Synthesis and thermoelectric properties of sintered skutterudite CoSb₃ with a bimodal distribution of crystal grains

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Abstract. We have synthesized sintered skutterudite CoSb₃ composed of large and small crystal grains. The sintered materials with larger crystal grains tend to show lower electrical resistivity, while those with smaller grains possess lower thermal conductivity. The possibility of enhancing thermoelectric performance by producing sintered materials with a bimodal distribution of crystal grain sizes so that they possess both low electrical resistivity and thermal conductivity is discussed. The electrical resistivity and Seebeck coefficient generally increase as the ratio of small particles increases. The sample with a mass ratio of small particles of 30% possesses the largest power factor of the sample. The thermal conductivity decreases as the ratio of small particles increases. As a result, the samples containing a higher ratio of smaller particles show higher ZT.

1. Introduction

In the face of impending environmental and energy problems, thermoelectric energy conversion of heat to electricity has attracted the attention of many researchers. Skutterudite compounds are known as potential thermoelectric materials [1-3]. Skutterudite compounds can be represented as MX₃, where M is Co, Rh or Ir and X is P, As or Sb. Most binary skutterudite compounds possess a reasonably large Seebeck coefficient (S) and good electrical conductivity (σ), resulting in a large power factor (S²×σ) comparable to state-of-the-art thermoelectric materials. However, their thermal conductivity (κ) remains too high to make skutterudite compounds efficient thermoelectric materials [3].

The total thermal conductivity κₜ₉₉ of a material consists of a lattice κₚ₉ and carrier contributions κ₉₉. κ₉₉ generally increases as the number of carriers in a material increases. κₚ₉ decreases when phonons are scattered by disorder in a material, for example, by grain boundaries. The degree of phonon scattering depends on the density of the disorder; the more disorder present in a material, the more strongly phonons are scattered. The minute grains in sintered materials effectively improve phonon scattering at grain boundaries, resulting in reduced thermal conductivity [4].

On the other hand, electron or hole carriers are scattered at grain boundaries, so sintered materials with smaller crystal grains generally have larger electrical resistivity. As a result, it is difficult to realize both low electrical resistivity and thermal conductivity in sintered materials composed of crystal grains of a single size, i.e., with a single-modal distribution of crystal grains. In sintered materials composed of a mixture of large and small crystal grains, electron or hole carriers can pass through the large crystal grains without being disturbed, while phonons are scattered at the grain boundaries between small crystal grains because phonons do not follow a path like carriers. Therefore,
both low electrical resistivity and thermal conductivity can be attained in sintered materials with a bimodal distribution of crystal grains.

From this viewpoint, Zhao et al. investigated the thermoelectric properties of Bi$_2$Te$_3$ containing nano- and microsized crystal grains, which were synthesized by mechanical milling for different times and spark plasma sintering [5]. Mechanical milling grinds alloys or intermetallic compounds into fine powders using a ball or vibration mill. In this study, we have synthesized sintered CoSb$_3$ with a bimodal distribution of crystal grains by mechanical milling and hot pressing. The thermoelectric properties of the resulting CoSb$_3$ compounds have been investigated.

2. Experiment
The method used to prepare the samples is summarized in Figure 1. CoSb$_3$ was synthesized by direct reaction of the constituent elements. Co (Rare Metallic Co., Ltd., Japan, 99.9 at.% purity) and Sb (Rare Metallic Co., Ltd., Japan, 99.9999% at.% purity) powders were mixed in the desired ratio, evacuated in a silica ampoule and then heated at 1073 K for 24 h. After the reaction was completed, the ampoule was opened and the products were ground with a mortar and pestle into fine powders. For large particles of CoSb$_3$, the obtained powders were classified by a sieve into particles with diameters between 32 and 63 $\mu$m. For small particles of CoSb$_3$, the obtained powders were mechanically milled. CoSb$_3$ powder (about 10 g) was placed in a zirconium pot with a volume of about $45 \times 10^{-6}$ m$^3$ with 10 zirconium balls with a diameter of 10 mm. The pot was filled with Ar gas. Mechanical milling was carried out for 20 h using a planetary ball mill (P-6, Fritsch, Germany). The obtained large and small particles were weighed with the desired mass ratios of large particles to small particles of 100-x : x, where x=0, 30, 70 and 100. The weighed powders were agitated ultrasonically in ethanol for 10 min. Dry mixed powders were obtained after the evaporation of ethanol. The mixed powders were packed into graphite dies and hot-pressed at 923 K for 1 h under a vacuum of $10^{-3}$ Pa and pressure of 50 MPa.

Phase identification of the obtained samples was performed by X-ray diffraction at room temperature. The Seebeck coefficient and electrical resistivity of the sintered samples were simultaneously measured by the standard four probe dc method in under a flow of Ar gas for the temperature range from room temperature to about 773 K. The thermal diffusion coefficient ($\lambda$) of the samples was measured by the laser flash method using a thermal constant analyzer (TC7000, ULVAC, Japan). The specific heat ($C_p$) of the samples was measured by a differential scanning calorimeter (DSC-50, Shimadzu, Japan). The density ($d$) of the samples was measured by the Archimedes method.

