Polyol Process Synthesis of CoSb₃ Thermoelectric Nanoparticles

Keisuke Isogai ¹, Takashi Itoh ²

1. Department of Materials Science and Engineering, Nagoya University, Nagoya, Japan
2. EcoTopia Science Institute, Nagoya University, Nagoya, Japan

Abstract: The cobalt-antimony skutterdite compounds have relatively high power factor at around 380 °C, but they have relatively high thermal conductivity. Nanostructuring is expected to lower the lattice thermal conductivity by phonon scattering on the grain boundary, improving the thermoelectric performance of the materials. In this study, we aim at synthesizing CoSb₃ thermoelectric nanoparticles by using polyol process for constructing the nanostructural body of the materials. The polyol process that synthesizes nanoparticles is one of liquid-phase process using polyol as a solvent. The CoSb₃ nanoparticles were synthesized in mole ratio of Co(OOCCH₃)₂·4H₂O to SbCl₃ of 1:4.5 at reaction temperature of 240 °C in the solvent of tetra ethylene glycol. The reaction products were characterized by XRD, EDX, SEM, and TEM. Extremely small particles with about 10 nm in diameter mainly existed in the reaction products. The minimum particle size was 3-5 nm. The nanoparticles were identified as the CoSb₃ compounds.

Keywords: Polyol Process, Nanoparticle Synthesis, Thermoelectric Materials, Skutterdite Compound

1. INTRODUCTION

Recently, the scarcity of energy by exhaustion of fossil fuel and the environmental problem like as global warming have become serious, and the energy resource which can be substituted for the fossil fuel is needed. More than 60 % of the thermal energy supplied from the power plant is discharged as waste heat at present. Unfortunately, an effective collection technique of the waste heat has not been established, because the waste heat has relatively low temperature and is the low-grade thermal energy. Thus, the thermoelectric power generation which can directly convert thermal energy to electric energy is a promising candidate for the collection technique of waste heat.

Principle of thermoelectric power generation is based on the Seebeck effect that the temperature difference between two different metals or semiconductors creates the thermopower. The power generation is a very clean and very quiet system that does not make exhaust gases and harmful substances. In addition, because it has no scale effect, it can convert thermal energy to electric energy with even a small amount of heat and possesses a feature of high output current density. It also has other advantages that it is lightweight, small size, long life and maintenance free because there is no drive section. Thus, the thermoelectric power generation will be paid more and more attention due to environmental problem and energy saving [1]. However, compared to the conventional energy generation systems, the conversion efficiency of thermoelectric devices is too low, and the performance of the thermoelectric materials has given a restriction to its applications.

The thermoelectric performance of a material at a given temperature is evaluated by the dimensionless figure of merit ZT defined with a following equation,

\[ ZT = \frac{\alpha^2 T}{\rho \kappa} \]

where \( \alpha \) is the Seebeck coefficient, \( T \) the absolute temperature, \( \rho \) the electrical resistivity, and \( \kappa \) the thermal conductivity, respectively. The thermal conductivity \( \kappa \) of thermoelectric semiconductors consists of contributions from electrons and phonons, with the majority contribution coming from phonons. It is expressed with the following equation,

\[ \kappa = \kappa_e + \kappa_L \]

where \( \kappa_e \) and \( \kappa_L \) are the electron and lattice thermal conductivities, respectively.

The thermoelectric materials having good performance in middle temperature range (300-600 °C) are required for power generation by using waste heat. The cobalt antimonite compound CoSb₃ is a promising thermoelectric material in the middle temperature range [2]. The CoSb₃ has skutterdite structure. The skutterdite compounds possess large Seebeck coefficient and good electrical conductivity. The thermal conductivity of the compounds is, unfortunately, too high to obtain a good thermoelectric performance. A lot of efforts have been made to reduce the thermal conductivity of the skutterdite compounds like as the filled skutterdite [3].

To obtain nanostructured materials is one of the approaches for lowering the thermal conductivity by increase of the phonon scattering. Fabricating the nanosized particles and consolidating the nanoparticles are required for making the nanostructured sintered body. The polyol process that exploits the polyalcohol solvents having high boiling point, which also act as the mild reducing agents during heating, is one of the methods of nanoparticles synthesis in liquid phase [4]. In this paper, we report with respect to the synthesis and the structural control of the CoSb₃ nanoparticles by using polyol process.

2. EXPERIMENTAL DETAILS

Three kinds of materials, that is, Co(OOCCH₃)₂·4H₂O, SbCl₃ and the poly vinyl pyrrolidone (PVP, 170 mg) as a surface stabilizer were dissolved in the tetra ethylene glycol (TEG, 20 ml) as a solvent by sonication and magnetic stirring. After the solution was strongly agitated by Ar gas bubbling at room temperature for longer than 45 min, the reducing agent NaBH₄ (30 mg) dissolved in

Corresponding author: K. Isogai, h072105m@mbox.nagoya-u.ac.jp
TEG (5 ml) was added slowly, and the CoSb₃ compound was synthesized by heating to 240 °C in Ar gas. The synthesized particles in the solution were settled by centrifugation, washed with ethanol and dried under atmosphere.

