RAMAN STUDY OF UNFILLED SKUTTERUDITE $CoSb_3$ UNDER HIGH PRESSURE

M. Komura[1], T. Kume[1], S. Sasaki[1], H. Shimizu[1],
R. Viennois [2], L. Girard[3], D. Ravot[3]

1- Materials Science and Technology Gifu University, 1-1 Yanagido, Gifu, Japan
2 - DPMC, Université de Genève, 24 Quai Ernest Ansermet, CH-1211 Genève 4, Switzerland
3- LPMC, Université Montpellier II, Place Eugène Bataillon, F-34095 Montpellier, France

Filled skutterudite compounds have been considered as potential candidates for thermoelectric applications. These cubic materials (space group Im-3) can be expressed with a general formula $\square A_4B_{12}$ (A = Co, Fe, Ir, and B = P, As, Sb), where $\square$ represents vacancy for accommodating the guest atoms such as the rare-earth ions or other electropositive elements. The rattling of the guest atoms insides the oversized cages in the skutterudite causes a reduction of thermal conductivity, resulting in the phonon glass behavior. There are also binary skutterudites without guest atoms, such as $CoSb_3$. Because of their open structure, the skutterudite compounds are expected to indicate interesting behavior under high pressure. In fact, Kraemer *et al.* demonstrated that, above 20 GPa, $CoSb_3$ undergoes an irreversible isosymmetric transition to a phase that, on pressure release, exhibits a volume greater than that of pristine $CoSb_3$.

In the present paper, we present the first high pressure Raman study of $CoSb_3$. The five out of eight Raman signals related with Sb vibrations were clearly measured up to 35 GPa. As pressure increases, the discontinuous spectral change occurred two times; all the Raman lines showed abrupt broadening at 15.5 GPa, and further broadening and disappearance of the highest frequency peak took place at 27 GPa. The spectral shapes modified by pressure were found to be similar to those reported for the filled skutterudites at ambient pressure[2]. Namely, the spectra obtained at 15.5 GPa < P < 27 GPa resemble that of a partially filled skutterudite ($Ge_{0.05}Co_4Sb_{12}$), and those measured at P > 27 GPa do that of a fully filled skutterudite ($SnCo_4Sb_{12}$). These findings are consistent with the self-insertion reaction proposed by Kraemer; the pressurization causes a reaction from $CoSb_3$ to Sb_xCoSb_{3-x} for which a part of Sb atoms are removed from the framework, and fall into the site for the guest.

[1] A. C. Kraemer *et al., Phys. Rev.* B **75**, 024105 (2007).
[2] G. S. Nolas *et al., J. Appl. Phys.* **94**, 7441 (2003).

E-mail Presenting Author : komina86@yahoo.co.jp