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Crystal structures and phase transitions of inorganic-organic hybrid layered materials $(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2\text{MCl}_4$ ($\text{M} = \text{Cu}^{2+}$ and Mn^{2+})

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Because of the combination of the hydrogen bonds between halogen atoms in an inorganic part and nitrogen atoms in an organic part, a layered inorganic-organic hybrid perovskite $(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2\text{MCl}_4$ ($\text{M} = \text{Cu}^{2+}$, Mn^{2+} , Fe^{2+}) shows a various crystal structures [1, 2, 3]. To understand an interlayer spacing effect on a magnetic property, various systems have been developed. All three Cu-, Mn- and Fe-compounds crystallized in the same orthorhombic space group (Pbca, No. 61) at room temperature ($a = 7.207\text{\AA}$, $b = 7.301\text{\AA}$, $c = 39.413\text{\AA}$ for Mn-compound, $a = 7.302\text{\AA}$, $b = 7.327\text{\AA}$, $c = 38.635\text{\AA}$ for Cu-compound, and $a = 7.171\text{\AA}$, $b = 7.279\text{\AA}$, $c = 39.106\text{\AA}$ for Fe-compound, respectively). However, in the recent study [1], it is reported that Cu-compound should be ferroelectric, although the inversion center in the point group mmm prevents the spontaneous polarization. In addition, it is also claimed that Mn-compound should have an additional phase transition at 100K and below 100K the point group of Mn-compound is $\text{mm}2$ (Pbc21), where the ferroelectric property is allowed [4]. But from our own investigations on Mn- and Cu-compounds [2, 5] and also a recent study on Fe-compound [3] strongly suggest that Cu-, Mn- and Fe-compounds are not ferroelectric at room temperature but ferroelastic. In this study, we will show crystal structures of Mn- and Cu-compounds not only from neutron single crystal diffraction techniques but also other methods including temperature dependent X-ray powder diffraction results and domain structures under polarized microscope.

Reference

- [1] A. O. Polyakov et al., Chem. Mater., 24 (2012) 133.
- [2] S. H. Park et al., Dalton Trans., 41 (2012) 1237.
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- [5] G. Park et al., (2018) in preparation.

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