Structural instability of unfilled skutterudite compounds TX_3 (T = Co, Rh and Ir, X = As and Sb) under high pressure at room temperature

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Filled skutterudite compounds attracted many researchers' interest as strongly correlated electron systems. The skutterudite family includes binary, unfilled skutterudite compounds. These body centered cubic compounds (space group is $Im\bar{3}$) have a chemical formula TX_3 or $\square T_4X_{12}$, where T = Co, Rh and Ir (site 8*c*), X = As and Sb (site 4*g*) and the symbol $\square$ represents a vacancy (site 2*a*). In spite of the presence of large voids in the structure, earlier studies under high pressure indicate that the unfilled binary skutterudites are quite stable under high pressure. However, the structural change of $CoSb_3$ under high pressure has been reported, recently [1]. This structural change could be interpreted as a pressure-induced self-insertion reaction of $CoSb_3$, in which antimony atoms from the compound framework partially fill the 2*a* site. In order to confirm this phenomenon, we have studied the powder x-ray diffraction of $CoSb_3$ using synchrotron radiation, under high pressure at room temperature [2, 3]. We observed an unusual compression curve of $CoSb_3$ on the relative unit cell volume (V/V_0) versus pressure, where V_0 is the volume at ambient pressure. The volume reduction with pressure becomes to be saturated above a critical pressure (P_C) around 30GPa. While no major change such as the appearance of any new peak was observed in the profiles obtained at high pressures, the peak intensity ratio changes drastically above P_C. Further, upon pressure release, the cell volume becomes greater than that observed at increasing pressure. The sample recovered at ambient pressure has a greater volume than that of pristine sample. Similar behaviors have been observed for TSb_3 (T = Rh and Ir) and TAs_3 (T = Co, Rh and Ir). These results suggest that the pressure-induced structural change is a common feature of unfilled skutterudite. Structural instability of unfilled skutterudite compounds TX_3 (T = Co, Rh and Ir, X = As and Sb) is discussed.

[1] A. C. Kraemer *et al*., Phys. Rev. B, **75** (2007) 024105.
[2] K. Matsui *et al*., Journal of Physics: Conference Series **215** (2010) 012005.
[3] K. Matsui *et al*., Journal of Physics: Conference Series **273** (2011) 012043.