Figure 1. Flow chart showing the procedure followed to prepare samples.
The thermal conductivity ($\kappa$) was calculated from the measured $\lambda$, $C_p$ and $d$ using the relationship $\kappa = \lambda C_p d$.

3. Results and discussion

The X-ray diffraction patterns for the sintered samples with various ratios of particle sizes contained only diffraction peaks consistent with CoSb$_3$ with cubic skutterudite structure (data not shown).

Figure 2 shows SEM images of the sintered CoSb$_3$ with various ratios of particle sizes. As shown in Figure 2(a), the sample containing only large particles possesses more pores than the other samples. The relative density of the sample composed of only large particles is about 92%, while the relative densities of the other samples are between 96 and 98%. The crystal grain size is several tens of $\mu$m, which shows that the crystal grains do not grow during sintering. As the ratio of small particles is increased, the area occupied by the small particles increases, but the small particles gather together and so are not evenly dispersed. The sample containing only small particles exhibits a dense and homogeneous texture (Figure 2(d)), and some of the crystal grains grow during sintering.

The temperature dependence of the Seebeck coefficient for CoSb$_3$ with various ratios of particle sizes is shown in Figure 3. The Seebeck coefficient of all of the samples is positive, and it generally increases as the ratio of small particles in the samples increases. Previously, we reported that the Seebeck coefficient of half-Heusler ZrNiSn$_{0.98}$Sb$_{0.02}$ is increased by mechanical milling, which is because of the smaller grain size in the mechanically milled samples [4]. Yang et al. reported that CoSb$_3$ with small grains shows a larger Seebeck coefficient than that with larger grains, regardless of

![Figure 2. SEM images for sintered CoSb$_3$ with ratios of small particles of (a) 0%, (b) 30%, (c) 70% and (d) 100%.](image-url)
their similar carrier densities \[6\]. They considered that the increase in the Seebeck coefficient is mainly caused by potential barrier scattering. A potential barrier should form at grain boundaries when the typical grain size is sufficiently small. Carriers with high enough energy will overcome the potential barrier, while those of lower energy will be stopped or strongly scattered by the potential barrier at grain boundaries \[7,8\].

Figure 4 shows the temperature dependence of the electrical resistivity \(\rho\) for CoSb\(_3\). The electrical resistivity decreases with temperature, so these samples show semiconducting behavior. The electrical resistivities of these samples are larger than those of a previous report; Sharp \textit{et al.} reported that the electrical resistivity of CoSb\(_3\) at room temperature was 40 \(\mu\Omega\)m \[3\]. The relative density of their sample is 90\%, which is lower than that of our samples, so the larger electrical resistivity of our samples cannot be ascribed to their density. There may be a slight difference in the chemical compositions of the samples, which would affect their carrier density. The electrical resistivity generally increased as the ratio of small particles increased. In the samples containing higher ratios of

\begin{figure}[h]
  \centering
  \includegraphics[width=0.4\textwidth]{figure3.png}
  \caption{Temperature dependence of the Seebeck coefficient for CoSb\(_3\) samples containing various ratios of small particles.}
\end{figure}

\begin{figure}[h]
  \centering
  \includegraphics[width=0.4\textwidth]{figure4.png}
  \caption{Temperature dependence of the electrical resistivity for CoSb\(_3\) samples containing various ratios of small particles.}
\end{figure}

\begin{figure}[h]
  \centering
  \includegraphics[width=0.4\textwidth]{figure5.png}
  \caption{Electrical resistivity for CoSb\(_3\) samples as a function of mass ratio of small particles.}
\end{figure}

\begin{figure}[h]
  \centering
  \includegraphics[width=0.4\textwidth]{figure6.png}
  \caption{Temperature dependence of the power factor for CoSb\(_3\) samples containing various ratios of small particles.}
\end{figure}
small particles, the density of grain boundaries is higher, so this behavior is considered to be caused by carrier scattering at grain boundaries.

Figure 5 shows the electrical resistivity at 400 K as a function of the mass ratio of small particles in the samples. The sample with a ratio of small particles of 30% shows relatively low electrical resistivity, while for those containing >30% small particles, the electrical resistivity increases linearly with the ratio of small particles. Zhao et al. observed similar behavior for Bi₂Te₃ samples [5]. The electrical resistivity of their samples rapidly increased when the ratio of small particles exceeded about 60%, which was attributed to an effect similar to percolation.

The temperature dependence of the power factor for CoSb₃ samples containing various ratios of small particles is shown in Figure 6. The sample with a ratio of small particles of 30% shows the largest power factor of the samples over the whole temperature range. As mentioned above, as the ratio of small particles increases, both the Seebeck coefficient and electrical resistivity increase. This result shows that the sample with a ratio of small particles of 30% has relatively low electrical resistivity.

