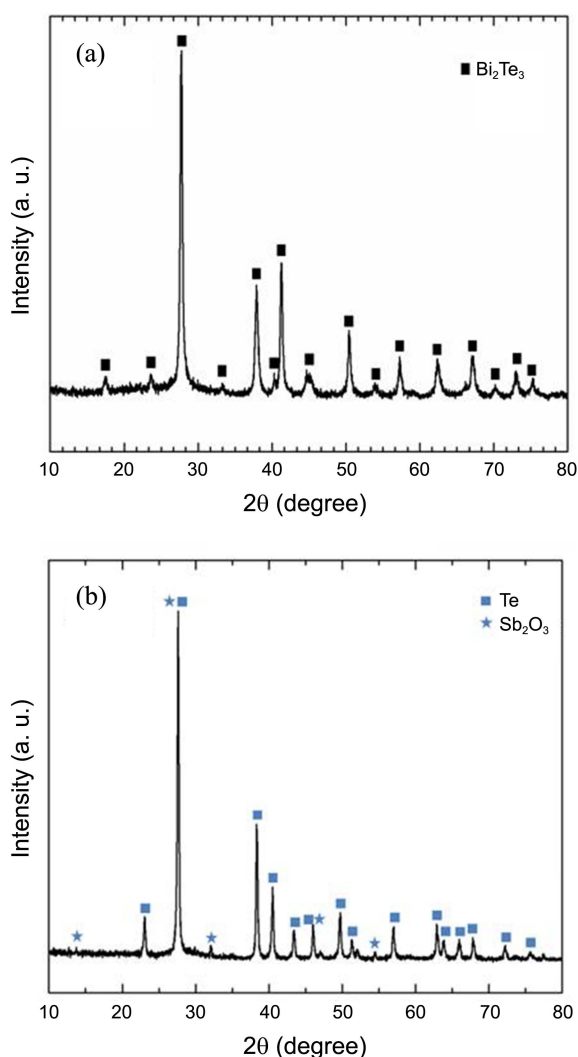
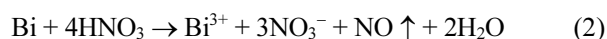
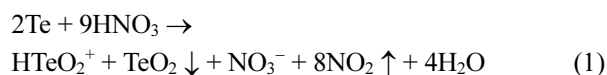


Figure 1. X-ray diffraction patterns of the synthesized nanopowders by chemical reduction process using solution containing Bi and Te ions (a) and precipitated white powders (b).

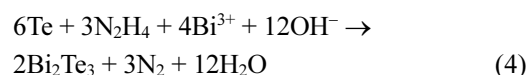
white powders was analyzed by XRD which are formed by the dissolving process with the HNO₃ solution, many unknown peaks appeared in the pattern. This was attributable either to amorphous structures, or impurities remaining despite the cleaning process. Therefore, we have analyzed the crystalline structure of the synthesized powders after more careful washing and chemical reduction processes, which are shown in Figure 1(b). The pattern could be indexed as two different crystalline structures: Te (JCPDS No. 79-0736) and Sb₂O₃ (JCPDS No. 75-1565).

The formation mechanism of the Bi₂Te₃, Te, and Sb₂O₃ structures can be understood by considering the two reactions, *i.e.*, dissolving and reduction. Since used TE chips such as n-type Bi₂Te₃ and p-type Bi_{0.5}Sb_{1.5}Te₃ were employed as the source materials, the following dissolving chemical reactions occurred in the HNO₃ aqueous solutions:

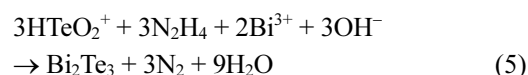


When the used TE chips were immersed into the acidic aqueous solutions, Bi³⁺ and HTeO₂⁺ ions dissolved, and TeO₂ powders were simultaneously precipitated. On the contrast, Sb is not dissolved by dilute acid solutions due to low solubility. However, this low solubility of Sb in the acidic solutions is increased with increasing concentration of the acidic solutions and with increasing temperature. For this reason, we used a highly concentrated acidic solution. *e.g.*, 68 wt %, and a relatively high temperature of 100 °C. Although, the Sb is dissolved by hot and concentrated acidic solutions, this is immediately oxidized and precipitated due to the high oxidation ability of HNO₃ solutions. The precipitated powder can be regarded as a mixture of Sb₂O₃ and Sb₂O₅. During the dissolving process, the Bi³⁺ and HTeO₂⁺ ions are dissolved, and antimony oxide and TeO₂ are precipitated into the HNO₃ solutions.

In order to synthesize nanoparticles by the chemical reduction, the precipitated particles were separated. And the reduction process of the Bi³⁺ and HTeO₂⁺ ions in solution was conducted using hydrazine. It has been reported that the reduction potential of HTeO₂⁺ to Te is more positive than that of Bi³⁺ to Bi.¹⁴ Therefore, the reduction reactions are divided into two sequential steps, the initial reduction of HTeO₂⁺ to elemental Te, and the further reaction of Te with Bi³⁺ to Bi₂Te₃.¹⁵



Thus, the overall reaction can be expressed as;



The XRD pattern of the synthesized nanopowders from the precipitated powders indicates crystalline structures of

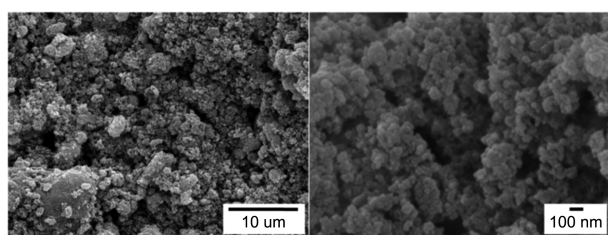


Figure 2. The SEM images of the synthesized Bi_2Te_3 nanopowder using chemical reduction with a used thermoelectric module.

