

## In-situ X-ray observation for the pressure-induced self-insertion reaction of $\text{CoSb}_3$ under high temperatures and high pressures

Chihiro SEKINE\*, Kazuki MATSUI, Kojiro ITO, Syuhei MITSUKA, Yusuke FUKUSHI  
Muroran Institute of Technology, Muroran, Hokkaido 050-8585, Japan

### Introduction

The unfilled skutterudite compounds  $\text{TX}_3$  ( $T = \text{Co, Rh, Ir}$ ,  $X = \text{P, As, Sb}$ ) and the filled skutterudite compounds  $\text{RT}_4\text{X}_{12}$  ( $R = \text{rare-earth element}$ ,  $T = \text{Fe, Ru, Os}$ ,  $X = \text{P, As, Sb}$ ) crystallize in a body centered cubic structure of space group  $\overline{Im}\overline{3}$  ( $T_h^5$ , No.204). The binary antimony-based compounds  $\text{TSb}_3$  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.

In spite of the presence of large voids in the structure, earlier studies under high pressure indicate that the binary skutterudite compounds are quite stable under high pressure. However, recently the structural change of  $\text{CoSb}_3$  in high pressure has been reported [1]. They reported that above 20 GPa,  $\text{CoSb}_3$  at room temperature undergoes an irreversible isosymmetrical transition to another phase that, upon pressure release, exhibits a volume greater than that of pristine  $\text{CoSb}_3$ . This anomalous behavior could be interpreted as a pressure-induced self-insertion reaction of  $\text{CoSb}_3$ , in which antimony atoms from the compound framework partially fill the voids. This phenomenon of  $\text{CoSb}_3$  has been verified by synchrotron powder X-ray diffraction [2]. Furthermore, the same phenomenon was observed at lower pressure (7.7GP) and higher temperature (550°C) [1]. In this study, we have tried to observe the pressure induced self-insertion reaction of unfilled skutterudite compounds  $\text{CoSb}_3$  in-situ at high temperatures and high pressures.

### 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 [3-5]. The sample of  $\text{CoSb}_3$  was prepared at 2GPa and 550°C using a cubic-anvil high-pressure apparatus.

### Results and Discussion

Figure 1 shows x-ray diffraction patterns of  $\text{CoSb}_3$  at 8GPa under high temperatures. Figures (b) and (a) show the diffraction patterns at 500°C before annealing and after annealing at 550°C for 15 min, respectively. The diffraction peaks for skutterudite structure appear doubled and displaced toward lower energy. This result suggests the coexistence of two isosymmetrical phases of  $\text{CoSb}_3$  and that one phase of them has larger volume than that before annealing. We have succeeded to observe the pressure-induced isosymmetrical structural change of unfilled skutterudite compounds  $\text{CoSb}_3$  in-situ at 8GP and 550°C. This result supports pressure-induced self-insertion reaction model proposed in ref. [1].

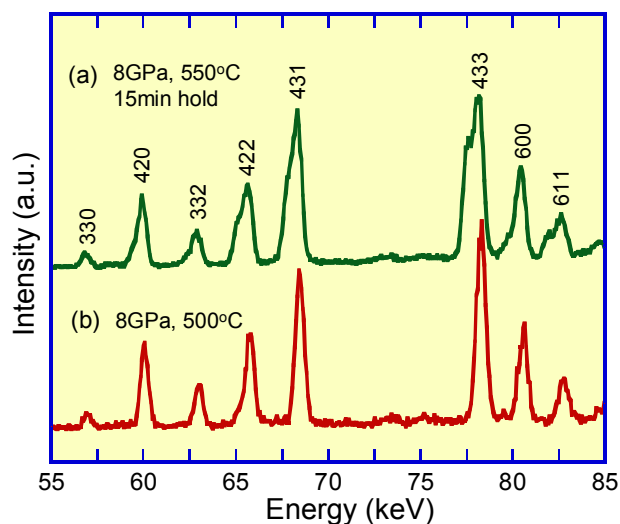


Fig. 1. X-ray diffraction patterns of  $\text{CoSb}_3$  at 8GPa under high temperatures.

### References

- [1] A. C. Kraemer *et al.*, Phys. Rev. B 75 (2007) 024105.
- [2] K. Matsui *et al.*, J. Phys.: Conf. Ser. 215 (2010) 012005.
- [3] C. Sekine *et al.*, Rev. High Press. Sci. Technol. 16, 336 (2006).
- [4] C. Sekine, KEK Proceedings 2007-7, 22 (2007).
- [5] C. Sekine *et al.*, J. Phys.: Conf. Ser. 215 (2010) 012141.

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