Crystal Structure and Phase Transitions in Lead-halide Perovskite Semiconductor

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$C_5H_{10}NH_2PbBr_3$ is a lead-based inorganic-organic one-dimensional semiconductor. It has a perovskites structure consisting of semiconducting parts which are composed of one-dimensional chains of face-sharing lead-iodide octahedra and barrier parts composed of $C_5H_{10}NH_2^+$ molecules. The lead-iodide chain is isolated by the organic molecules to be a quantum wire, so this material can be regarded as a naturally self-organized one-dimensional system. The precise crystal structure of $C_5H_{10}NH_2PbBr_3$ has not been reported yet. We have performed X-ray diffraction measurement and found that the structure is monoclinic with space group of $P2_1$ ($z = 2$) at R.T., and transformed to orthorhombic $C222_1$ ($z = 4$) above 400 K. Detailed information on the structures, especially on the organic molecule is quite important to understand its optical property and mechanism of the phase transition. In this study, we have performed single-crystal neutron diffraction experiment at R.T. using a four-circle neutron diffractometer, T22, FONDER.

The lattice parameters obtained in the present experiment are $a = 9.8206$ Å, $b = 7.8663$ Å, $c = 15.0283$ Å and $\beta = 102.317$, which are consistent with those obtained from our X-ray measurement. The structure is analyzed using program SHELXL-97, where positional parameters for Pb and I are fixed at our X-ray results and those of atoms in organic molecule are determined by 378 independent reflections with $|F| > 4\sigma$. The final reliable factor is $R = 15.1\%$ which is rather high because the number of reflections is insufficient for 216 structural parameters and there is a rotational disordering in six-membered rings in the organic molecule. Figures show molecular conformations of six-membered rings composed of one nitrogen and five carbon atoms. The X-ray data (a) shows chair forms while neutron data (b) shows boat and skewed-boat form which are less stable than chair forms. The twisting motion between the two identical boat conformers is considered to play an important role on the phase transition. Structural analysis measurement for high temperature phase by using neutron diffraction is planned for further investigation on this system.

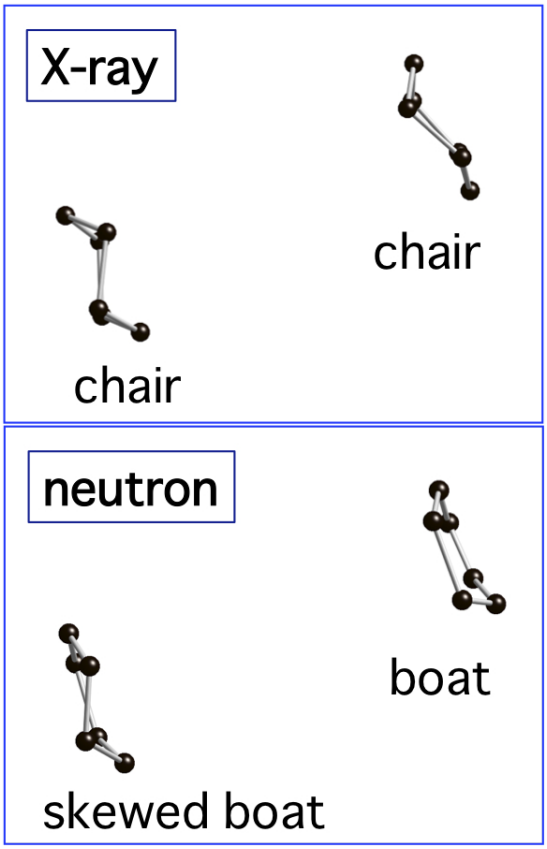

Fig. 1. (a)Molecular conformation of six-membered rings obtained by (a)X-ray and (b)neutron data.