Experimental report

21/12/2021

Proposal: **7-02-204**

Council: 4/2020

Title: Dynamics of New Cubic Stabilised Hybrid Perovskites

Research area: Chemistry

This proposal is a new proposal

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Samples: (CH3NH3)1-xPbI3+y

Instrument	Requested days	Allocated days	From	To
IN16B	4	2	05/07/2021	07/07/2021

Abstract:

Hybrid perovskites, composed of an organic cation, inside a post transition metal halide framework, have emerged as simple, low cost solar cell materials, with power conversion efficiencies that are competitive with silicon. The commercial viability of perovskite solar cells is yet to be proven with stability being the major limiting factor. These hybrid perovskites are highly sensitive to environmental conditions and quickly degrade under the mildest of thermal treatment. The root cause of decomposition in MAPbI3 is likely to be the volatility of the MA+ cation, and much research has thus focused on controlling the thermal and chemical stability. We have recently developed a number of procedures to chemically manipulate the MAPBI3 structure to produce new phases with potentially improved photovoltaic properties, as well as heightened stability. We propose to study two new MA1-xPbI3+y phases where pristine MAPbI3 has been chemical modified to posses very different more favourable chemical and physical properties.

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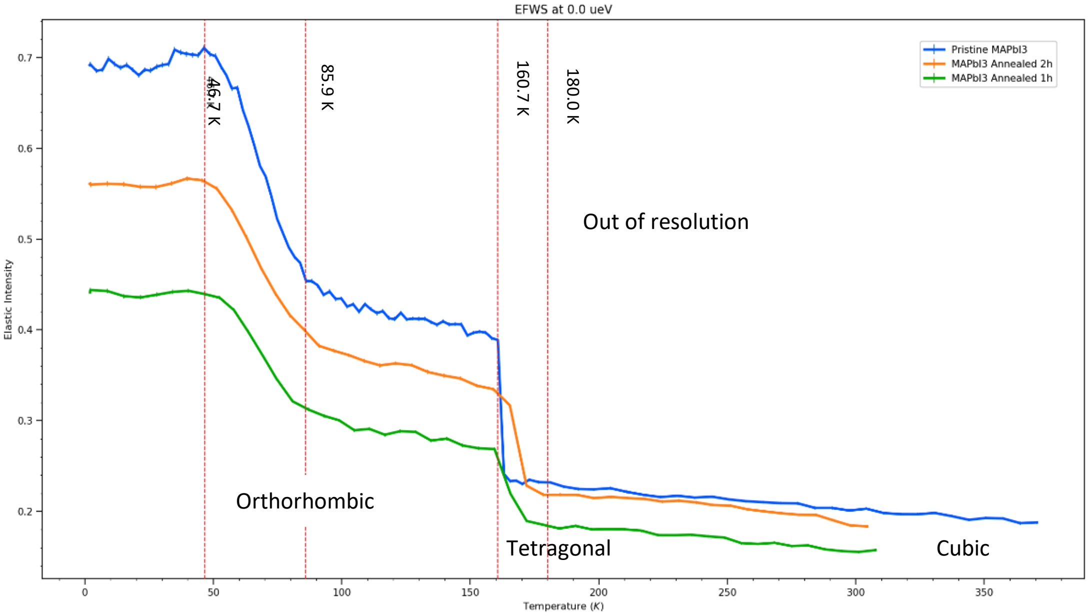
The aim of this experiment was to study the methylammonium (MA) cation dynamics in MA deficient/treated version of $MAPbI_3$ in comparison to one sample of pristine $MAPbI_3$. Due to Covid-19 travel restrictions, only one PhD student alone was able to attend this experiment as they were already working in France. During the two days of beamtime, we were able to measure one sample of pristine $MAPbI_3$ and two versions of MA deficient $MAPbI_3$, achieved by our vacuum annealing post synthetic treatment.

REMARK: The is a preliminary report and so any comments made here are not definitive as the analysis of this data is still in progress.

For this experiment we started by measuring the FWS at 0 μeV, 3 μeV and 6 μeV from 2 – 350 K.

Figure 1. Elastic Full Window Scans of Pristine $MAPbI_3$, annealed 1h, and annealed 2h, at 0.0 μeV.



At 0 μeV we find that the temperature of the orthorhombic to tetragonal transition temperature seems to have shifted slightly between the pristine, 1h annealed, and 2h annealed samples. These temperatures are listed in Table 1. A change in the dynamics of these three systems is clearly seen which actively disagrees with the results published by A.M.A Leguy *et al*. (2015). However, they are so far in agreement with results from T. Chen *et al*. (2015).

We can see that above 180 K, the dynamics in these systems are too fast to be measured and go out of the resolution of IN16B. This was also noted by the beamline scientist that it would have been more productive to have the BATS setup for this experiment which was scheduled earlier in the beamline cycle.

