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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 reducing. When the waste thermoelectric chips are immersed into a high concentration of HNO$_3$ aqueous solution at 100 °C, oxide powders, e.g., TeO$_2$ and Sb$_2$O$_3$, are precipitated in the Bi$^{3+}$ and HTeO$_3^-$ ions contained solution. By employing a reduction process with the ions contained solutions, Bi$_2$Te$_3$ nanoparticles are successfully synthesized. Due to high reduction potential of HTeO$_3^-$ to Te, Te elements are initially formed and subsequently Bi$_2$Te$_3$ nanoparticles are formed. The average particle size of Bi$_2$Te$_3$ was calculated to be 25 nm with homogeneous size distribution. On the other hand, when the precipitated powders reduced by hydrazine, Sb$_2$O$_3$ and Te nanoparticles are synthesized because of higher reduction potentials of TeO$_2$ to Te. After the washing step, the Sb$_2$O$_3$ are clearly removed, results in Te nanoparticles.

Key Words : Thermoelectric materials, Bi$_2$Te$_3$ nanoparticles, Te nanoparticles, Chemical reduction, Recycling

Introduction

Alloy materials based on bismuth-telluride (Bi$_2$Te$_3$) have attracted much attention in academic researches and industrial applications because of its easy processing and stable performance.$^{1-4}$ The Bi$_2$Te$_3$ 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, $\sigma$ 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.$^7$ 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.$^8$

Phonon scattering depends on the average size and shape of the nanoparticles, the control of which is essential for achieving enhanced $ZT$ values.$^9$ 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 Bi$_2$Te$_3$, and they require relatively high temperature, complex processing and expensive and/or toxic precursors. In contrast, using chemical methods, (such as polylol, 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.$^{10-13}$ Despite these achievements, however, cost-issues have not yet been solved.

We report a low production cost process for the Bi$_2$Te$_3$ 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 Bi$_2$Te$_3$ 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 (HNO$_3$, 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 %, N$_2$H$_4$·H$_2$O) solutions were used as a reduction agent. In order to synthesize Bi$_2$Te$_3$ nanoparticles, 20 mL of the hydrazine hydrate solution was carefully dropped into the HNO$_3$ 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 Kα 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 particles, the hydrazine solutions were directly dropped onto the surface of the precipitated 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 Bi0.5Sb1.5Te3 were employed as the source materials, the following dissolving chemical reactions occurred in the HNO3 aqueous solutions:

$$2\text{Te} + 9\text{HNO}_3 \rightarrow \text{HTeO}_3^{2+} + \text{TeO}_2 \downarrow + 8\text{NO}_2 \uparrow + 4\text{H}_2\text{O} \quad (1)$$

$$\text{Bi} + 4\text{HNO}_3 \rightarrow \text{Bi}^{3+} + 3\text{NO}_3^- + \text{NO} \uparrow + 2\text{H}_2\text{O} \quad (2)$$

When the used TE chips were immersed into the acidic aqueous solutions, Bi3+ and HTeO32+ 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 HTeO32+ 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 HTeO32+ ions in solution was conducted using hydrazine. It has been reported that the reduction potential of HTeO32+ 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 HTeO32+ to elemental Te, and the further reaction of Te with Bi3+ to Bi2Te3.15

$$2\text{HTeO}_3^{2+} + \text{N}_2\text{H}_4 \rightarrow 2\text{Te} + \text{N}_2 + 2\text{H}_2\text{O} + 2\text{OH}^- \quad (3)$$

$$6\text{Te} + 3\text{N}_2\text{H}_4 + 4\text{Bi}^{3+} + 12\text{OH}^- \rightarrow 2\text{Bi}_2\text{Te}_3 + 3\text{N}_2 + 12\text{H}_2\text{O} \quad (4)$$

Thus, the overall reaction can be expressed as:

$$3\text{HTeO}_3^{2+} + 3\text{N}_2\text{H}_4 + 2\text{Bi}^{3+} + 3\text{OH}^- \rightarrow \text{Bi}_2\text{Te}_3 + 3\text{N}_2 + 9\text{H}_2\text{O} \quad (5)$$

The XRD pattern of the synthesized nanopowders from the precipitated powders indicates crystalline structures of
the Te and Sb$_2$O$_3$. This can be explained by the reduction potentials of TeO$_2$ to Te and Sb$_2$O$_3$ to Sb. The standard reduction potential ($E^\circ$) and redox equilibrium (log $K$) of TeO$_2$ to Te, Sb$_2$O$_3$ to Sb, and Sb$_2$O$_3$ 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. This means that the Te nanoparticles are formed by chemical reduction, but Sb is not produced, remaining as an oxide structure, e.g., Sb$_2$O$_3$. However, the Sb$_2$O$_3$ are easily dissolved by washing with water, results in Te nanoparticles.

Figure 2 shows the FE-SEM images of the synthesized Bi$_2$Te$_3$ nanoparticles. 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 spectroscopy (EDX) in a SEM. The atomic percentage of elements presented in the synthesized Bi$_2$Te$_3$ 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 nanoparticles sample (Figure 1(b)) is calculated to be 0.79 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 nanoparticles. 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$_2$Te$_3$ and Te nanoparticles. A particle size distribution of 20 nm to 40 nm of the Bi$_2$Te$_3$ 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$_2$Te$_3$ 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$_2$Te$_3$ phase. The 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$_2$Te$_3$ phase. The lattice distance of the HR-TEM image (Fig. 3(d)) was measured as 0.32 nm, which is similar to the Bi$_2$Te$_3$ phase. 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$_2$Te$_3$ 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$_2$Te$_3$ and Te powders were easily synthesized. The average particle size of the Bi$_2$Te$_3$ 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$_2$Te$_3$. We expected that our recycling process has a potential for application to other materials and for synthesis of nano-sized powders.

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References