EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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://wwws.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 form 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.

ESRF	**Experiment title:** Real-time X-ray diffraction for in situ analysis of the crystallization process of MPbX3 (M= organic or inorganic cation, X= Cl, Br, I) high-efficiency perovskite solar cells	**Experiment number**: **SC-4932**
Beamline: ID10	**Date of experiment**: from: 06 Sep 2018 to: 11 Sep 2018	**Date of report**: 28. Feb 2020
Shifts: 15	**Local contact(s)**: **Andrei Chumakov**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Compositional engineering of organic-inorganic lead halide perovskites is one of the key methods to achieve high solar cell efficiency. As stated in the proposal, we have determined different compositions of $MPbX_3$ (M = $CH_3NH_3^+$, $CH(NH_2)_2^+$, or Cs^+ and X= Cl, Br, I or a mixture) with different mixing ratios for M and X.

The following X-ray scattering experiments were done at beamline ID10 of the ESRF with a photon energy of 22 keV under N_2 atmosphere. The beam size was 20 µm in vertical direction and 100 µm in horizontal direction. GIWAXS data was measured under an angle of incidence of 0.02…0.2° with a PILATUS 300k area detector.

Since the analysis of the data is still in progress, we present only some important findings in this report. As an example in Fig.1 we show post growth GIWAXS data of mixed perovskite films with different cation ratio. The films are crystalline with reflections matching a single perovskite structure. Depending on mixing ratio we find a slight shift of the lattice constant of the cubic perovskite structure. The shift of the lattice constant is induced by a larger molecular cation, which expands the lattice. In addition, we find different amounts of PbI_2 and hexagonal $FaPbI_3$ polytypes. Since these two additional phases strongly impact the device performance of perovskite solar cells, we track the also the nucleation of these in real-time during annealing.

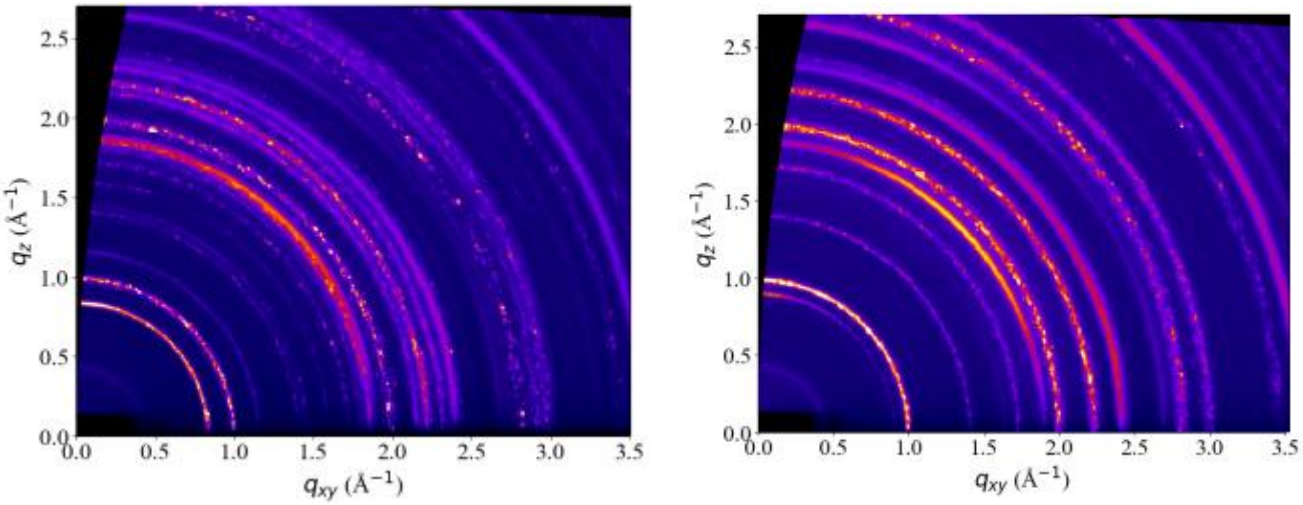

Fig 1: Comparison of GIWAXS data at the end of film growth from two films with different cation. Angle of incidence was 0.2° and each image was assembled from 6 images measured with a PILATUS 300k detector.

Fig. 2 shows the integrated Bragg peak intensity from different crystal phases during annealing of the perovskite precursor measured by GIWAXS. Before annealing (t = 0) we observe already crystallized PbI_2 in the precursor film. Immediately at the start of annealing (t = 50 s) we observe a strong increase in PbI_2 nucleation. This is followed by an increase of nucleation of the cubic perovskite phase. At later times (t = 100…600) we see a complete conversion of the crystalline PbI_2 into the cubic perovskite structure. We also observe the nucleation of the 6H polytype of $FAPbI_3$ in competition to the cubic perovskite structure.

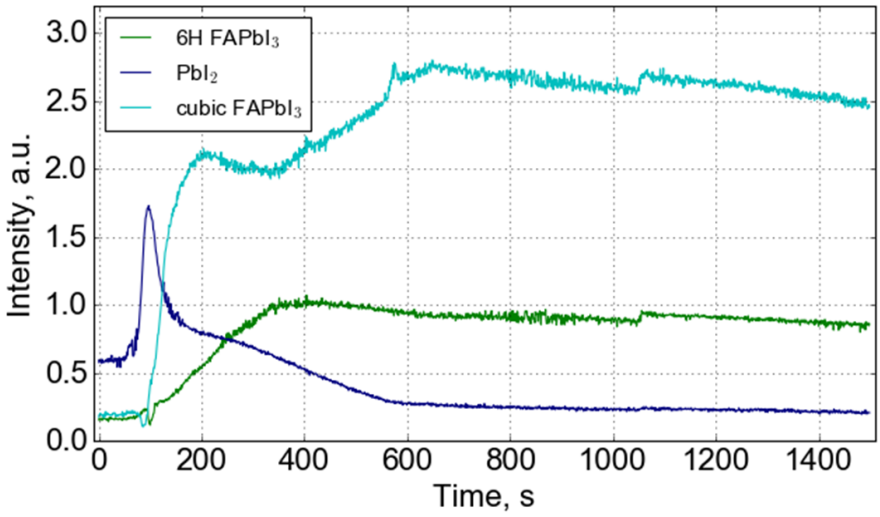

Fig. 2: Bragg peak intensity from different crystal phases during annealing of the perovskite precursor measured by GIWAXS. The annealing starts at t = 50 s.

As stated in the proposal, we were able to measure the crystal formation dynamics for several material compositions. The crystal formation dynamics were measured in real-time during annealing by grazing incidence X-ray diffraction (GIWAXS) to determine the crystal quality, in terms of peak width and orientation distribution. The analysis of these data is still ongoing. With these *in situ* real-time measurements, we expect to obtain a detailed understanding of the structural aspects of perovskite crystal formation from solution in a 1-step conversion process.

We wish to acknowledge the excellent collaboration with the beamline staff, which made this challenging experiment a success.