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| ESRF | **Experiment title:**<br>Crystallization dynamics of hybrid perovskites studied by in situ X-ray microscopy | **Experiment number**:<br>CH-4974 |
| **Beamline**:<br>ID01 | **Date of experiment**:<br>from: 19/04/2017 to: 23/04/2017 | **Date of report**:<br>25/09/2017 |
| **Shifts:**<br>15 | **Local contact(s)**:<br>Tao Zhou | *Received at ESRF:* |


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## Report:

In this experiment, we aimed to study the crystallization dynamics of hybrid perovskites using *in situ* FFDXM. For that, we spin-coated the perovskite precursor on appropriate substrates in the chemical lab at the ESRF before tranferring it under $N_2$ to the furnace on the ID01 beamline. We measured a total of 14 samples in the 15 shifts that were given. On the first few samples we discovered that the hybrid crystallites formed during *in situ* annealing were too small to survive the beam damage during image acquisition, even under constant $N_2$ flux. The half-life time (Fig. 1) of these crystallites was around 500 sec under the beam regardless of the nature of the exposure (500 times 1 sec or 50 times 10 sec).

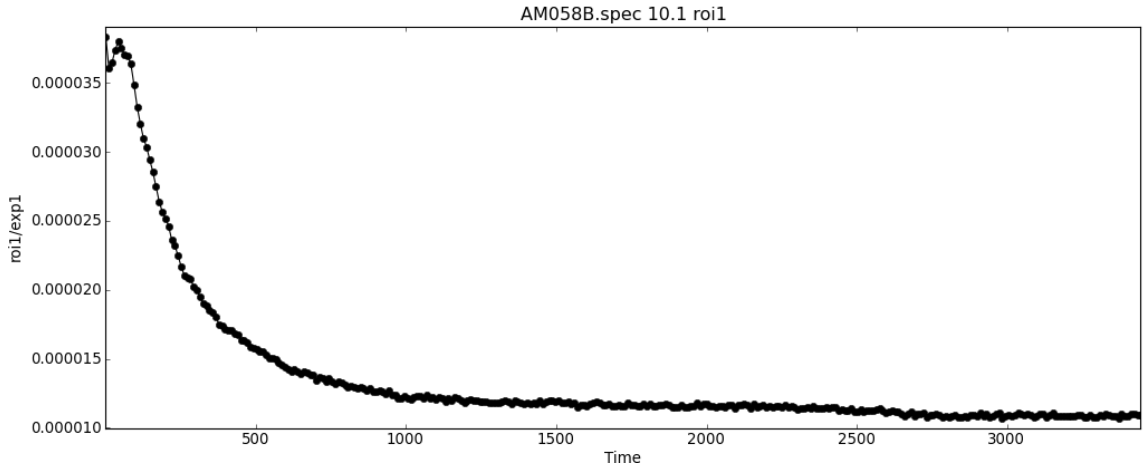


*Figure 1 : Timescan in diffraction mode of the MAPI signal showing the crystallites being destroyed under the beam.*

To tackle this, we split the remainder of the beam time into two parts. The first part involves the statistical mapping of the spatial distribution and spatial correlation of MAPI, MAPbCl and $PbI_2$ on samples deposited *ex situ* on FTO covered glass substrates containing a layer of poly-crystalline (pc) $TiO_2$ (analysis still in

progress). The use of this type of substrates is interesting because it can potentially be applied in the low cost production of perovskite solar cells, despite the small size of the perovskite crystallites obtained. The second part was devoted to the *in situ* study of the hybrid perovskite crystallization on single-crystalline (sc) $TiO_2$ substrates (analysis completed). The use of sc-$TiO_2$ substrates allows much larger crystallites to be obtained, although the cost of the substrate is also significantly higher. The large crystallites can sustain more than 20 min of constant beam exposure without deteriorating. *Ex situ* mapping was also performed to study the correlation and transformation between the (004) oriented and (220) oriented MAPI obtained on sc-$TiO_2$ substrates.

