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In-situ observation for crystallization of skutterudite compounds under high temperatures and high pressures

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Introduction

The skutterudite compounds have been actively studied as potentially useful thermoelectric materials. The compounds have also attracted much attention of their wide variety of strongly correlated electron behaviors. A number of groups have grown single crystals of various skutterudite compounds. In the growth process, Sb or Sn was typically used as flux because skutterudite compounds are incongruent melting compounds at ambient pressure. The sizes of the grown crystals, however, are limited and only few skutterudite compounds have been able to be crystallized by flux method. Larger single crystals are necessary in order to study their fundamental properties. High-pressure synthesis technique may be beneficial to solve these issues. In this study, we have tried to observe crystallization processes of skutterudite compounds in-situ at high temperature and high pressure. We could obtain some information about the single crystal growth of CoP_3 and $CoSb_3$ under high pressure.

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 of CoP_3 and $CoSb_3$ are polycrystalline powder samples prepared under high pressure.

Results and Discussion

Figure 1 shows x-ray diffraction patterns of $CoSb_3$ at 2.5GPa and at various temperatures where solid circles indicate the characteristic x-ray for Sb. The diffraction peaks completely disappeared and only a halo pattern was observed at 860ºC. This indicates that the compound has melted at this temperature. With decreasing temperature, $CoSb_3$ recrystallized and the same diffraction patterns were observed. The result suggests that $CoSb_3$ is congruent melting compound under high pressure in contrast to the result at ambient pressure. This is a great advantage for growing single crystals. We carried out the same experiments for CoP_3. The melting points under high pressure are summarized in Table 1.

Table 1: Melting points of skutterudite compounds CoP_3 and $CoSb_3$ at high pressure.

Compounds	Pressure (GPa)	Melting point (ºC)
CoP_3	3.8	1350-1400
$CoSb_3$	2.5	820-840

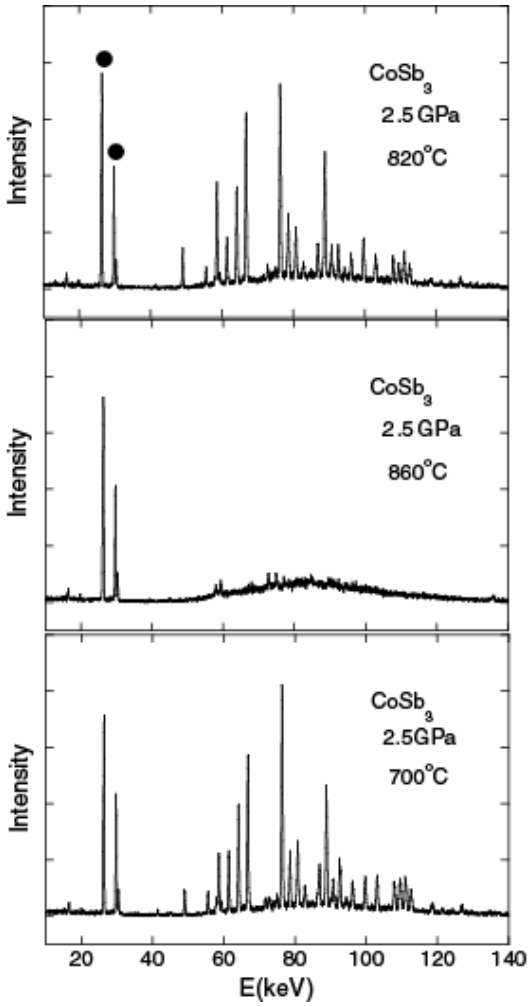

Fig. 1. X-ray diffraction patterns of $CoSb_3$ at 2.5GPa and at various temperatures.

References

[1] C. Sekine et al., Memoirs of Muroran Institute of Technology 55, 15 (2005).
[2] C. Sekine et al., Rev. High Press. Sci. Technol. 16, 336 (2006).

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