NE5C/2009G030

In-situ x-ray observation for the pressure-induced self-insertion reaction of $RhSb_3$ under high temperatures and high pressures

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Introduction

The unfilled skutterudite compounds TX_3 (T = Co, Rh, Ir, X = P, As, Sb) crystallize in a body centered cubic structure of space group $Im\bar{3}$ (T^5_h No.204). The structure has a vacancy, which can be partially occupied by rare-earth ions. In spite of the presence of large voids in the structure, earlier studies indicate that the binary skutterudite compounds are quite stable under high pressure. However, recently the structural change of $CoSb_3$ in high pressure has been reported [1]. They reported that above 20 GPa, $CoSb_3$ at room temperature (RT) undergoes an irreversible isosymmetric transition to another phase that, upon pressure release, exhibits a volume greater than that of pristine $CoSb_3$. This anomalous behavior could be interpreted as a pressure-induced self-insertion reaction of $CoSb_3$, in which antimony atoms from the compound framework partially fill the voids. This phenomenon of $CoSb_3$ has been verified by synchrotron powder x-ray diffraction and similar behaviors have been observed for isostructural compounds $RhSb_3$ and $IrSb_3$ [2]. Furthermore, the same phenomenon of $CoSb_3$ was observed at lower pressure (7.7GP) and higher temperature (550ºC) [1]. In this study, we have tried to observe the pressure induced self-insertion reaction of unfilled skutterudite compound $RhSb_3$ 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]. The sample of $RhSb_3$ was prepared at 2GPa and 550ºC using a cubic-anvil high-pressure apparatus.

Results and Discussion

Figure 1 shows x-ray diffraction patterns of $RhSb_3$ at 8GPa and room temperature. Figures (a) and (b) show the diffraction patterns before and after annealing at 550ºC for 30 min, respectively. Figure 2 shows the temperature dependence of the relative shift (E/E_0) for 422, 431, 433 Bragg peaks of $RhSb_3$. The peaks show a significant shift toward lower energy around 400ºC. This result suggests that the self-insertion reaction occurs around this temperature at 8GPa. Consequently, the annealed sample at RT has a larger volume than that before annealing because the diffraction peaks appear displaced toward lower energy.

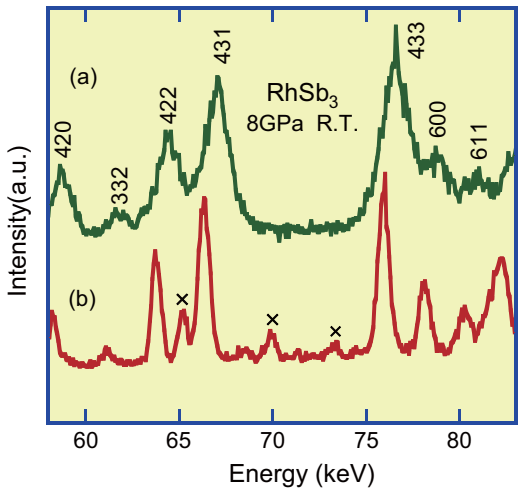

Fig. 1. X-ray diffraction patterns of $RhSb_3$ at 8GPa and RT. (a) before heating (b) after heating. The cross indicates an impurity phase of $RhSb_2$.

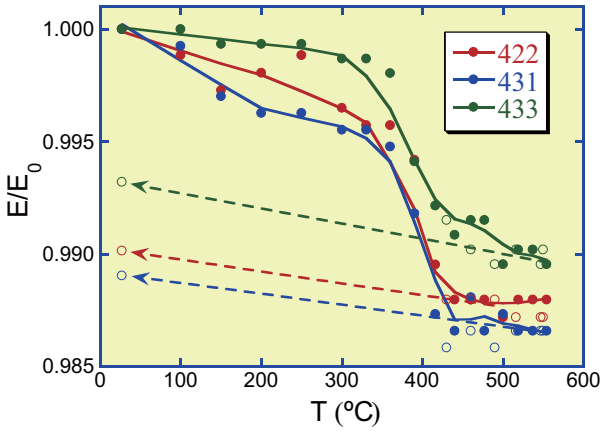

Fig. 2. Temperature dependence of the relative energy (E/E_0) shift normalized at RT for 422, 431, 433 Bragg peaks of $RhSb_3$.

References

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