Below is shown a short demonstration of the data analysis:

For *in situ* crystallization, the sample was heated to 115°C. Stationary scans were performed on different areas of the sample to 1) acquire more statistical information on the crystallization dynamics on the entire sample surface and to 2) mitigate the possible beam damage on smaller crystallites. The result (after noise substraction) on one area is shown in fig. 2.

We have collected data at different stages (time) of crystallization on 31 areas covering a total surface of 0.3 $mm^2$. The majority of the crystallization was achieved within 5 min after heating to 115°C. Earlier formation does not necessarily lead to larger crystallites. A thicker precursor layer (near the edge of the sample) seems to result in the formation of more and larger crystallites. Only small crystallites were formed between 5 min to 10 min after heating to 115°C. These results are currently being processed for the modelling of the nucleation process.

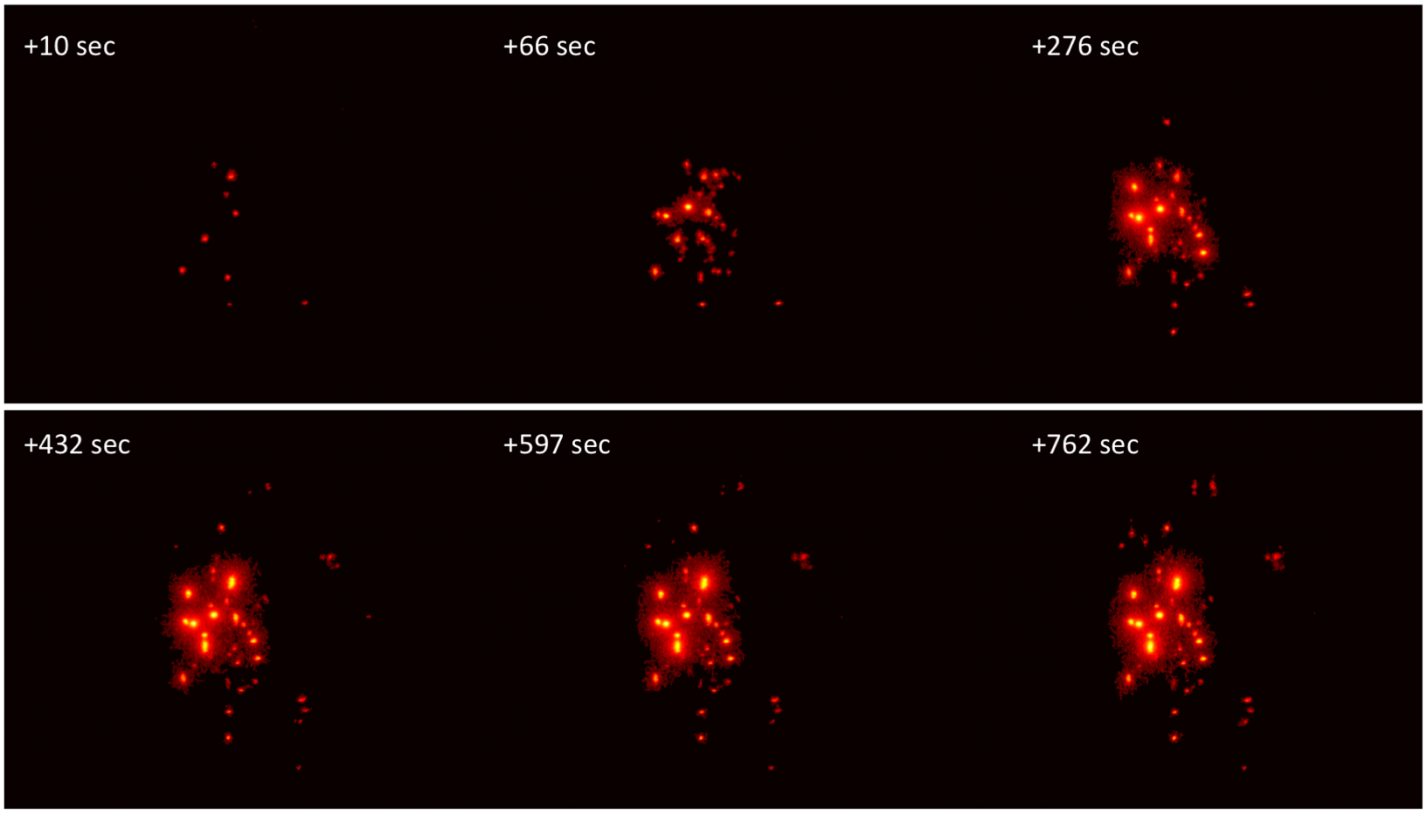


