NE5C/2007G083

In-situ X-ray observations for crystallization of TSb_3 (T=Co, Rh and Ir) under high temperatures and high pressures

Chihiro SEKINE*, Takao KACHI, Tomoo YOSHIDA, Ryota ABE
Takahiro NAMIKI, Keita AKAHIRA, Kojiro ITO
Muroran Institute of Technology, Muroran, Hokkaido 050-8585, Japan

Introduction

The binary antimony-based skutterudites, $CoSb_3$, $RhSb_3$ and $IrSb_3$, crystallize in a body centered cubic structure of space group $Im\bar{3}$ (T^5_h No.204). These materials show excellent thermoelectric properties though their lattice thermal conductivities are quite large. The skutterudite structure has a vacancy, which can be partially occupied by rare-earth ions. The rare-earth ions inside the cages in the skutterudite framework rattle and scatter phonons and thus reduce the lattice thermal conductivity. Therefore, filled skutterudite compounds, where rare-earth ions inserted into the lattice voids, have been actively studied as potentially useful thermoelectric materials. High-pressure synthesis technique is one of the useful methods to prepare high quality samples of skutterudite. In this study, first of all, we have tried to observe synthesizing processes of undoped $CoSb_3$, $RhSb_3$ and $IrSb_3$ in-situ at high temperature and high pressure to obtain synthesis conditions for these compounds.

Experimental

In-situ x-ray diffraction patterns were taken by an energy-dispersive method using the synchrotron radiation. High pressure was applied using the multi-anvil high-pressure apparatus, MAX80, installed at the beam line AR NE5C. Pressure was determined by the lattice constant of NaCl internal pressure marker. The details of the in-situ observation method were described in our reports [1, 2]. The starting materials are mixture of each metal and antimony powder.

Results and Discussion

Figure 1 shows x-ray diffraction patterns of synthesizing process of $CoSb_3$ at 3.5GPa. Figure 1(a) shows a pattern of starting materials (Co:○, Sb:△) where solid circles indicate the characteristic x-ray for Sb.

Table 1: Synthesis conditions of skutterudite compounds $CoSb_3$, $RhSb_3$ and $IrSb_3$ at high pressure.

Compounds	Pressure (GPa)	Temperature (ºC)
$CoSb_3$	2.0	650-850
	3.0	600-750
	3.5	550-750
$RhSb_3$	2.0	600-690
	4.0	570-650
$IrSb_3$	2.0	600-680

We observed the diffraction peaks for skutterudite structure at 540ºC (fig. 1(b)). Then, the peaks of impurity phase appeared at 760ºC (fig. 1(c)). In series of the experiments, we could obtain the synthesis condition of $CoSb_3$ under high pressure. We also carried out the same experiments for $RhSb_3$ and $IrSb_3$. The synthesis conditions under high pressure are summarized in Table 1.

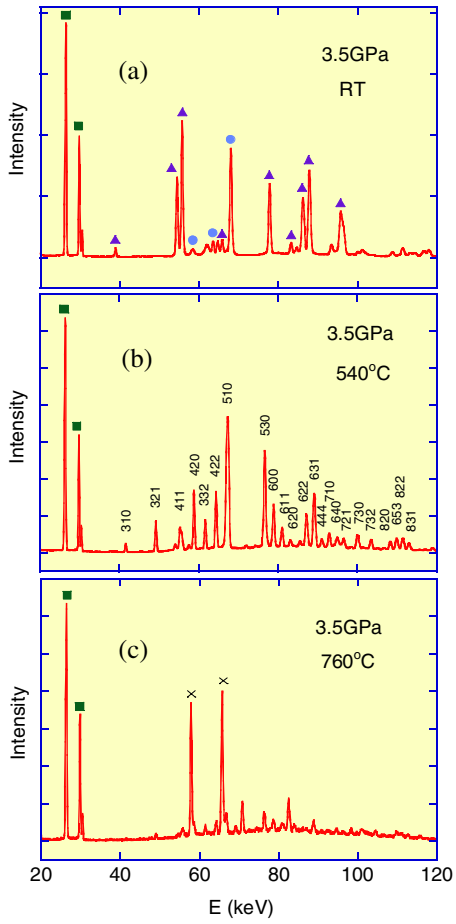

Fig. 1. X-ray diffraction patterns of synthesizing process of $CoSb_3$ at 3.5GPa. Peaks marked with crosses correspond to impurity phase.

References

[1] C. Sekine *et al.*, Rev. High Press. Sci. Technol. 16, 336 (2006).
[2] C. Sekine, KEK Proceedings 2007-7, 22 (2007).

* sekine@mmm.muroran-it.ac.jp