EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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:** Combined nanoscale strain and halide composition mapping in perovskite layers deposited on silicon for tandem solar cells	**Experiment number**: MA-5734
Beamline: ID13	**Date of experiment**: from 17/06/2023 to 19/06/2023 and from 27/06/2023 to 29/06/2023	**Date of report**: 13/09/2023
Shifts: 18	**Local contact(s)**: MEDJAHED Asma	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

MA-5734 experiment was performed in June 2023 in two individual sessions: from 17/06/2023 to 19/06/2023 and from 27/06/2023 to 29/06/2023. The samples were hybrid halide perovskite (HHP) with the chemical composition $Cs_{0.15}Fa_{0.85}Pb(I_{0.83}Br_{0.17})_3$ as optimized at CEA/INES deposited on two types of silicon substrates: flat Si substrates and pyramid textured Si as described in the proposal. Pristine thin layers were studied, obtained through different deposition processes and conditions. Samples obtained by spin-coating were investigated: two of them were deposited on flat Si substrates, each being annealed for a different time (5 min or 1h at 100 ºC), to investigate the effect of the annealing on the strain, grain orientation, halide distribution as well as the distribution of PbI_2. This crystalline compound is known to have to different origins: untransformed precursor or degradation product of the perovskite. Additionaly, perovskite thin films were also deposited on textured Si substrates by two different techniques, spin coating and slot die coating. The former is the most widely used technique in laboratory but it leads to non-uniform layers when aiming for the large area deposition required for industrial applications. The latter allows rapid and well-controlled large area deposition. Finally, cross-sections of a solar cell based on a perovskite layer spin coated on flat silicon was prepared for depth-resolved investigations. The experiment being held 3 month ago, the data is still under investigation. We present here the first results extracted.

1. Experimental set-up and raw data

During the experiment, nano-scanning XRD and XRF were simultaneously measured, with the aim of mapping both structural and chemical information on our samples. In terms of chemical information, we particularly focus on halide distribution. The experiment was conducted at an energy of 15.2 keV. A beam of around 70 nm in size was used and the flux was estimated at 4.5 10^{10} ph/s. The raw data for XRD, measured with the Eiger 4M detector and XRF, measured with the Vortex-EM detector are shown in Figure 1. The grain size was measured by SEM to a few hundreds of nanometers, the focused nano-beam allowed to image individual grains, as shown by the sarcity of the spots on the Eiger image.

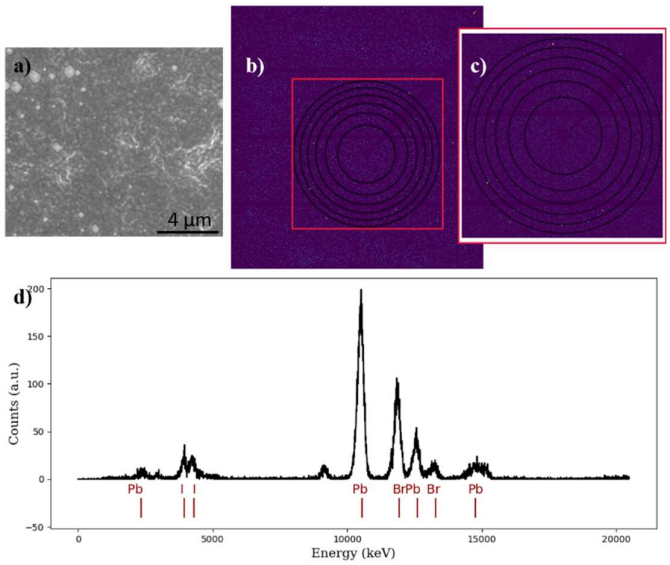

Figure 1 a) SEM image of a typical sample, showing a few 100nm in grain size. b) Example of an Eiger image measured on an HHP sample. The black circles point to the position of the expected perovskite Debye Scherrer rings. c) close up on the Eiger image, allowing the shwo the scarcity of the diffraction spots observed in one measurment point. d) Example of XRF spectra measured, with the attribution of the different peaks to the chemical elements giving rise to it.

