Phase transition in a lead-based inorganic-organic perovskites C5H10NH2PbI3

Miwako Takahashi(A), Munehiko Nakatsuma(A), Kunimitsu Kataoka(A), Takurou Kawasaki(A), Ken-ichi Ohshima(A), Yukio Noda(B)
(A)IMS., Univ. of Tsukuba, (B)IMRAM, Tohoku Univ.

C5H10NH2PbI3 has a lead-based inorganic-organic perovskites structure consisting of semiconducting parts which are composed of one-dimensional chains of face-sharing lead-iodide octahedra and barrier parts composed of C5H10NH2+ 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 crystal structure at room temperature is orthorhombic with space group of C2221. It has been shown by Raman scattering, DSC and optical absorption measurements that the structure undergoes temperature-induced successive phase transitions: phase I at room temperature, phase II for 255.5K to 284.5K, phase III for 250K to 255.5K and phase IV below 250K, which involve rotational/orientational ordering of the organic C5H10NH2+ parts. However, its precise structure has not been determined yet. We have been studying structures and phase transitions in this material by combining the data obtained by neutron and x-ray diffraction techniques, and found interesting structural changes take place in the successive phase transitions. The lattice parameters show step-like changes at the transition temperatures with considerable large contraction along direction vertical to lead-iodide chain while it expands along the chain. Below 285K in phase II, 400 peak is found to separates in two indicating that the crystal lattice changes from orthorhombic to monoclinic. The angle between the splitting peaks increases linearly with decreasing temperature down to 255K and decreasing again up to room temperature without any hysteresis. Below 255K, diffuse peaks appear at the reciprocal points at which reflection is forbidden in the C-centered lattice. These results show that the large structural changes are accompanied with the successive phase transitions. Structural analysis measurement for the phase II has been performed by using a single crystal diffractometer T2-2, FONDER. Since creation of twined crystals in the process of phase transitions is inevitable, Bragg peak intensities were measured at 280K just below the transition temperature where monoclinic angle is close to 90 degree and intensities from twined crystals were integrated together. The intensity data at phase II has been analyzed with the model of monoclinic P21/n which has been suggested by X-ray measurement. The refinement was not successful and structure at phase I gives better R value. Powder diffraction measurement was also performed by using HERMES. The obtained data shows quite high background due to the incoherent scattering from H atoms. Figure 1 shows diffraction pattern at room temperature analyzed by the Rietveld method "RIETAN-2000" [1]. The Rietveld analysis for the data at low temperatures is now going on.

[1] F. Izumi and T. Ikeda, Mater. Sci. Forum, 321-324 (2000) 198-203.

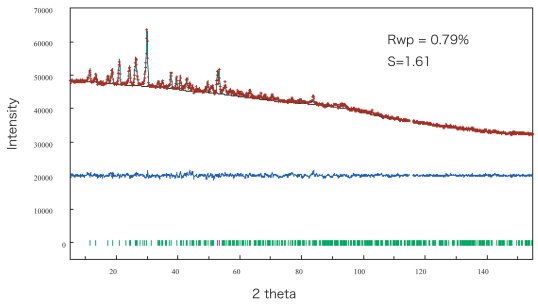

Fig. 1. Diffraction pattern at phase I analyzed by Rietveld method.