ESRF	**Experiment title:** Simultaneous elemental, XBIC and XEOL mapping for unravelling anisotropic charge collection in 2D layered perovskite X-ray detectors	**Experiment number**: MA-5519
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Report:

During this experiment we successfully performed two sets of measurements on 2D hybrid organic/inorganic halide perovskites $(PEA)_2PbBr_4$ (PEA = $C_6H_5C_2H_4NH_3$+) film and crystals. We used a photon energy of 29.5 keV because some restrictions needed to be imposed to the aperture of the undulator gap of id16B that prevent reaching the 17.5keV requested. The beam spot size was 50nm × 50nm. We acquired simultaneous X-ray Fluorescence (XRF) and X-ray Beam Induced Current (XBIC) maps. XRF was measured using two silicon drift detectors at about 15° from the plane perpendicular to the beam. The typical XRF spectrum from $(PEA)_2PbBr_4$ is reported in figure 1a, with highlighted the available Pb, Br and Au emission lines. The XBIC signal was measured with a modulation technique by chopping the beam at 1 kHz and using a lock-in amplifier in current mode; measurements were performed at 0V, 1V, 5V and 10V of external bias voltage.

First, we performed *in-plane* measurements on the perovskite films, where we probed the current flowing parallel to the 2D perovskite plane, by placing the sample perpendicular to the X-ray beam. The films were deposited by spin coating on interdigitated gold contacts with channel length 5µm and width 0.8mm. We measured 4 samples with films with different grain size obtained by solution engineering (i.e. different solvents and addition of antisolvent), from ~2µm to ~100µm. Performing maps with dimensions of 6 µm x 6 µm or 10µm x10 µm, we were able to map the charge collection. After some preliminary tests up to 10V, we chose 1V as optimized bias value to avoid degradation induced by the bias stress in combination with the high-flux beam. We were able to map Pb and Br to monitor the grain position, alongside with Au to locate the electrodes. Moreover, it was possible to observe a nontrivial contribution of the grain boundaries. Figure 1b shows an example of Pb XRF map in one sample with large grains, while Figure 1c shows the corresponding XBIC map. During the data analysis we will extract the stoichiometric ratio between Pb and Br, and the X-ray Charge Collection efficiency maps from XBIC ones.

Then, we performed *out-of-plane* measurements on $(PEA)_2PbBr_4$ single crystals. We irradiated the sample edge in the direction parallel to the crystallographic stacked planes to probe XRF and XBIC perpendicular to them. A dedicated sample holder was 3D printed for this experiment, to rotate and align the sample (Fig. 1e). Samples were grown from solution as thick crystals and exfoliated on kapton tape (crystal thickness 60 µm). Chromium planar contacts were evaporated onto the sample, then we cut the sample to obtain a sharp lateral face perpendicular to the crystal planes (Fig 1d).

A preliminary step was to find the best configuration for the sample alignment. Angular rotating scans were performed to optimise the alignment below 0.2 degrees from the direction perpendicular to the sample planes, then long linescans (up to 30um) were performed along the cut edge of the crystal. We observed an exponential decay of the current signal (in figure 1f one of the XBIC linescans), alongside a constant Pb XRF value (not

shown in the figure). We roughly quantified the charges drift length in the out-of-plane direction by fitting a decaying exponential to the XBIC profile $y=a+e^{-(x/b)+c}$, where b=(1.72±0.04)µm, as shown in Figure 1f. Considering the very interesting result of this first out-of-plane measurements, we plan, on the next proposal, to perform such characterization both on single crystals and on polycrystalline perovskite films with different crystal orientation and optimized top-bottom electrode geometry. We will take advantage of the above experience to speed up and improve the crucial alignment procedure. Moreover, the use of lower energy beam (17.5 keV) will improve the XBIC intensity (higher absorption of thin films). Finally, we plan to add XEOL to the XRF/XBIC acquisitions. We tried to perform XEOL measurements, but the geometry and size of the samples (not optimized for out-of-plane measurements) did not allow a good alignment with the XEOL setup mounted. We designed with the local contact a new sample geometry to solve this issue. Simultaneous acquisition of XBIC and XEOL signals would be important to identify radiative-loss centers, that are competitive with charge trasport porcess, fundamental to develop efficient detectors.

