

## MS10-P04

## Rotational dynamics of methyl ammonium ions and hydrogen-bonding in orthorhombic $\text{CH}_3\text{NH}_3\text{PbI}_{2.94}\text{Cl}_{0.06}$ by means of neutron scattering and IR investigations

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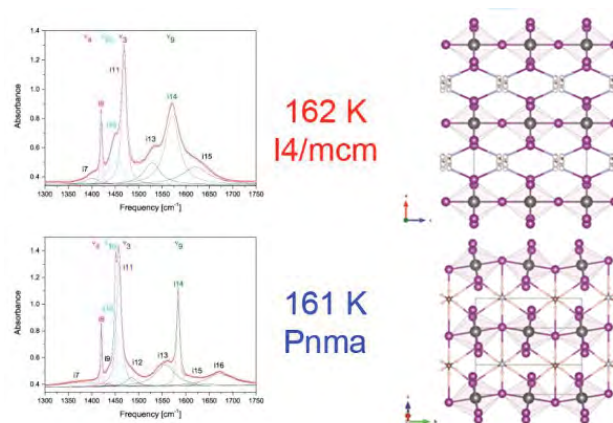
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Perovskites with  $\text{ABX}_3$ -structure show huge possibilities for element substitution on the A-, B- and X-sites, resulting in a broad variety of physical properties. One field of interest is chlorine-substituted methyl ammonium lead triiodide in which A is the organic unit  $[\text{CH}_3\text{NH}_3]^+$ , B =  $\text{Pb}^{2+}$  and  $\text{X} = \text{I}_{3-x}\text{Cl}_x$ .

We chose to substitute 2 % of the iodine in  $\text{MAPbI}_3$  with chlorine since recent investigations with synchrotron XRD showed that only a narrow range of up to 2.5 % of the iodine in  $\text{MAPbI}_3$  can be substituted with chlorine. At the same time, only up to 1 % of the iodine in  $\text{MAPbCl}_3$  can be substituted, meaning there is a large miscibility gap. [1]

The aim of the quasi-elastic neutron scattering (QENS) investigations presented here is to understand the inter-relationship of the static and the dynamic structure of  $\text{MAPbX}_3$  by comparing the temperature-dependent methyl ammonium rotational dynamics of  $\text{MAPbI}_3$ ,  $\text{MAPbI}_{2.94}\text{Cl}_{0.06}$  and  $\text{MAPbCl}_3$ . Combining the QENS results with the analysis of temperature-dependent IR vibrational spectra of  $\text{MAPbI}_3$ ,  $\text{MAPbI}_{2.94}\text{Cl}_{0.06}$  and  $\text{MAPbCl}_3$  helps us understand the influence of the rotational dynamics of the methyl ammonium cation on the hydrogen-bonding layers in the orthorhombic low temperature phase. Recently, the presence of layers with X...H-N hydrogen-bonds in the orthorhombic phase of  $\text{MAPbX}_3$  was discussed to explain the drastic changes of MA IR vibrational modes across the tetragonal-orthorhombic phase transition (Fig. 1). The transformation of the 2-dimensional orthorhombic hydrogen-bond layers into a more 3-dimensional arrangement in the tetragonal phase is an important feature, providing deeper insight into the mechanisms that lead to a free-rotating MA molecule in the inorganic host structure. [2]

In recent QENS investigations on  $\text{MAPbI}_3$  [3], two quasi-elastic components were identified in the tetragonal ( $161.5 \text{ K} < T < 327 \text{ K}$ ) and cubic ( $T > 327 \text{ K}$ ) phase. It was interpreted that, in the cubic and tetragonal phases, the MA ion exhibits four-fold rotational symmetry perpendicular to the C-N axis ( $C_4$ ) along with three-fold rotation parallel to the C-N axis ( $C_3$ ), while only  $C_3$  rotation was present in the orthorhombic  $\text{Pnma}$  phase ( $T < 161.5 \text{ K}$ ). [3] Here, we reinvestigate the suggested jump-models for  $\text{MAPbI}_3$  and show the validity of the proposed QENS interpretation for  $\text{MAPbI}_{2.94}\text{Cl}_{0.06}$  and  $\text{MAPbCl}_3$ .



### References:

- [1] Franz et al., submitted to Acta Crystallogr. B, 2018
- [2] Schuck et al., J. Phys. Chem. C, 2018, 122, 5227
- [3] Li et al., Nature Communications 2017, 8, 16086

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