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High-temperature and high-pressure phase diagram of $RhSb_3$

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Introduction

The skutterudite compounds have been actively studied as potentially useful thermoelectric materials. The compounds have also attracted many researchers' interest as strongly correlated electron systems. The binary unfilled skutterudite compounds with a body centered cubic (space group *Im*3) have a general formula TX_3 or T_4X_{12} (T=Co, Rh and Ir, X=P, As and Sb, site 24*g*), where the symbol represents a vacancy (site 2*a*). While earlier studies have indicated that the unfilled skutterudite compounds are quite stable under high pressure, a pressure induced structural change at room temperature of unfilled skutterudite compounds has been reported recently [1-3]. These behaviors could be interpreted as a pressure-induced self-insertion reaction, in which antimony atoms from the compound framework partially fill the voids (site 2*a*) at room temperature. Furthermore, similar behaviors have also been reported under high temperature and high pressure [1, 4]. In this study, we have tried to observe structural changes of the unfilled skutterudite compound $RhSb_3$ in-situ at high temperature and 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 a 6-6 compression system and the multi-anvil high-pressure apparatus (MAX80) installed at the beam line AR NE5C. We used Tr. 27mm WC anvil for first stage anvil and Tr. 4mm WC anvil for second stage anvil. The boron epoxy was used for pressure medium. Pressure was determined by the lattice constant of NaCl internal pressure marker. High quality polycrystalline samples of $RhSb_3$, used as stating materials, were synthesized at 2GPa and 550°C, using a cubic-anvil high-pressure apparatus.

Results and discussion

Figure 1 shows x-ray diffraction patterns of $RhSb_3$ at 6GPa and room temperature (a) and 640°C (b). The peaks of $RhSb_3$ appear doubled (indicated by arrows) and displaced toward lower energy at 640°C. This suggests that the self-insertion reaction occurs. Peaks for an impurity phase ($RhSb_2$) also observed between 67 and 75keV, indicated by cross symbol at 640°C. The temperature dependence of peak positions of $RhSb_3$ show a significant shift toward lower energy around 500°C at 6GPa. Similar behavior was also observed around 400°C under 8GPa [4]. From these results, the high-temperature and high-pressure phase diagram of unfilled skutterudite $RhSb_3$ was obtained as shown in Figure 2.

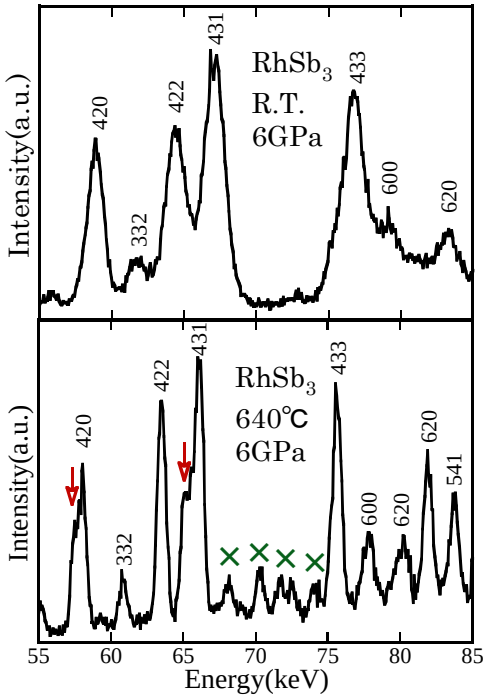

Fig.1. X-ray diffraction patterns of $RhSb_3$ at 6GPa and room temperature (a) and 640°C.

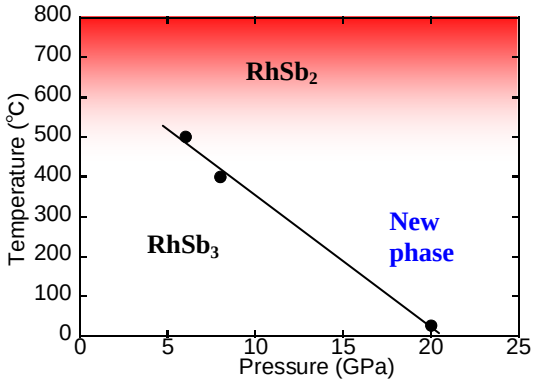

Fig. 2. High-temperature and high-pressure phase diagram of $RhSb_3$

Reference

[1] A. C. Kraemer *et al.*, Phys. Rev. B, **75** (2007) 024105.
[2] K. Matsui *et al.*, PF activity report (2009) 196.

[3] K. Matsui *et al*., PF activity report (2010) 224.
[4] C. Sekine *et al*., PF activity report (2010) 222.
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