the Te and Sb_2O_3 . This can be explained by the reduction potentials of TeO_2 to Te and Sb_3O_5 to Sb. The standard reduction potential (E°) and redox equilibrium ($\log K$) of TeO_2 to Te, Sb_2O_5 to Sb_2O_3 , and Sb_2O_3 to Sb are $E^\circ = 0.53$ V and $\log K = 35.8$, $E^\circ = 0.69$ V and $\log K = 22.7$, and $E^\circ = 0.15$ V and $\log K = 7.7$, respectively.¹⁶ This means that the Te nanopowders are formed by chemical reduction, but Sb is not produced, remaining as an oxide structure, e.g., Sb_2O_3 . However, the Sb_2O_3 are easily dissolved by washing with water, results in Te nanopowders.

Figure 2 shows the FE-SEM images of the synthesized Bi_2Te_3 nanopowders. Spherical nanoparticles were clearly observed with a homogeneous size distribution of 20–30 nm, in micron-size agglomerations. This result is in good agreement with the nanoparticle size calculated from the XRD results. The quantitative ratios of the synthesized nanopowders are determined by energy dispersive X-ray spectrometry (EDX) in a SEM. The atomic percentage of elements presented in the synthesized Bi_2Te_3 nanopowders sample (Figure 1(a)) is calculated to be 40.84 at % for Bi and 59.16 at % for Te, respectively. On the other hand, in the case of Te nanopowders sample (Figure 1(b)) is calculated to be 0.79

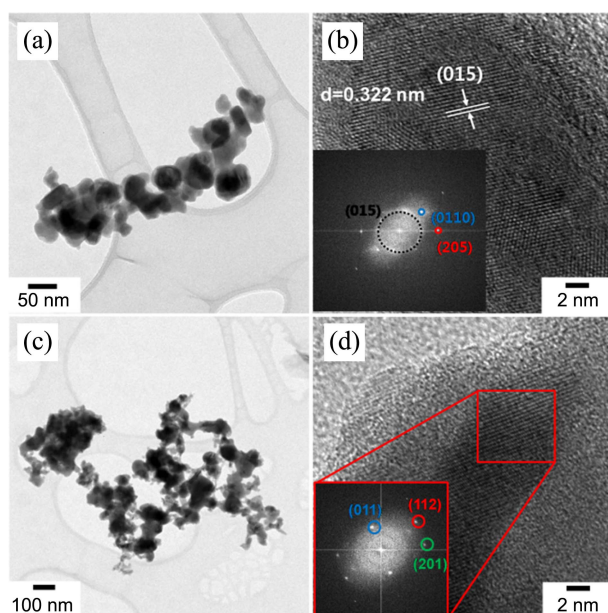


Figure 3. TEM images of the synthesized Bi_2Te_3 (a) and Te (c) nanopowder by chemical reduction process using the used thermoelectric module and HR-TEM images and FFT patterns of the Bi_2Te_3 (b) and Te (d).

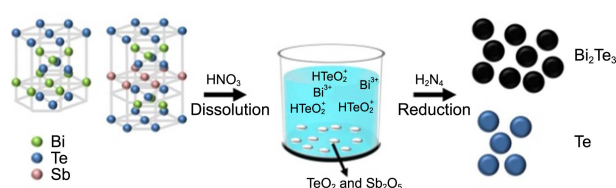


Figure 4. A schematic diagram of the experimental concept.

at % for Bi, 2.09 at % for Sb and 97.12 at % for Te, respectively. Compared with the XRD results, it was confirmed that a low concentration of Bi is included into the nanopowders. In further detailed analysis, the synthesized nanoparticles were characterized by HR-TEM.

Figure 3 shows the HR-TEM images and the fast Fourier transform (FFT) analysis of the synthesized Bi_2Te_3 and Te nanoparticles. A particle size distribution of 20 nm to 40 nm of the Bi_2Te_3 was observed, as shown in Figure 3(a), and the lattice distance of the HR-TEM image was 0.322 nm, which corresponds with the (015) plane of the Bi_2Te_3 phase. The FFT patterns of the HR-TEM image (inset of Figure 3(b)) are consistent with the d values of the (015), (0110), and (205) lattice planes of the Bi_2Te_3 phase. On the other hand, the synthesized Te nanoparticles (Fig. 3(c)) have a more broad size distribution, from 10 nm to 100 nm, than that of the Bi_2Te_3 . The lattice distance of the HR-TEM image (Fig. 3(d)) was measured as 0.32 nm, which is similar to the Bi_2Te_3 . However, the FFT patterns of the HR-TEM image (inset of Fig. 3(d)) are clearly consistent with the d values of the (011), (201), and (112) lattice planes of the Te phase. Furthermore, during the washing process with water, the antimony oxides are clearly removed. From the result of TEM analysis, it was clearly confirmed that nano-sized single crystalline Bi_2Te_3 and Te particles were synthesized by the chemical reduction using a recycling process without any other compounds. A schematic diagram of this study was summarized in Figure 4.

Conclusion

In order to use waste TE chips, we have investigated a low-cost and simple recycling process. Using this recycling process, nano-sized Bi_2Te_3 and Te powders were easily synthesized. The average particle size of the Bi_2Te_3 was calculated to be 25 nm, with homogeneous size distribution and spherical shape. On the other hand, the synthesized Te nanoparticles have a more broad size distribution, from 10 nm to 100 nm, than that of the Bi_2Te_3 . We expected that our recycling process has a potential for application to other materials and for synthesis of nano-sized powders.

Acknowledgments. The present research was conducted by the research fund of Dankook University in 2011.

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