2. On the beam induced damage of HHP

Extensive efforts have been dedicated during the experiment to investigate the beam induced degradation of HHP. First of all, setting the energy to 15.2 keV in comparison to the 13 keV used for preliminary tests not only allowed for the measurement of the fluorescence of the Br but also was observed to decrease the beam induced damage. Moreover, various measurement conditions were tested to optimize the measurement methodology in order to minimize beam damage and allow for the obtention of reliable data. Figure 2 shows the effect of the repetition of mapping, with two different steps keeping constant the counting time.

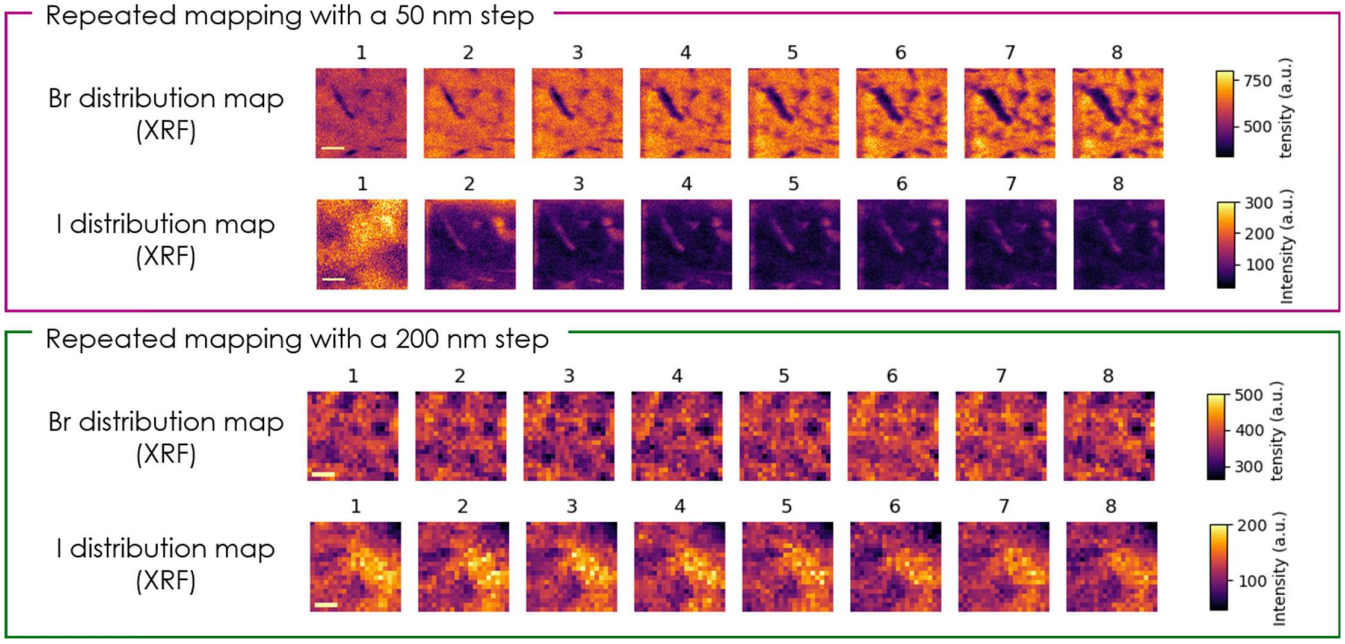

Figure 2 Evolution of the halide distribution while raster scans are repeated on the same region, for two different steps keeping constant the counting time. For each group of images, the same color scale is used to better visualize the evolution of the distribution over the repetitions.

The first parameter investigated was the nature of the scan. On ID13, 2 different mapping modes are available: meshes and raster scans. During the former, the shutter is closed between each measurement point. During the

latter, the shutter remains open as a line of the map is measured, it is then closed while the translation motors move the sample to the starting point of the next line: once there, the shutter is opened again for the measurement of this line. No real difference between these two types of measurements was observed, and since the raster scans are a lot faster than the meshes, we opted for raster scanning the sample.
The more stricking influence found was on the step size taken between each measurement point of a map. Three different step sizes were tested: 50 nm, 100 nm and 200nm. The evolution of the distribution of both the I and the Br in function of the repeated scans is showed in figure Figure 2. For sake of reliability of the measured data, 200 nm step has to be preferred.

