Experimental report

20/11/2017

Proposal: 7-02-167 **Council:** 4/2016

Title: Rotational dynamics of methyl ammonium ions in the hybrid organic-inorganic perovskite CH3NH3PbI2.94Cl0.06 by means of QENS investigations

Research area: Materials

This proposal is a new proposal

Main proposer: Goetz SCHUCK

Experimental team: Frederike LEHMANN
Susan SCHORR
Goetz SCHUCK

Local contacts: Jacques OLLIVIER
Hannu MUTKA

Samples: CH3NH3PbI3
CH3NH3PbI2.94Cl0.06
CH3NH3PbCl3

Instrument	Requested days	Allocated days	From	To
IN5	4	3	21/11/2016	24/11/2016

Abstract:

Perovskites with ABX3 – structure show a huge possibility on element substitutions on A-, B- and X-site which leads to a broad variety of physical properties. In recent years the interests become focused on hybrid perovskites as a future optoelectronic material. Our main field of interest is chloride substituted methyl ammonium lead triiodide in which A is the organic unit [CH3NH3]+ = MA, B = Pb2+ and X = I3-xClx . The aim is to get an inside into the interrelationship of static and dynamic structure of MAPbI3-xClx and MAPbCl by studying the temperature dependent methyl ammonium dynamics by means of QENS investigations in order to understand the influence of chloride on the rotational dynamics of the methyl ammonium cation.

EXPERIMENT n° 7-02-167

Instruments involved:

IN5 from 21/11/2016 to 24/11/2016

IN4 from 23/11/2016 to 24/11/2016

Title:

Rotational dynamics of methyl ammonium ions in the hybrid organic-inorganic perovskite $CH_3NH_3PbI_{2.94}Cl_{0.06}$ by means of QENS investigations

Götz Schuck,[1] Frederike Lehmann,[1,2] Susan Schorr [1,3]

1 Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

2 Universität Potsdam, Institut für Chemie, Karl-Liebknecht-Straße 24-25, D-14476 Potsdam OT Golm, Germany

3 Freie Universität Berlin, Institut für Geologische Wissenschaften, Malteserstr. 74-100, 12249 Berlin, Germany

Local Contact: Hannu MUTKA and Jacques OLLIVIER

The aim of this experiment was to investigate the influence on the rotational dynamics of CH_3NH_3 (abbreviated as MA) molecules when Cl is incorporated into the crystal structure of $MAPbI_3$. This report is preliminary since the analysis of the data presented here is still in progress.

IN5

Three samples ($MAPbI_3$, $MAPbCl_3$, $MAPbI_{2.94}Cl_{0.06}$ = 2 % Cl) where measured at 70K, 130K, and 190K using a resolution of 2.25 Å and 4.8 Å (Fig. 1). $MAPbI_3$ was additionally measured with a resolution of 8 Å at 30 K, 70 K, 100 K and 160 K. It was possible to obtain quasi elastic data for all three samples. The obtained spectra give the impression, that the samples are not suffering on degrading issues as previously reported [1]. The quasi elastic data have proven to be essential for completing and obtaining a relaxation map of $MAPbI_{2.94}Cl_{0.06}$ in the temperature region of the orthorhombic-tetragonal phase transition.

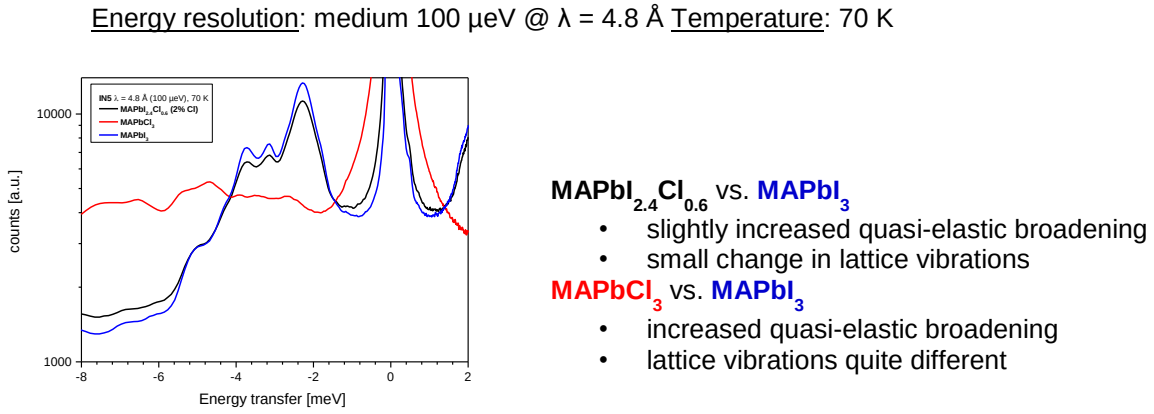

Figure 1: Displays the recorded quasi elastic scattering spectra at 70 K with a medium resolution of 4.8 Å measured on the IN5

We will give more detail in a final report once we have submitted a paper on these important results.

