



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal: <https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Variable Induced Defects in Hybrid Perovskites	Experiment number: CH 5861
Beamline: BM01	Date of experiment: from: 21 st April 2021 to: 23 rd April 2021	Date of report: 20 th July 2021
Shifts: 6	Local contact(s): Dr Charlie McMonagle	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Jessica Dawber Professor Mark Green University of Kent, Canterbury, Kent, CT2 7NH, UK		

Report:

Hybrid organic-inorganic perovskites have attracted attention in the development of efficient photovoltaic devices due to their low cost synthesis and power conversion efficiencies that are competitive to silicon. These compounds of general formula ABX_3 (A = organic cation; B = transition metal; X = halogen), with the most commonly studied perovskite being methylammonium lead iodide, $MAPbI_3$ ($MA = CH_3NH_3$) [1,2]. $MAPbI_3$ exists in three temperature dependent morphologies (shown below) and certain research has shown that the cubic phase is the most efficient structure for photovoltaic devices [3, 4]. Despite its promising photovoltaic capabilities in research, these solar cells have not yet made it to the commercial market - largely due to its instability when in contact with moisture or at elevated temperatures [5]. One such suggestion for improving stability is suppressing or shifting the transitions of $MAPbI_3$ or even stabilising the high temperature cubic phase at room temperature [3]. We have been developing a number of post-synthetic annealing treatments that have shown to alter structure of $MAPbI_3$ at room temperature.



Due to the COVID-19 pandemic and lockdown in France during the beamtime schedule, users were unable to be present for this experiment and so measurements were carried out by the local contact Dr Charlie McMonagle, with contact occurring remotely between himself and the us as the users. During this time we were able to study several of these the samples of $MAPbI_3$ that we had previously treated post-synthetically, where the annealing time had been varied. Each of these samples were packed into capillaries and measured from 100 K – 400 K with a wavelength of 0.64114 Å. This temperature range allowed us to observe all three phase transitions that occur in $MAPbI_3$ so we could study any differences between pristine $MAPbI_3$ that is reported in literature.

Initial measurements were taken at 300 K, Figure 1a highlights a section of the pattern for each sample where there is noticeable suppression of the 211 reflection with increasing treatment time. The suppression of this reflection is synonymous with the increasing presence of a cubic phase within the samples. This hypothesis is further supported by the peak shape evolution that is seen in Figure 1b where as treatment time is increased, a merging of the doublets seen between $11.6^\circ - 11.8^\circ$ and $12.9^\circ - 13.2^\circ$ to a single peak.

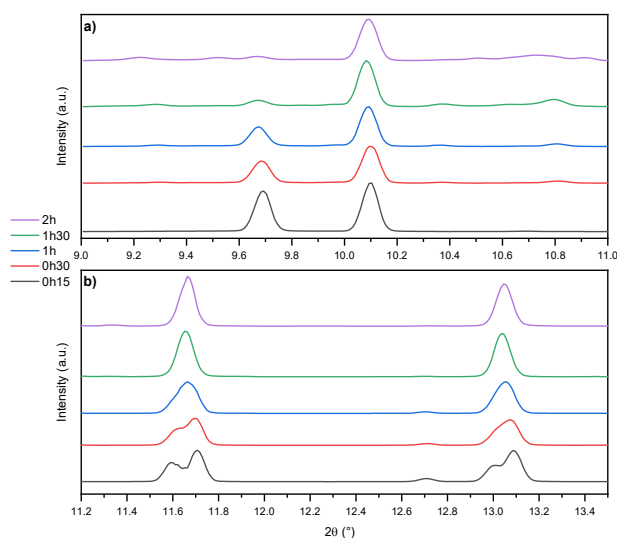


Figure 1. a) Observed decrease in peak intensity 211 reflection with increasing the annealing time of treatment. b) evolution of peak shape from ‘tetragonal’ doublet to ‘cubic’ singlet peak with increasing annealing time of each sample. Patterns were measured at 300 K.

We also observed a shifting of the tetragonal to cubic transition temperature, which was dependent on how long MAPbI₃ had been exposed to the post-synthetic treatment. The contour plot seen in Figure 2 illustrates this lowering of the tetragonal to cubic phase transition temperature upon heating from 300 K – 400 K, and further lowering of this temperature when cooling down from 400 K which suggests there is a hysteric effect of these transitions in the treated samples. Another possible reason for this supposed lowering of the phase transition temperature is that the sample may have been a slightly different temperature than the cryostat reported value. We use Table 1 to show the estimated temperature at which these transitions occur for each sample, however the difference in temperature between each measurement is 4 K and so further work would need to be done to gain more precise data the transition temperature for each sample. Further support for this shifting of the transition temperature is shown in Figure 3, where sequential refinements of the data for each sample were performed based on the tetragonal phase of MAPbI₃. From this the lattice parameters were extracted and the ratio between the c and a lattice parameters have been plotted as a function of temperature. Doing this enables us to see more clearly the temperature at which the material transitions from a tetragonal to cubic structure.

