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Pressure effect on binary phase diagram

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Introduction

A skutterudite $CoSb_3$ has attracted an attention as a thermoelectric material. For the reason above, a binary Co-Sb phase diagram has investigated well [1]. According to the Co-Sb phase diagram, the Co-Sb system has three compounds: CoSb, $CoSb_2$, and $CoSb_3$. These compounds melt or solidify as follows:

CoSb <-> Liq.

$CoSb_2$ <-> CoSb + Liq. <-> Liq.

$CoSb_3$ <-> $CoSb_2$ + Liq. <-> CoSb + Liq. <-> Liq.

Thus, CoSb is a congruent compound and the other two are incongruent compounds. According to the reaction described above, $CoSb_3$ crystallizes from a melt through CoSb and $CoSb_2$. Recently it has been reported that $CoSb_3$ can be grown directly from a supercooled melt with chemical compositions of 25 at. % Co and 75 at. % Sb at high pressures [2], which is different from a solidification process at atmospheric pressure.

In this study, we observe melting and solidification processes of Co-Sb compounds, CoSb, $CoSb_2$ and $CoSb_3$ at high pressures..

Experimental

CoSb was synthesized by Ar-arc melting of a 1:1 molar mixture of Co and Sb. $CoSb_2$ and $CoSb_3$ were synthesized by a solid state reaction of a 1:2 molar mixture of Co and Sb and a 1:3 molar mixture of Co and Sb, respectively. X-ray diffraction measurements at high pressures and high temperatures were performed in the beam line PF-AR-NE5C. High pressure was applied using the multi-anvil high-pressure apparatus MAX80. WC anvils with a square flat-surface size of 6 x 6 mm^2 were used. A powdered sample was loaded in the h-BN capsule. The temperature was measured by an alumel-chromel thermocouple attached to the sample capsule. The pressure was evaluated from the lattice parameter of a NaCl internal pressure marker. The X-ray diffraction patterns were measured by an energy-dispersive method. The lattice parameters were obtained by the least-squares fitting of the indexed pattern.

Results and Discussion

Fig. 1 shows x-ray diffraction patterns of $CoSb_3$ in heating at 4.4 GPa. The circles, squares, and triangles represent reflections from $CoSb_3$, $CoSb_2$ and CoSb, respectively. The synthesized sample contains a small amount of $CoSb_2$ as an impurity phase. $CoSb_3$ exhibit no structural transitions in pressurization up to 4.4 GPa at room temperature. In heating at 4.4 GPa, reflections from $CoSb_2$ beomes larger and those from $CoSb_3$ disappear at 1070 K. At 1380 K, reflections from CoSb appears and then those disappear. These results suggest that $CoSb_3$ melts at 4.4 GPa as follows: $CoSb_3$ -> $CoSb_2$ + Liq. -> CoSb + Liq. -> Liq., which is qualitatively the same as a melting process of $CoSb_3$ at atmospheric pressure. In cooling, no reflection appears down to 970 K and then the reflections from $CoSb_3$ appears at 920 K. This result is consistent with the previous results [2]. $CoSb_3$ was observed at room temperature and atmospheric pressure.

We are now investigating the recovered sample using SEM.

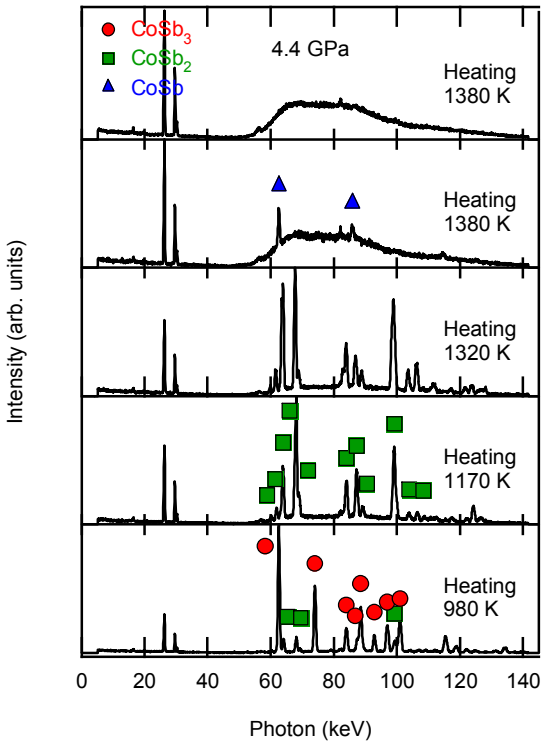

Fig. 1. X-ray diffraction patterns of $CoSb_3$ in heating at 4.4 GPa.

References

[1] P. Feschotte, and D. Lorin, J. Less-Common Met. **155**, 255 (1989).

[2] C. Sekine et al., J. Phys. Conf. Series 215, 012141 (2010).

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