Phonon modes at low energy < 20 meV could be measured and show clear differences of spectra comparing the different samples (Fig. 1).

IN4

In additional experiments at IN4 it was possible to perform a temperature-dependent measurement of the inelastic spectra of $MAPbI_3$ between 10 K and 194 K (with temperature step of about 8 K) in an energy range up to 25 meV (Fig. 2). It could be observed that the elastic intensity indicates a change of the MA dynamics that are in agreement with preliminary results published by D. Djurado [1]. The normalised elastic intensity that is shown in Fig. 3, clearly indicates the orthorhombic/tetragonal phase transition at 162 K. The MA libration at 11.7 meV showed drastic changes around the orthorhombic-tetragonal phase transition (Fig. 4a and b). This discontinuous behaviour is likely to be connected to the temperature-dependent frequency behaviour of combinational modes at around 1680 cm^{-1} that could be observed recently in IR vibrational spectra of $MAPbI_3$ [2].

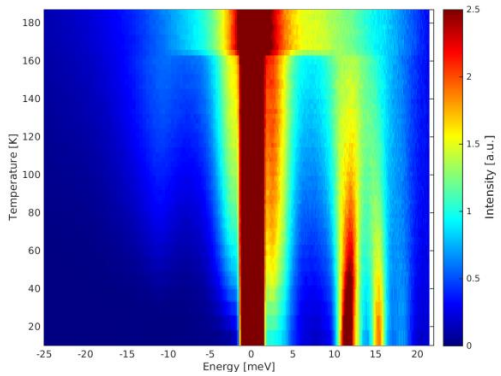

Figure 2: Displays inelastic scans of $MAPbI_3$ taken on the IN4

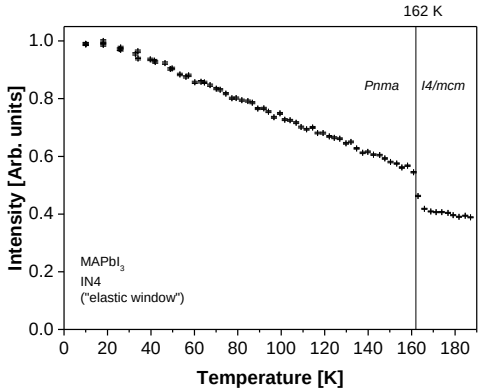

Figure 3: Displays the normalized elastic intensity of the elastic peak of $MAPbI_3$ taken on the IN4

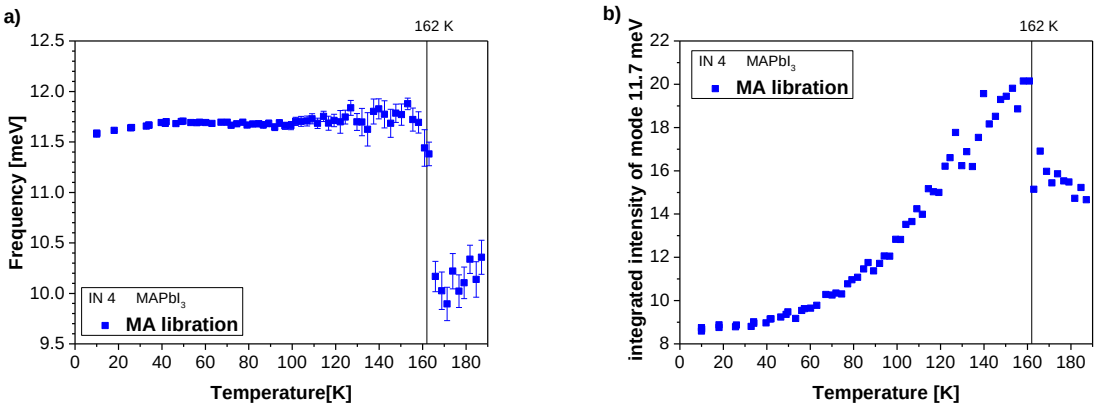

Figure 4: Displays a) temperature-dependent frequency and b) temperature-dependent integrated intensity of MA libration mode of $MAPbI_3$ measured on the IN4

[1] ILL Experimental report 7-04-140, 2016

[2] G. Schuck, D.M. Többens, M. Koch-Müller, I. Efthimiopoulos and S. Schorr, submitted to J. Phys. Chem. C