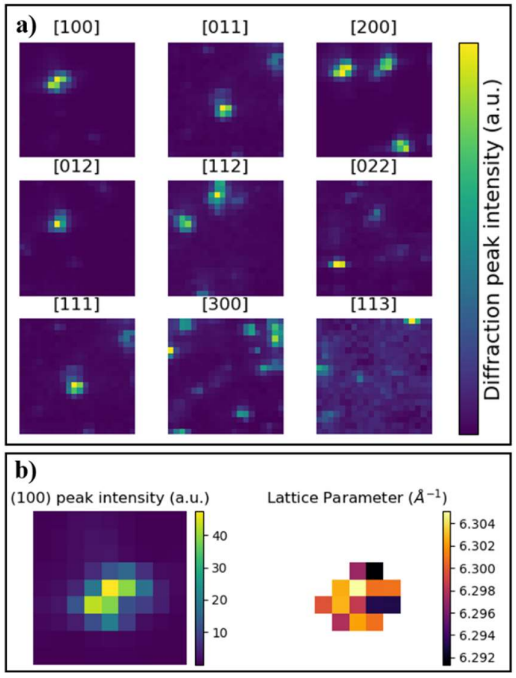

Figure 3 a) Illustration of the various grain orientation in a mapped region (4x4 µm²). b) Zoom on the region displaying a grain oriented along the perovskite [100] direction. The lattice parameter is calculated for each measurement point taken inside the grain, showing the lattice parameter distribution inside the grain.

3. Grain orientation and lattice parameter

As explained in the first paragraph of this report, few diffraction spots were observed on each measurement point. This allows to extract the orientation of individual grains in the mapped region. An example is shown in Figure 3.a). The maps represented in this figure were measured on a HHP layer deposited on a flat Si substrate.
It shows that for most of the grains imaged here, multiple measurement points are taken, allowing eventually to map the inhomogeneities at the grain level. Further data processing is in progress.

For each grain, the lattice parameter can be calculated. An example is shown in Figure 3.b) where the grain oriented along the HHP [100] direction (shown in Figure 3.a) is studied. The lattice parameter is represented next to the peak intensity. The lattice parameter was calculated for measurement points showing at least 10 % of the maximum intensity measured on the (100) peak in this grain. The result shows a large inhomogeneity in lattice parameter inside an individual grain. However these are only preliminary results.

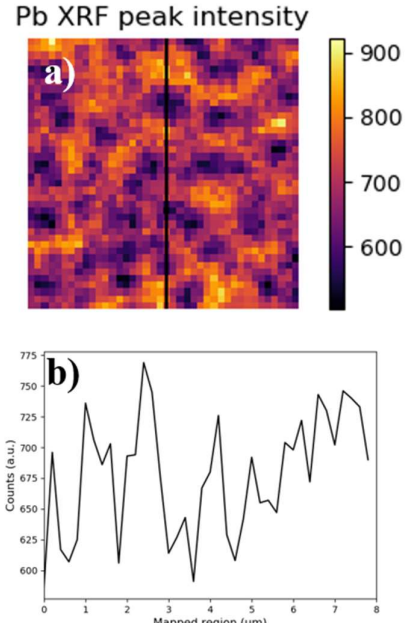

Figure 4 a) Localization of the pyramids with the intensity of the Pb XRF peak intensity. The mapped region is 8x8 µm². b) Cut in the map showing the variation in the Pb peak intensity.

4. Localizing the pyramids on textured Si substrates

As explained in the introduction of the report and in the proposal, one of our aims is to investigate HHP layers deposited on silicon wafers with micron scale pyramid-textured surface, and more precisely the influence of the pyramids on the perovskite microstructure. Figure 4 shows an example of Pb XRF maps which gives access to the localization of the pyramids; this was confirmed by comparing to transmission maps (transmission is minimum for maximum Pb XRF intensity) and to similar measurements performed on perovskite layers deposited on flat silicon, which do not show any micron scale intensity variation (not shown here). The XRF maps will then be compared to the lattice parameter and orientation maps.