*Figure 2 : FFDXM images during in situ crystallization on one area of the sample.*

For *ex situ* (rocking scan) mapping of the preferential oriented crystallites, we use a peak search algorithm (clustering algorithm to be tested in the future) to identify the position and size of crystallites of different orientations (i.e. mosaicity). The crystallites are shown in their contours, with different color corresponding to different orientations. The idea is to understand if there is a spatial correlation between preferentially oriented crystallites and those that are not. An example is shown in Fig. 3 left, only the large crystallites are shown here for clarity. Some crystallites were overlapping as they were formed on top of each other. On Fig. 3 right the complete map of the same area is shown, including crystallites as small as 500 nm.

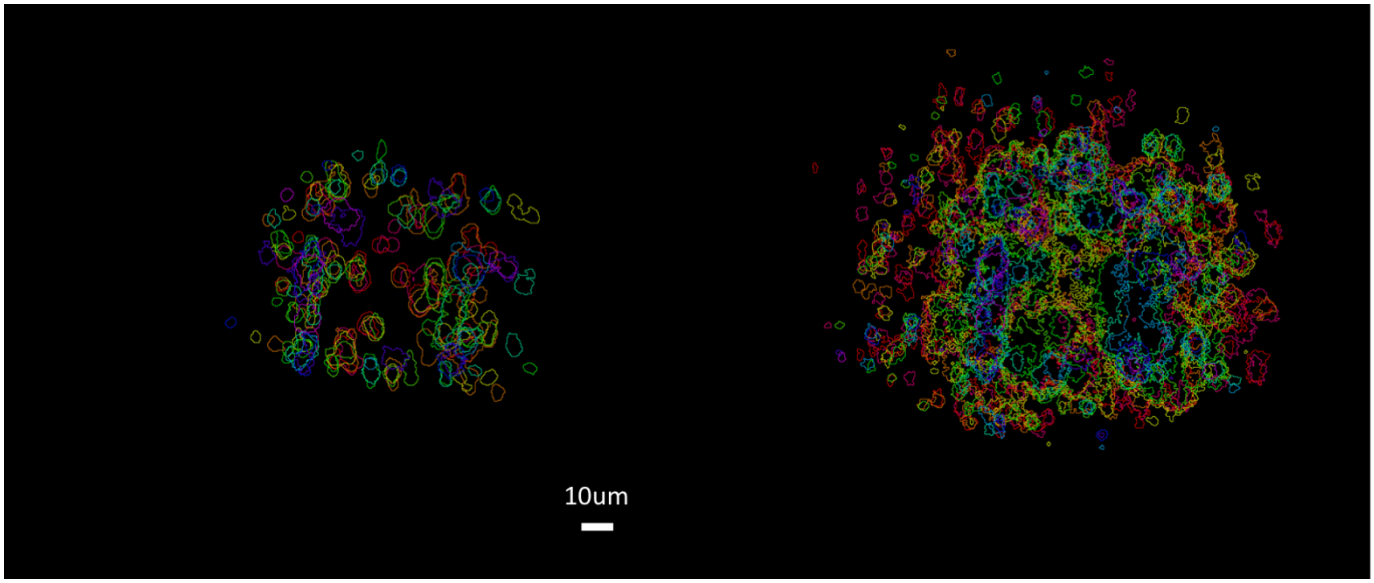


*Figure 3 : Mosaicity map of the crystallites, (left) only large ones are shown for clarity, (right) the complete map*

