

Pressure-induced irreversible isosymmetric transition of unfilled skutterudite compound CoSb_3

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Introduction

The skutterudite compounds have been actively studied as potentially useful thermoelectric materials. The compounds crystallize in a body centered cubic structure of space group $\text{Im}\bar{3}$ and the binary compounds have a general formula TX_3 ($T=\text{Co, Rh and Ir}$, $X=\text{P, As and Sb}$, site 24g) or $\square\text{T}_4\text{X}_{12}$ where the symbol \square represents a vacancy (site 2a). In spite of the presence of large voids in the structure, earlier studies indicate that the binary skutterudites are quite stable under high pressure. However, the structural change of CoSb_3 in high pressure has been reported [1], recently. Therefore, we have studied the powder x-ray diffraction of CoSb_3 using synchrotron radiation, under high pressure in order to confirm this phenomenon and we have verified this phenomenon for CoSb_3 [2]. In this paper, we will report this result.

Experimental

Using a cubic-anvil high-pressure apparatus, CoSb_3 were prepared at 2GPa and 550°C. The high-pressure diffraction experiments were performed at the beam line BL-18C. The powder x-ray diffraction pattern of CoSb_3 was measured with a diamond-anvil cell (DAC) and the imaging plate up to 43GPa at room temperature. Pressure in the DAC was determined from a pressure shift in the sharp R-line fluorescence spectrum of ruby. A 4:1 methanol-ethanol solution was used as pressure medium.

Result and discussion

Figure 1 shows x-ray diffraction patterns of CoSb_3 at several pressures. No major change such as the appearance of any new peak was observed in the profiles of CoSb_3 obtained at pressures up to 43GPa. This indicates that there is no change in crystal structure type within this pressure range. Although the sample was compressed normally up to 28 GPa, the intensity of 110, 200 and 211 Bragg peaks was drastically suppressed at 37 GPa (Fig. 1(c)). Furthermore, the suppressed intensity of these peaks was maintained at the diffraction pattern after decreasing pressures (Fig. 1(d)). This result suggests any pressure-induced isosymmetric structural change of CoSb_3 .

Figure 2 shows the relative unit cell volume (V/V_0) of CoSb_3 versus pressure. V_0 is the volume at ambient pressure. Above 28 GPa, upon increasing pressure, the volume reduction with pressure becomes to be saturated and the volume decreases again in the range of over 38GPa. Further, upon pressure release from above 43

GPa, the cell volume becomes greater than that observed at increasing pressure. This effect is irreversible, and the sample recovered at ambient pressure exhibits a volume about 2.3% greater than that of pristine CoSb_3 . This result is consistent with the previous report [1]. The bends around 10 GPa are due to solidification of the 4:1 methanol-ethanol solution used as pressure medium.

We will study also this phenomenon for other skutterudite compounds.

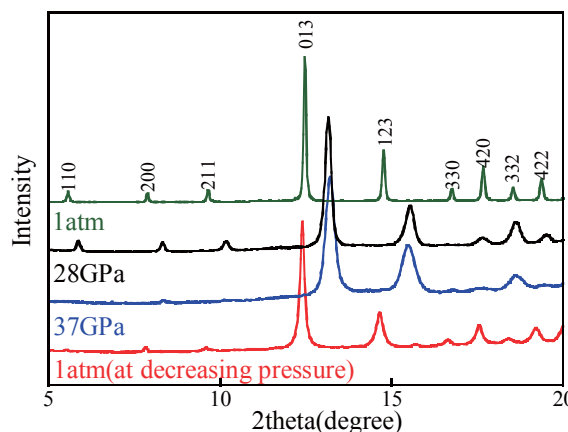


Figure 1 X-ray diffraction patterns of CoSb_3 at (a) 1 atm, (b) 28 GPa, (c) 37 GPa and (d) 1 atm (at decreasing pressure).

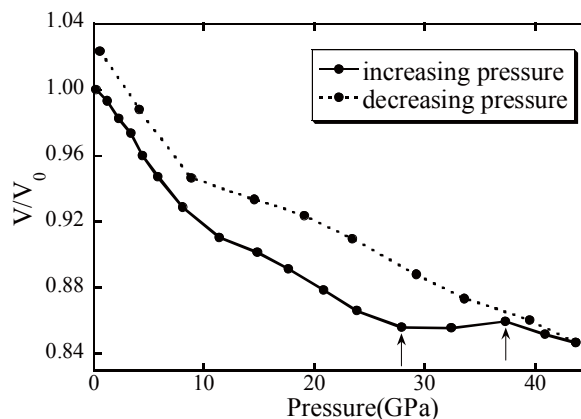


Figure 2 Pressure dependence of the relative unit cell volume for CoSb_3 .

Reference

- [1] A. C. Kraemer *et al.*, Phys. Rev. B, **75**, 024105 (2007).
- [2] K. Matsui *et al.*, J. Phys.: Conf. Ser. **215** 012005 (2010).

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