In-situ observation of synthesizing process of
Mm₉Co₄Sb₁₂ utilizing x-ray diffraction under high
temperatures and high pressures

Chihiro Sekine¹, Hirotaka Kato¹, Masatoshi Kanazawa¹, Yukihiro
Kawamura¹, Keiki Takeda¹, Mizushi Matsuda¹, Kunihiro Kihou²,
Chul-Ho Lee², and Hirotada Gotou³

¹Muroran Institute of Technology, Muroran, Hokkaido 050-8585, Japan
²National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki
305-8568, Japan
³Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan
E-mail: sekine@mmm.muroran-it.ac.jp

Abstract. The antimony-based partially-filled skutterudite compound Mm₉Co₄Sb₁₂
(Mm=mischmetal) are expected for n-type thermoelectric materials with high-performance and
low-cost. In order to prepare high-quality samples of the compound, synthesizing processes at
high pressures and high temperatures have been studied by means of in-situ x-ray diffraction
measurements using synchrotron radiation and a cubic-anvil high pressure apparatus. In se-
ries of the experiments, we could obtain the optimum condition for synthesizing the compound
under high pressure.

1. Introduction

The skutterudite compounds have attracted much attention owing to their potential as improved,
next generation thermoelectric materials [1, 2, 3]. The binary compound CoSb₃ crystallizes with
the CoAs₃-type structure of space group Im3 (T₅₄h, No. 204) [4]. This structure has eight formula
units, including two voids, per cubic unit cell. The material shows excellent thermoelectric
properties (large Seebeck coefficients and high hole mobilities)[5]. The dimensionless figure-
of-merit, $ZT$, of thermoelectric materials is given by a combination of electrical and thermal
transport coefficients, $ZT=S^2\sigma T/\kappa$, where $S$ is the Seebeck coefficient, $T$ is the absolute
temperature, $\sigma$ is the electrical conductivity, and $\kappa$ is the thermal conductivity, which has both
electronic and lattice components, $\kappa_{el}$ and $\kappa_{lat}$ respectively. Although the power factor, $S^2\sigma$,
for CoSb₃ is quite large, the lattice thermal conductivity, $\kappa_{lat}$ is too high. However, the filling
of the voids partially in the binary skutterudite structure with rare-earth $(R)$ ions can reduce
$\kappa_{lat}$ greatly[3]. The $R$ ions are located inside the oversized cages, formed by twelve Sb ions,
and the undersized ions are believed to show random motion (rattling) around the equilibrium
positions. Thus, it produces a large phonon scattering, reducing the lattice thermal conductivity
$\kappa_{lat}$. Owing to the reduced thermal conductivity, partially-filled skutterudite compounds show
excellent thermoelectric performance. Recently, however, the use of rare earth metals has serious
problems about cost and supply amount. Therefore, we focus to mischmetal (Mm) as the
void-filling ions. Mischmetal is an alloy of rare earth elements in various naturally occurring
proportions. A typical composition includes approximately 50% Ce and 25% La, with small amounts of Nd and Pr. Mischmetal is low-cost compared with individual rare earths because the extraction processes is unnecessary.

A preparation of high-quality samples for the antimony-based skutterudite compounds is quite difficult at ambient pressure because the high vapor pressure of Sb and impurity phases tend to be formed easily. High-pressure synthesis technique is one of the useful methods to prepare high quality samples of skutterudites. In this study, we have tried to observe synthesizing processes of \(\text{Mm}_x\text{Co}_4\text{Sb}_{12}\) \((\text{Mm}=\text{mischmetal})\) in-situ at high temperature and high pressure to obtain the optimum condition for synthesis.

2. Experimental

In-situ x-ray diffraction patterns were taken by an energy-dispersive method using synchrotron radiation and a solid-state detector. High pressure was applied using a multi-anvil assembly 6-6 (MA6-6) with a cubic-anvil high-pressure apparatus, the MAX80 system, installed at the beam line AR-NE5C, at Photon Factory (PF) in High Energy Accelerator Research Organization (KEK) (Tsukuba, Japan) (Fig. 1). The MA6-6 consists of six small second-stage anvils with an anvil guide, and can be compressed by a cubic-anvil apparatus (Fig. 2) [6]. The truncated edge length (TEL) of the second-stage anvil made of tungsten carbide is 6 mm. The anvil guide is made of tool steel (SUS304), with an outer edge length of 28 mm. The anvil guide has holes along one of the diagonal direction for access to the incident and exiting x-rays. The TEL of the first-stage anvil is 27 mm. The sample container made of boron-epoxy is formed a cube of 9 mm on an edge. The starting materials, which are mixture of Mm, Co and Sb, are put into a BN crucible. The crucible with a graphite heater is inserted in a cube-shaped boron-epoxy solid pressure medium. Pressure was determined by the lattice constant of NaCl internal pressure marker. The details of the in-situ observation method were described in Ref. 7.

\(\text{Mm}_x\text{Co}_4\text{Sb}_{12}\) \((x=0.2, 0.4, \text{and } 0.6)\) samples were prepared at high temperatures and high pressures using a wedge-type cubic anvil high-pressure apparatus. The sample cell assembly is similar to that used for the high-pressure synthesis of P-based filled skutterudite compounds [8]. The prepared samples were characterized by powder x-ray diffraction using Co K\(\alpha_1\) radiation and silicon as a standard. Resistivity was measured by a standard dc four-probe method. Seebeck coefficient and thermal conductivity were measured with a thermal transport option of Quantum Design PPMS.

