NE5C/2007G083

In-situ X-ray observations for crystallization of unfilled and filled skutterudite compounds under high temperatures and high pressures

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

Introduction

The unfilled skutterudite compounds TX_3 (T=Co, Rh, Ir, X=P, As, Sb) and the filled skutterudite compounds RT_4X_{12} (R=rare-earth element, T=Fe, Ru, Os, X=P, As, Sb) crystallize in a body centered cubic structure of space group $Im\overline{3}$ (T^5_h No.204). The binary antimony-based compounds TSb$_3$ show excellent thermoelectric properties though their lattice thermal conductivities are quite large. The binary 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, we have tried to observe synthesizing processes of unfilled skutterudite compounds $CoSb_3$, $RhSb_3$, $IrSb_3$ and RhP_3 and filled skutterudite compound $SmRu_4Sb_{12}$ 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 or phosphorus powder.

Table 1: Synthesis conditions of unfilled and filled skutterudite compounds at high pressure.

Compounds	Pressure (GPa)	Temperature (°C)
$CoSb_3$	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
RhP_3	2.0	1000-1060
$SmRu_4Sb_{12}$	2.0	700-760

Results and Discussion

Figure 1 shows x-ray diffraction patterns of synthesizing process of $RhSb_3$ at 2.0GPa. Figure 1(a) shows a pattern of starting materials (Rh:△, Sb:×) where solid and open squares indicate the characteristic x-ray for Sb and Rh, respectively. The diffraction peaks for skutterudite structure began to appear at 520°C (fig. 1(b)). Then, all diffraction peaks were assigned to $RhSb_3$ at 760°C (fig. 1(c)). We also carried out the same experiments for other skutterudites. The synthesis conditions under high pressure are summarized in Table 1.

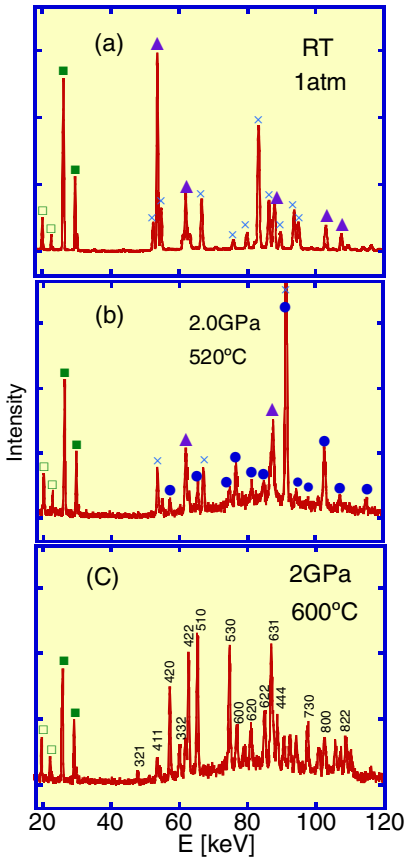

Fig. 1. X-ray diffraction patterns of synthesizing process of $RhSb_3$ at 2GPa.

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