Experimental report

12/09/2016

Proposal: 7-04-140 **Council:** 10/2014

Title: Local dynamics and vibrational states in hybrid H & D methylammoniumlead iodide perovskite MA+PbI3-

Research area: Materials

This proposal is a new proposal

Main proposer: David DJURADO

Experimental team: Peter REISS
Maria MENDEZ MALAGA
Stephanie POUGET
Mathilde BOUCHARD
David DJURADO

Local contacts: Bernhard FRICK
Jacques OLLIVIER
Mohamed ZBIRI
Alexandre IVANOV

Samples: CH3NH3PbI3
CD3NH3PbI3
CD3ND3PbI3

Instrument	Requested days	Allocated days	From	To
D20	1	0		
IN16B	4	1	06/05/2015	08/05/2015
IN5	4	6	25/06/2015	01/07/2015
IN6	4	0		
IN1 LAG	3	3	20/09/2015	23/09/2015

Abstract:

We aim to fully investigate vibrational and dynamics properties by inelastic (INS) and quasielastic (QENS) incoherent neutron scattering in methyl ammonium lead iodide perovskite. This family of materials shows high performance as sensitizer in photovoltaic cells, when incorporated in a mesoscopic heterojunction with TiO2, and an organic hole transporter. Although this material is known since the 1950’s, only few dynamics studies have been done in the past, without any attempt to probe the time ranges covered by QENS. It turns out that the knowledge of this dynamics is of prime importance to understand in details the electronic properties of this material. This would allow in the future to design new related materials without toxic elements such as lead and with better stability to humidity. In order to try to differentiate precisely the evolution of the dynamics of the methyl ammonium group as a function of the temperature we will do the same study on fully and partially hydrogenated (deuterated) compounds.

EXPERIMENT n°7-04-140

Instruments involved : IN16B : from 06 to 08 /05 /2015

IN5 from 25/06 to 01/07/2015

IN1 from 20/09 to 23/09/2015

Title: Local dynamics and vibrational states in hybrid H & D methylammonium lead iodide perovskite MA+PbI3-

David Djurado, Peter Reiss, Renaud Demadrille, Stéphanie Pouget, Mathilde Bouchard, Dmitry Aldakov.

INAC – SPrAM- (UMR CNRS-CEA-UGA) and MEM, CEA Grenoble – 17 rue des Martyrs- 38054 – Grenoble –cedex9

The aim of this experiment was to extract the characteristics of local diffusion of the Methyl Ammonium (MA) cation in different phases of MAPBI3 from 40 to 350K in the time windows from 1ns to 0.1 ps.

We took advantage to have also the partially deuterated phase CD3NH3PBI3 in order to try to differentiate the dynamics of CH3 and NH3 groups.

REMARK: This report is very preliminary and any comment made here is far from being definitive since the analysis is still in progress.

IN16B

For this experiment we started by measuring EFWS and IFWS (2µeV) on IN16B from 2 to 350K.

We obtain the results of figures 1 And 2.