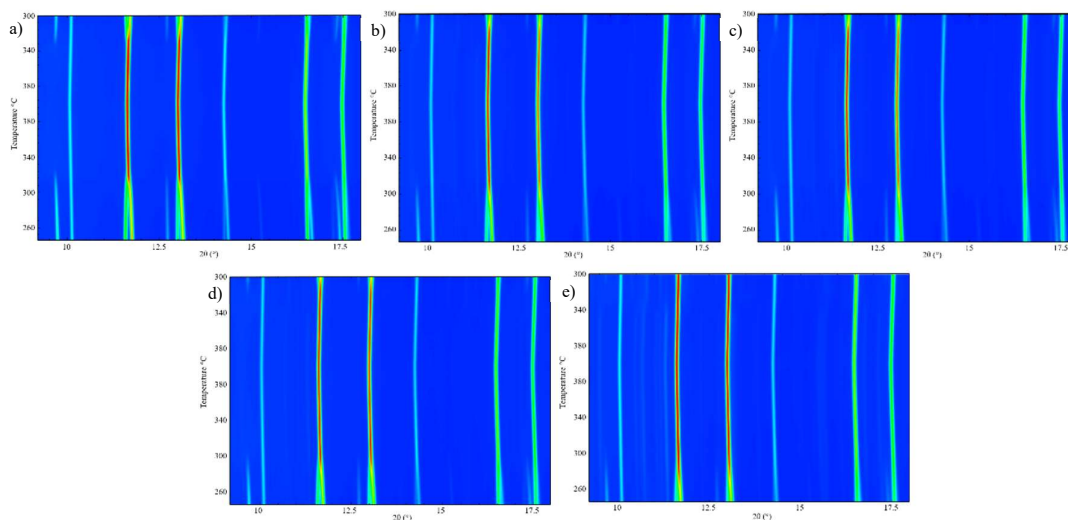


Figure 2. 2D contour plots displaying the differences at which MAPbI₃ transitions between the tetragonal and cubic phases with increasing time of the post-synthetic treatment. a) 0h15; b) 0h30; c) 1h; d) 1h30; e) 2h.

Despite clear shifting in the high temperature phase transition, we are unable to see any observable temperature shift for the lower transition between the tetragonal to orthorhombic phases. Each sample went through the transition to the orthorhombic phase at 160 K, which is the temperature that has previously been reported for pristine MAPbI₃. This leads us to believe that this post synthetic treatment does not have an effect on the structure of MAPbI₃ at lower temperatures.

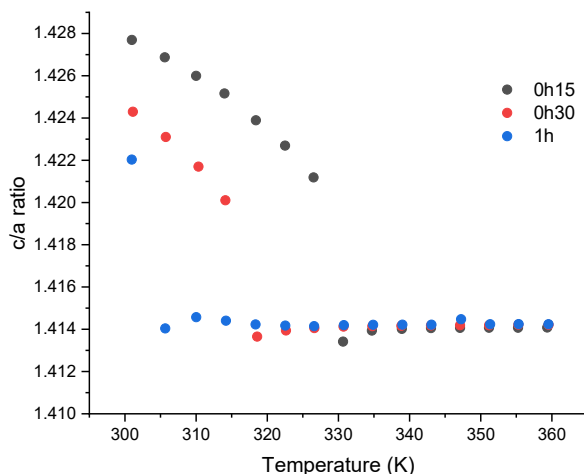


Figure 3. Plot of c/a lattice parameter ratio vs temperature for 0h15, 0h30, and 1h treated sample in order to demonstrate the shift in tetragonal to cubic phase transition temperature.

Table 1: Differences between the tetragonal (T) to cubic (C) transition temperature when heating or cooling the treated samples.

Treatment Time	T - C transition heating / K	C – T transition cooling / K
0h15	326	314
0h30	314	306
1h	305	294
1h30	300	279
2h	300	274

References:

1. N. G. Park. *Mater Today*, 2015, 18:65–72.
2. M. Liu, M. B. Johnston MB, H. J. Snaith, *Nature*, 2013, 501:395.
3. B. Salhi, Y. S. Wudil, M. K. Hossain, A. Al-Ahmed and F. A. AlSulaiman, *Renewable Sustainable Energy Rev.*, 2018, 90, 210–222.
4. G. Niu, X. Guo and L. Wang, *J. Mater. Chem. A*, 2015, 3, 8970–8980.
5. T. T. Ava, A. Al Mamun, S. Marsillac, G. Namkoong, *Appl. Sci.*, 9, 188, (2019).