

## Crystal Structures and Phase Transitions of the Methylammonium Tin Halide Perovskites

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Methylammonium Tin Halide Perovskites  $\text{CH}_3\text{NH}_3\text{SnX}_3$  ( $\text{MASnX}_3$ , X: halide) are candidates of lead-free light-absorbing materials for photovoltaic devices. They undergo successive phase transitions caused by tilting or distorting of the  $\text{SnX}_6$  octahedra and orientational ordering of the organic MA cation. The structures of low temperature phases are still controversial due to the difficulty of accurate determination for the orientation of organic cation. In this study, neutron diffraction measurements were performed on  $\text{MASnX}_3$  with X=I, Br to determine the structures at low temperature phases and elucidate the ordering mechanism of the organic cation through the phase transitions.

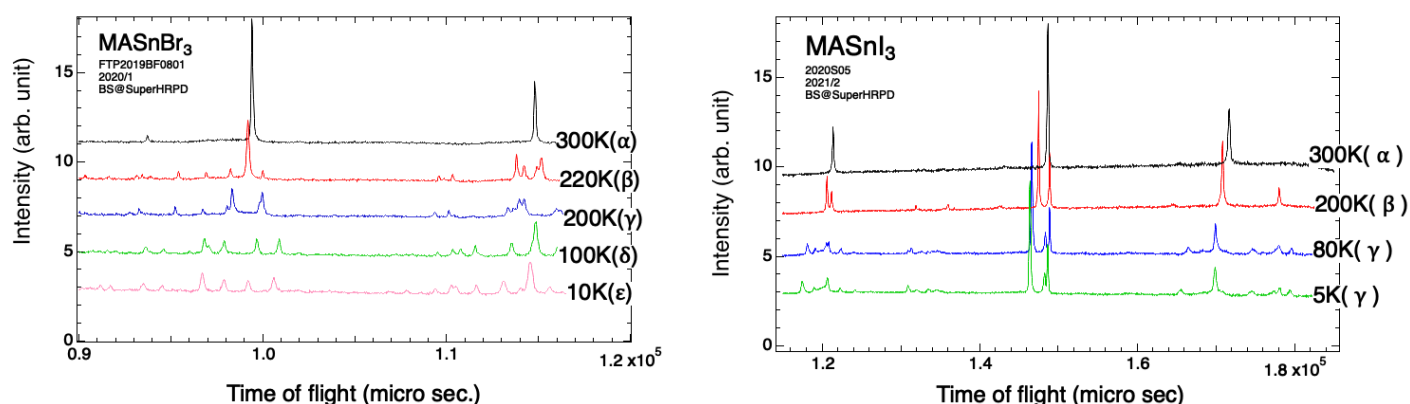


Figure 1. Neutron powder diffraction patterns of  $\text{MASnX}_3$  at different temperatures for (a) X = Br and (b) X = I.

Time-of-flight neutron diffraction data were collected using single crystal diffractometer SENJU (BL18) and Super High Resolution Powder Diffractometer SuperHRPD (BL08) installed at Materials and Life Science Experimental Facility, J-PARC. As shown in Fig.1(a), diffraction patterns observed at five phases of  $\text{MASnBr}_3$  are distinctly different from each other, showing that the crystal structure changes successively through the four phase transitions. The result requires reconsideration of the structures of  $\gamma$ ,  $\delta$  and  $\epsilon$  phases in which no perceptible structural changes have been observed between  $\beta - \gamma$  phases nor  $\delta - \epsilon$  phases[1]. For  $\text{MASnI}_3$ , three phases with different structures were recognized (Fig.1(b)) as previously reported[2][3]. Structure of the lowest temperature phase remains uncertain, but a drastic change of the diffraction pattern between  $\beta$  and  $\gamma$  phases indicates that the structural symmetry is reduced considerably from tetragonal to triclinic system. Single crystal structural analysis at the cubic  $\alpha$  phase reveals that the center of mass of the MA molecule locates off-center of the cubic unit cell, and nuclear density of the molecule synthesized by the maximum-entropy method shows anisotropic distribution along cubic axis. These tendencies appear more remarkable in  $\text{MASnBr}_3$ , indicating stronger effect of organic-inorganic interaction in the X = Br crystal.

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