The reaction products were characterized by the X-ray diffraction (XRD), the energy dispersive X-ray spectroscopy (EDX), the scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

In order to investigate the effect of reacting time (holding time) on the synthesis of CoSb₃ nanoparticles, we attempted to synthesize the nanoparticles at 240 °C for 5, 10, 20 and 30 min of the holding time, respectively. The mixing ratio of raw materials Co(OOCCH₃)₂·4H₂O and SbCl₃ was fixed (Co(OOCCH₃)₂·4H₂O : SbCl₃ = 1 mmol : 4.5 mmol).

Next, we changed the prepared total amount of two raw materials to investigate the effect of the total amount on the synthesized nanoparticles. The compositions of the two raw materials used in this study are listed in Table 1. In this case, the holding time at 240 °C was fixed by 10 min.

Table 1 Four kinds of experimental conditions on total amount of two raw materials

<table>
<thead>
<tr>
<th>Total amount</th>
<th>Co(OOCCH₃)₂·4H₂O</th>
<th>SbCl₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.85 mmol</td>
<td>0.7 mmol</td>
<td>3.15 mmol</td>
</tr>
<tr>
<td>5.5 mmol</td>
<td>1 mmol</td>
<td>4.5 mmol</td>
</tr>
<tr>
<td>16.5 mmol</td>
<td>3 mmol</td>
<td>13.5 mmol</td>
</tr>
<tr>
<td>27.5 mmol</td>
<td>5 mmol</td>
<td>22.5 mmol</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

3.1. Influence of holding time on synthesized nanoparticles

Figure 1 shows the XRD patterns of CoSb₃ nanoparticles synthesized by the polyol process at 240 °C for 5, 10, 20 and 30 min of the holding time, respectively. The skutterudite CoSb₃ phase was identified in all conditions regardless of the holding time. The phases of Sb and CoSb₃ were also identified as impurities.

The TEM images are shown in Figure 2. Comparing between the samples synthesized for 10 and 30 min of the holding time, the difference in particle size was hardly found. It indicates that the CoSb₃ nanoparticles are stable and the crystal growth of them does not occur at 240 °C. The light gray area as shown in Figure 2(d) existed in all samples. From EDX analysis, it was found out that this area consists of amorphous SbCl₃ of the raw material. In the sample synthesized by polyol process at 240 °C for 5 min, a small amount of CoSb₃ nanoparticles and a large amount of amorphous SbCl₃ existed.

3.2. Influence of total amount of raw materials on synthesized nanoparticles

Figure 3 shows the XRD patterns of CoSb₃ nanoparticles synthesized by polyol process at 240 °C for 10 min with different total amounts of the two raw materials as shown in Table 1. In the samples synthesized from total amount 3.85 mmol and 5.5 mmol of total amount of the raw materials, the CoSb₃ phase is mainly identified. Though there are peaks of CoSb₃ in the samples synthesized with 16.5 and 27.5 mmol of the total amount, the main peaks are those of Sb₅O₇Cl₁₂ phase. The reduction process is imperfectly finished as the total amount of raw materials increase.

The TEM images are shown in Figure 2. There was little change in size of the nanoparticles synthesized with the different total amount of raw materials.

3.3. Particle size, lattice constant and chemical composition of synthesized compound

The nanoparticles synthesized by polyol process at 240 °C for 10 min with 5.5 mmol of total amount of raw materials (Co(OOCCH₃)₂·4H₂O : SbCl₃ = 1 mmol : 4.5 mmol) are shown as TEM images in Figure 4(a). A majority of nanoparticles has the particle size of tens nm, and the size of finest nanoparticles is about 3-5 nm. The
lattice constant estimated from the selected-area diffraction pattern in Figure 4(b) was \(a=9.03\) Å, which was in good agreement with the literature value of CoSb$_3$ \((a=9.034\) Å) [5]. The typical atomic percentages of Co and Sb evaluated from EDX analysis are 29.2 % and 70.8 %, respectively. This result has a little difference from stoichiometric compositions of Co and Sb in the CoSb$_3$ compound.

4. CONCLUSIONS
In this study, the synthesis and structural control of the CoSb$_3$ nanoparticles were investigated. The results are summarized as follows.

The CoSb$_3$ nanoparticles were synthesized by using polyol process. The changes in the size of the particle synthesized under the difference conditions of the holding time and the total amount of raw materials were hardly found out. The reduction process was imperfectly finished as the total amount of raw materials increased. A majority of nanoparticles had the particle size of tens nm and the size of the finest nanoparticles was about 3-5 nm.

REFERENCES
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