5. Cross-section samples for depth resolved studies

Finally, the last part of this experiment was to measure cross-sections of full devices. The device architecture if shown in 5.a). Cross-section samples with a thickness of about 30 µm-thick were prepared by diamond saw and Focused Ion Beam (FIB) cutting (5.b). A photograph

of the set up is shown in 5.c). After identifying the regions of interest thanks to the on-axis microscope of ID13, the sample was carefully aligned with the X-ray beam based on the fluorescence and transmission intensities. Raster scans were performed. Figure 5.d-g) shows Br and I XRF maps as well as mapping of the intensity of the perovskite (100) and PbI2 (002) diffraction peaks obtained from the radial integration of the Eiger images. Unfortunately, the preparation process appeared to be quite destructive for the perovskite as evidenced in figure 5-f. However, these first cross-section investigations allowed us to develop methodologies for the sample alignment, as well as for XRF and XRD measurements. Our laboratory will soon be equipped with a femtosecond laser which has been shown to be a quite efficient cutting technique for HHP. We also hope to soon be able to carry out cross-section measurements in better conditions.

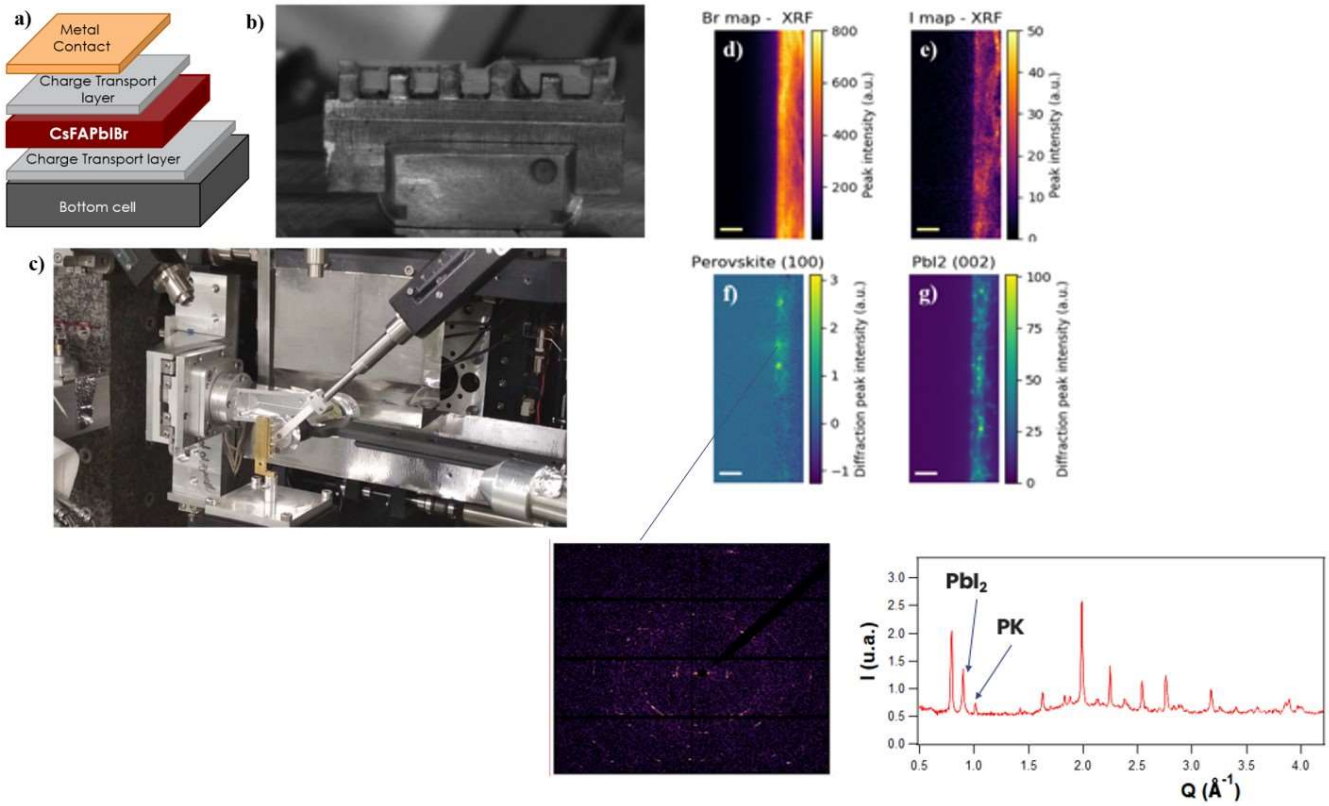

Figure 5