**Figure 1.** A photograph of MA6-6 in first stage anvils of the MAX80 system. 1, first stage anvil; 2, hole for x-ray.

**Figure 2.** A photograph of MA6-6. 1, pressure medium; 2, second stage anvil; 3, anvil guide; 4, preformed gasket; 5, wood spacer.
Figure 3. X-ray diffraction patterns of synthesizing process of Mm\textsubscript{0.4}Co\textsubscript{4}Sb\textsubscript{12} at 4.5 GPa. Solid triangles, open triangles and open circles designate the Bragg peaks of Co, Ce and Sb, respectively. Solid squares indicate the characteristic x-ray for Sb. Solid circles designate the Bragg peaks of Mm\textsubscript{0.4}Co\textsubscript{4}Sb\textsubscript{12}. Crosses indicate the peaks of an impurity phase. (a) The starting materials at room temperature, (b) 560°C, (c) 760°C and (d) 820°C.

3. Results and discussion

Figure 3(a) shows x-ray diffraction patterns of the starting materials, which are mixture of each metal and antimony powder in the atomic ratio of Mm : Co : Sb = 0.4 : 4 : 12, at room temperature and 4.5 GPa. Open triangles, solid triangles, and open circles designate the Bragg peaks of Ce, Co and Sb, respectively. Solid squares indicate the characteristic x-ray for Sb. With increasing temperature, the Bragg peaks of the starting materials faded out, and then the peaks of the skutterudite structure were observed above 450°C. At 560°C, all diffraction lines were indexable using the skutterudite structure (closed circles in Fig. 3(b)). Then, the peaks of an impurity phase, which are indicated by crosses, appeared at 760°C (Fig. 3(c)). This indicates that decomposition products of Mm\textsubscript{0.4}Co\textsubscript{4}Sb\textsubscript{12} (such as CoSb\textsubscript{2}) were generated above this temperature. Elevating temperature up to 820°C, the Bragg peaks disappeared and only the peaks of the characteristic x-ray for Sb were observed (Fig. 3(d)). This indicates that the sample is fully liquid at this temperature. In series of the experiments, we found an appropriate temperature range of 560-760°C for synthesizing Mm\textsubscript{x}Co\textsubscript{4}Sb\textsubscript{12} at 4.5 GPa.

We have actually synthesized Mm\textsubscript{0.4}Co\textsubscript{4}Sb\textsubscript{12} at 4.5 GPa and 600°C using a wedge-type cubic anvil high-pressure apparatus based on the synthesis condition obtained by the in-situ experiments. Figure 4 shows a powder x-ray diffraction pattern of Mm\textsubscript{0.4}Co\textsubscript{4}Sb\textsubscript{12} prepared under high pressure. While a small amount of impurity phase (metallic Sb) was detected, most of the observed diffraction lines were indexable using the skutterudite structure. The lattice constant determined by a least-squares fit to the data was 9.0714 Å. We have also synthesized Mm\textsubscript{0.2}Co\textsubscript{4}Sb\textsubscript{12} and Mm\textsubscript{0.6}Co\textsubscript{4}Sb\textsubscript{12} under the same condition. The x-ray diffraction patterns of the compounds Mm\textsubscript{0.2}Co\textsubscript{4}Sb\textsubscript{12} and Mm\textsubscript{0.6}Co\textsubscript{4}Sb\textsubscript{12} indicate that the main phase consists of the filled skutterudite. The lattice constants of Mm\textsubscript{0.2}Co\textsubscript{4}Sb\textsubscript{12} and Mm\textsubscript{0.6}Co\textsubscript{4}Sb\textsubscript{12} were determined in the same manner and found to be 9.0531 and 9.0853 Å, respectively. The inset of Fig. 4 plots
the lattice constants of $\text{Mm}_x\text{Co}_4\text{Sb}_{12}$ along with the value of CoSb$_3$ reported earlier [9]. The lattice constant of $\text{Mm}_x\text{Co}_4\text{Sb}_{12}$ becomes large linearly with increasing $x$. This suggests that the partially-filling of Mm to CoSb$_3$ was succeeded up to $x = 0.6$ at least. Furthermore, we have evaluated the thermoelectric properties of $\text{Mm}_{0.6}\text{Co}_4\text{Sb}_{12}$ and CoSb$_3$, prepared under high pressure, as a reference. The seebeck coefficient of $\text{Mm}_{0.6}\text{Co}_4\text{Sb}_{12}$ shows negative value, which means n-type conductivity, while CoSb$_3$ is a p-type conductor. The temperature dependence of the dimensionless figure of merit $ZT$ for CoSb$_3$ and $\text{Mm}_{0.6}\text{Co}_4\text{Sb}_{12}$ is shown in Fig. 5. $\text{Mm}_{0.6}\text{Co}_4\text{Sb}_{12}$ shows a large $ZT$ value of 0.07 compared with CoSb$_3$ at 300K. Therefore, the partially-filled skutterudite compound $\text{Mm}_x\text{Co}_4\text{Sb}_{12}$ are expected for n-type thermoelectric materials with high-performance and low-cost.

**Figure 4.** X-ray diffraction pattern of $\text{Mm}_{0.4}\text{Co}_4\text{Sb}_{12}$ prepared under high pressure. Cross indicates the peak of an impurity phase (metallic Sb). The inset shows lattice constants $a$ of $\text{Mm}_x\text{Co}_4\text{Sb}_{12}$ along with the value reported earlier for CoSb$_3$ [9].

**Figure 5.** Temperature dependence of the dimensionless figure of merit $ZT$ for CoSb$_3$ and $\text{Mm}_{0.6}\text{Co}_4\text{Sb}_{12}$.

**4. Summary**

We could obtain the optimum condition for synthesizing $\text{Mm}_x\text{Co}_4\text{Sb}_{12}$ under high pressure. In-situ x-ray experiments are excellent method for determining the condition for obtaining only target material without impurity phases for solid-phase reaction synthesis under high pressure.

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