For *ex situ* (radial scan) mapping of the correlation between (220) and (004) oriented crystallites we use once again fake color contour to indicate the orientation (structure) of the crystallites. The larger crystallites are often a mixture of (220) and (004) orientations, while pure (004) oriented (red, orange contour) and pure (220) oriented (blue, purple contour) crystallites can also be found. On Fig. 4 right the same area after beam exposure is shown. Concerning the two crystallite populations, up to now they have been considered as corresponding to two different structural orientations. But the ID01 measurements seems to indicate that the (004) oriented crystallites were transformed into (220) oriented ones, hinting that the different "orientations" are in fact different crystal structures that can be transformed to each other by either strain or stoichiometry modifications.

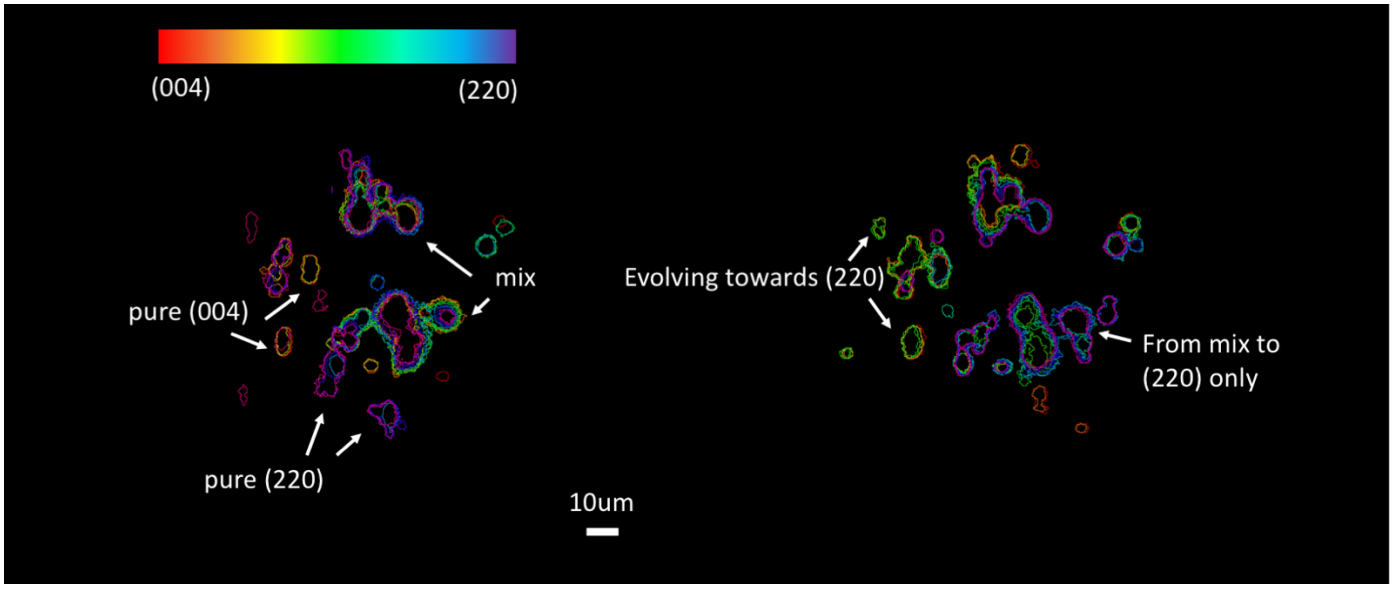


*Figure 4 : Structure map of the crystallites on the same area to see the beam effect.*

In summary, we were able to overcome many initial experimental setbacks mainly related to beam induced damage and mechanical stability of the sample mounted on the heating stage. After resolving these problems we have successfully performed *in situ* measurements during the crystallization process of hybrid perovskites (MAPI, MAPICl) as well as *ex situ* mosaicity and structure mapping of the samples statistically on a large surface area. The results obtained in this experiment are both scientifically of high interest and constitute a proof of concept for the applicability of FFDXM for the in-depth analysis of this emerging class of optoelectronic materials constituted by hybrid perovskites.