The temperature dependence of the thermal conductivity $\kappa$ for CoSb₃ samples containing various ratios of small particles is presented in Figure 7. The thermal conductivity also generally decreases as the ratio of small particles increases. As already mentioned, the total thermal conductivity $\kappa_{\text{total}}$ of the material consists of $\kappa_{\text{ph}}$ and $\kappa_{\text{car}}$. To determine whether the lattice or carrier conductivity governs the thermal conductivity of these samples, $\kappa_{\text{ph}}$ and $\kappa_{\text{car}}$ were estimated by the Wiedemann-Franz relationship. According to this relationship, $\kappa_{\text{car}} = LT/\rho$, where $L$ is the Lorentz number. We calculated $\kappa_{\text{car}}$ using a theoretical value of the Lorentz number for a metal with free electrons of $2.45 \times 10^{-8}$ W m⁻¹ K⁻¹ [9]. $\kappa_{\text{ph}}$ was obtained by subtracting $\kappa_{\text{car}}$ from $\kappa_{\text{total}}$.

Figure 8(a) and (b) show the temperature dependence of $\kappa_{\text{ph}}$ and $\kappa_{\text{car}}$ for CoSb₃ samples containing various ratios of small particles, respectively. The values of $\kappa_{\text{ph}}$ are much larger than those of $\kappa_{\text{car}}$, which shows that the thermal conductivity of this system is mainly dominated by the lattice. Both $\kappa_{\text{ph}}$$\kappa_{\text{car}}$

**Figure 7.** Temperature dependence of the thermal conductivity for CoSb₃ samples containing various ratios of small particles.

**Figure 8.** Temperature dependence of (a) $\kappa_{\text{ph}}$ and (b) $\kappa_{\text{car}}$ for CoSb₃ samples containing various ratios of small particles.
and $\kappa_{\text{car}}$ generally decrease as the ratio of the small particles increases, but considering the scale of the vertical axis, $\kappa_{\text{car}}$ can be regarded as almost constant independent of the ratio of small particles. The decrease of $\kappa_{\text{ph}}$ shows that phonons are efficiently scattered at the grain boundaries in the samples with a higher ratio of small particles. $\kappa_{\text{car}}$ gradually increases with temperature. This shows that the number of carriers increases with temperature, which coincides with the results for the electrical resistivity of the samples.

The dimensionless figure of merit $ZT$ was calculated from the Seebeck coefficient, electrical resistivity and thermal conductivity of the samples. Figure 9 shows the temperature dependence of $ZT$ for CoSb$_3$ samples containing various ratios of small particles. The sample with a ratio of small particles of 30% possesses the largest power factor of the samples (Figure 6). On the other hand, the higher the ratio of small particles in the sample, the lower its thermal conductivity (Figure 7). As a result, the samples with ratios of small particles of 70% and 100% show higher $ZT$. The maximum $ZT$ obtained in this study is 0.154 at 673 K for the sample containing only small particles.

4. Conclusions
To realize both low electrical resistivity and thermal conductivity, sintered skutterudite CoSb$_3$ with a bimodal distribution of crystal grain sizes was synthesized and its thermoelectric properties were investigated. The electrical resistivity generally increases as the ratio of small particles in the samples is increased, which is considered to be a result of carrier scattering at grain boundaries. The Seebeck coefficient also increases as the ratio of small particles is increased, while the thermal conductivity decreases. The sample with a ratio of small particles of 30% shows the largest power factor of those examined. As a result, the sample composed entirely of small particles shows the highest $ZT$.

The sample with a ratio of small particles of 30% shows relatively low electrical resistivity regardless of the small particles, but a clear influence of the bimodal distribution of crystal grain size on the thermoelectric performance of CoSb$_3$ was not observed in this study. SEM observations showed that the small particles in the sintered materials tended to aggregate. Improved dispersion of the small particles in the matrix may be necessary to enhance the thermoelectric performance of sintered materials with a bimodal distribution of crystal grain sizes.

On the other hand, Yang et al. reported that CoSb$_3$ nano/microcomposites, which are composed of nanosized CoSb$_3$ particles obtained by the polyol method and microsized CoSb$_3$ particles obtained by solid state reaction, exhibit $ZT$ almost twice that of the sample without nanosized particles [6]. The carrier density of nanosized CoSb$_3$ produced by polyol method is larger than that of microsized CoSb$_3$ formed by solid state reaction because the nanosized CoSb$_3$ contains excess Sb, so the electrical
The resistivity of the composites is much smaller than that of CoSb$_3$ without nanoparticles, regardless of its lower thermal conductivity. This result shows that control of the carrier density may be an effective way to enhance the thermoelectric performance of sintered materials with a bimodal distribution of crystal grain sizes.

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