In-situ X-ray observation of self-insertion reaction of unfilled skutterudite compounds under high pressure and high temperature

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Skutterudite compounds have been actively studied as potentially useful next-generation thermoelectric materials. The compounds crystallize in a body centered cubic structure of space group $Im\bar{3}$ and the unfilled binary compounds have a general formula $\square T_4X_{12}$ (T=Co, Rh and Ir, occupying site 8*c*, X = P, As and Sb, site 24*g*). Where, the symbol $\square$ means vacancy (site 2*a*). The previous studies under high pressure indicate that unfilled skutterudite compounds are quite stable under high pressure. However, a pressure-induced irreversible isosymmetric transition of $CoSb_3$ around 30 GPa at room temperature 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 site 24*g* partially fill the guest site (site 2*a*). Furthermore, it was reported that a similar behavior has been observed under high temperature at lower pressure [1]. In order to confirm this phenomenon, we have performed in-situ energy-dispersive x-ray diffraction of unfilled skutterudite compound $CoSb_3$ and isostructural compound $RhSb_3$ under high temperatures and high pressures using synchrotron radiation. Figure 1 shows x-ray diffraction patterns of $CoSb_3$ under 8 GPa at (a) 550°C and (b) 500°C. Inset shows the enlarged view in the energy range of 60-70keV. All peaks observed at 500°C appear doubled and shift to lower energy at 550°C. These results indicate the existence of a phase having larger lattice parameter. A similar behavior was observed for $RhSb_3$.

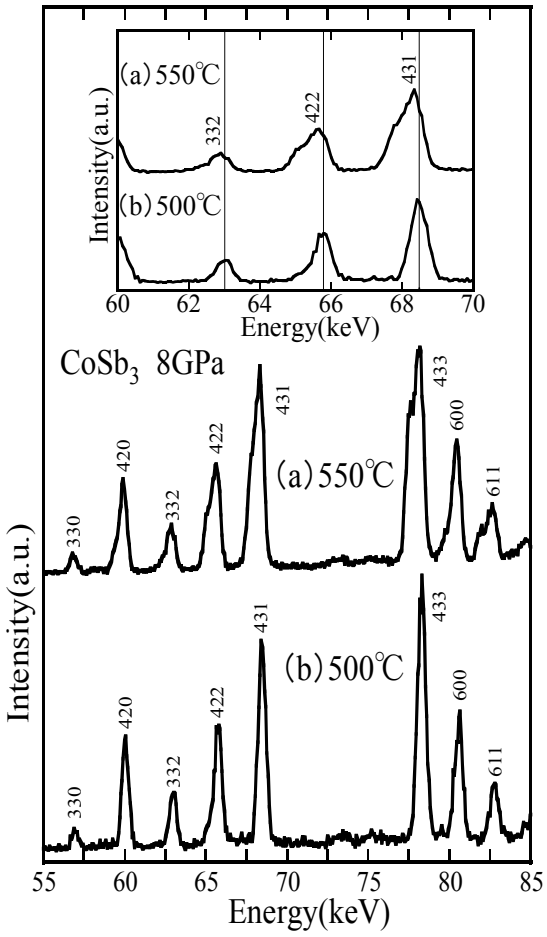

Figure 1. X-ray diffraction patterns of $CoSb_3$ under 8 GPa at (a) 550°C and (b) 500°C. Inset shows the enlarged view in the energy range of 60-70keV.

[1] A. C. Kraemer *et al.*, Phys. Rev. B, **75** (2007) 024105.