Table 1. Orthorhombic to Tetragonal Phase Transition Temperatures at 0.0 μeV.

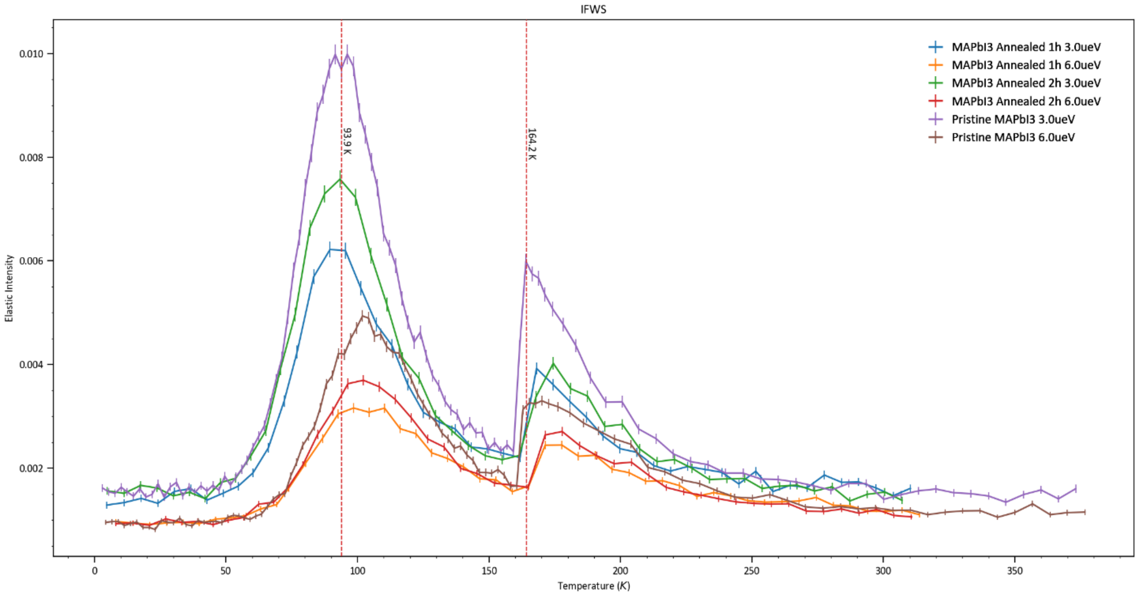
Sample	Transition T start (K)	Transition T end (K)	Difference (K)
Pristine	160.75	163.12	2.37
Annealed 1h	159.44	171.96	12.52
Annealed 2h	159.01	171.89	12.45

There is fairly large difference in intensity between the pristine and treated samples, and it was realized after the experiment that it is most likely due to the difference in sample mass. The availability of the pristine sample was considerably more than the 0.5 g of the treated samples. The sample mass should have been accurately weighed in the vials prior to the experiment. As another remark for any future experiments, a greater amount of each sample would be useful – however due to Covid restrictions in travel between UK and France, more sample could not be obtained prior to the experiment.

The slopes of the curves for each sample at around 160 K gives us some information on the speed of the faster dynamics of the organic cation as the transition phase occurs. It seems that the transition for pristine MAPbI3 is very quick, but for the treated samples the transition occurs across a couple of Kelvin (see Table 1).

As expected, the motions seem to be too fast above 170 K for the resolution of the instrument. This data is still under analysis so far.

Figure 2. Inelastic Full Window Scans of Pristine MAPbI$_3$, annealed 1h, and annealed 2h, at 3.0 μeV and 6.0 μeV.



Comparing the inelastic intensities of the pristine vs treated samples, again we see clear shifts of the orthorhombic to tetragonal phase transition temperatures at both 3 μeV and 6 μeV. These can be seen in Table 2. Once again, the large difference in intensity between the pristine and treated samples is most likely due to the difference in sample mass.

Table 1. Orthorhombic to Tetragonal Phase Transition Temperatures at 3.0 and 6.0 µeV.

Sample	**Transition T 3 µeV (K)**	**Transition T 6 µeV (K)**
Pristine	164.06	162.96
Annealed 1h	168.14	171.38
Annealed 2h	174.42	171.38

Quasi-elastic scattering spectra were also recorded for each sample at 2, 110, 170 and 200 K. This data is still under analysis.

References:

A. M. A. Leguy *et al.*, The dynamics of methylammonium ions in hybrid organic–inorganic perovskite solar cells. *Nat. Commun.*, 2015, 6, 7124, 10.1038/ncomms8124.

T. Chen *et al.*, Rotational dynamics of organic cations in the $CH_3NH_3PbI_3$ perovskite. *Phys. Chem. Chem. Phys.*, 2015,17, 31278-31286.