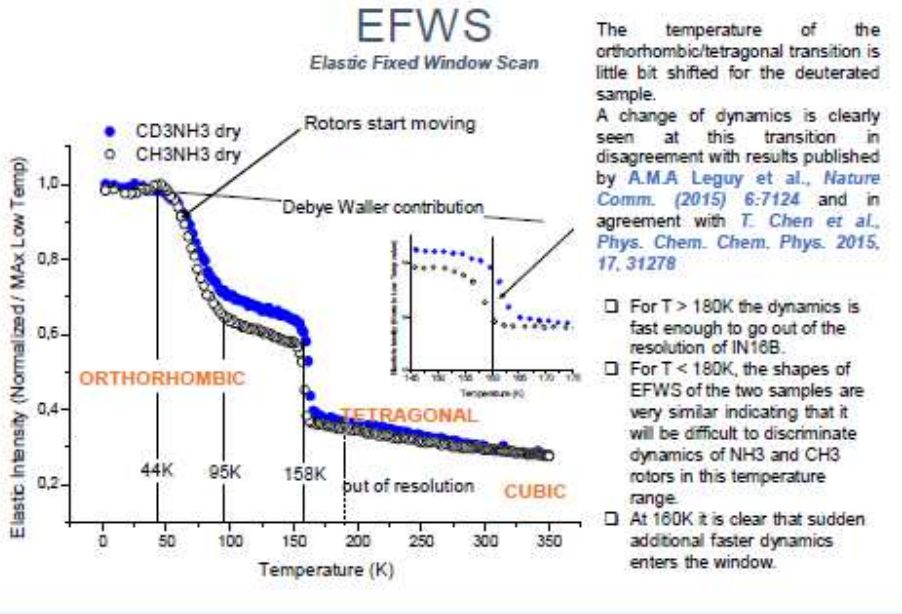


Figure 1: EFWS of CH3NH3PBI3 and CD3NH3PbI3

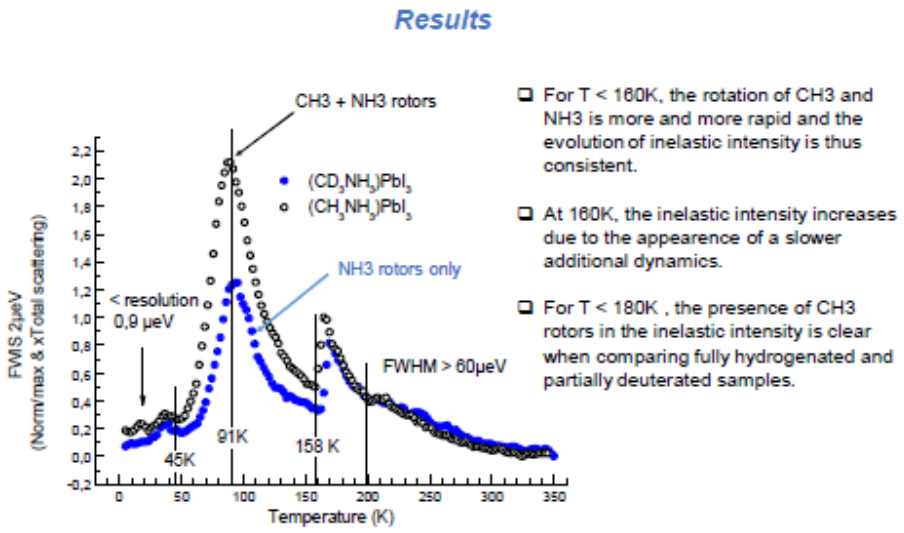


Figure 2: IFWS (2µeV) of CH3NH3PBI3 and CD3NH3PbI3

We could also record quasi elastic scattering spectra at 70, 90, 120, 150, 180 and 325K.

We could realize that the motions were clearly out of the resolution for T > 180K.

In this experiment we found at 2K excitations revealing some proton tunneling. This finding compelled to us to apply to obtain some additional time allocated from Director of ILL see experimental report of DIR 139 experiment.

IN5

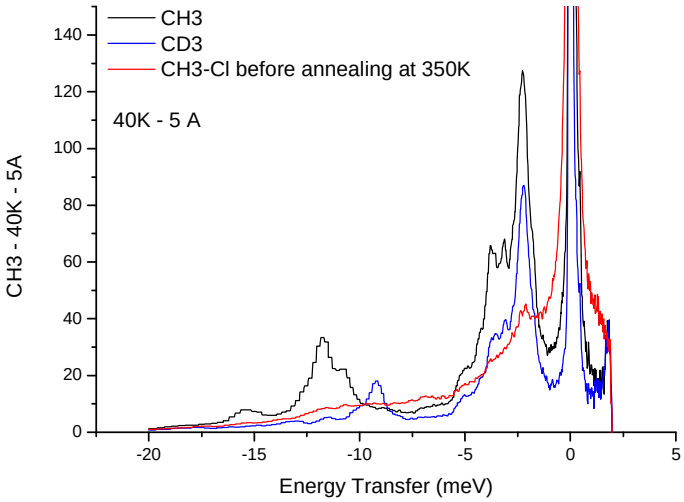
On IN5 we could perform a lot of quasielastic measurements on CH3NH3PbI3 and CD3NH3PbI3 and also to a phase containing chlorine like CH3NH3PbI(3-x)Clx.

Unfortunately for this Cl containing phase, we could checked later by performing neutron diffraction measurements on D1B on the same sample which did not have seen open air at all, that it is not stable at all and probably it was already degrading during IN5 measurements. Accordingly we do not give too much attention for the moment to these results.

By contrast for the twoother samples we could completely span the temperature range from 3K to 350K. We use mainly the 5Å wavelength and when applicable we alused a 7.5Å wavelength.

These measurements have revealed essential to complete and obtain a full relaxation map of the system, and we will give more details in a final report once we will have submitted a paper on these important results.

Let's note also that we could record on IN5 some phonon modes at low energy < 20meV and we can see the clear differences of spectra comparing the different samples. (figure 3).



Figures 3: Low energy phonon modes as recorded on IN5 for the three studied samples

IN1

Concerning IN1 we have recorded the inelastic spectra for CH3NH3PbI3 and CD3NH3PbI3 at 10, 90, 150 and 180K in an energy range from 7 to 500 meV. Up to now we did not have time to analyze these data which will be worth to analyze and comment in regard to different published contributions based on numerical calculations and recent Raman scattering measurements.