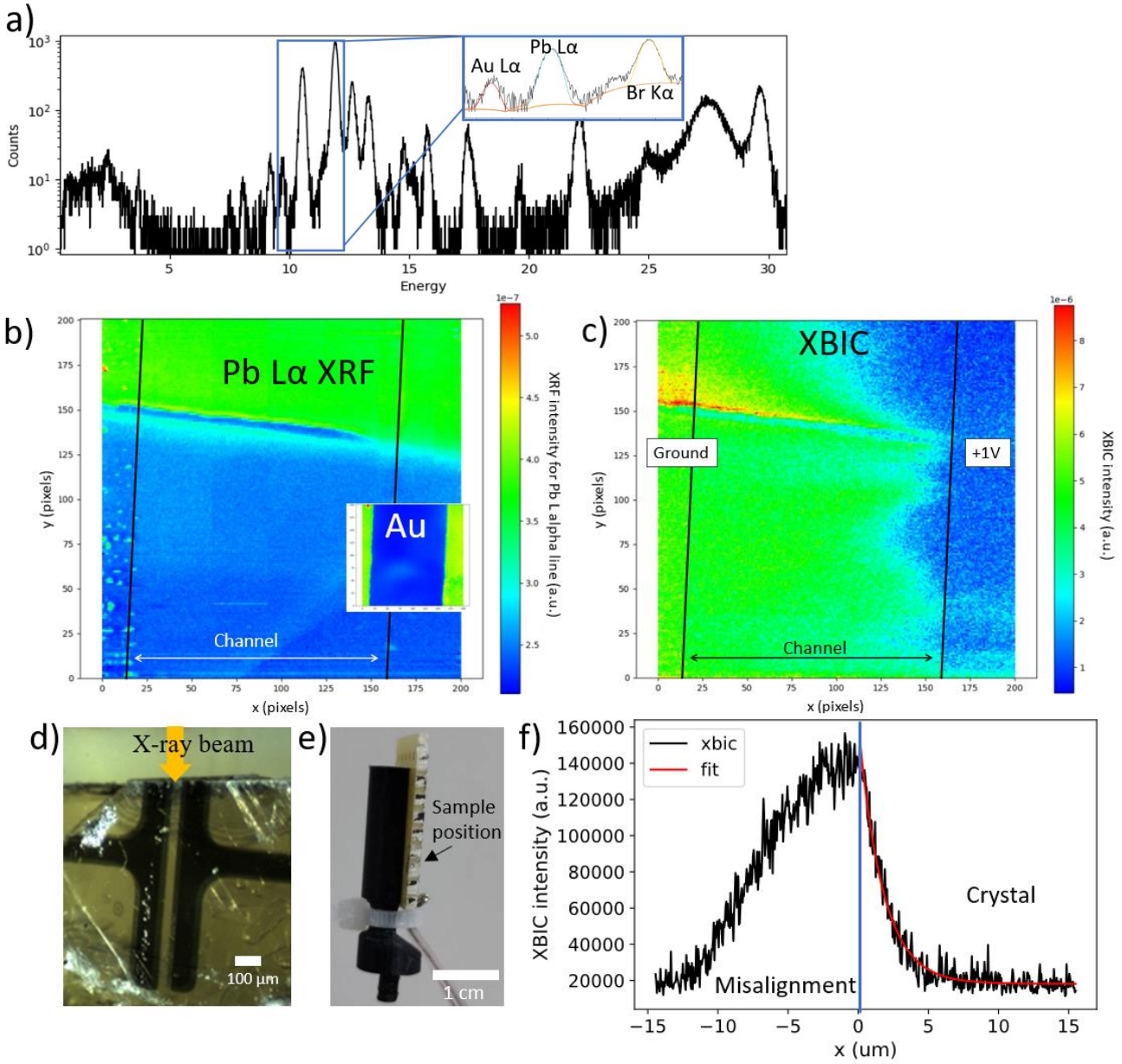

Figure 1 a) Example of a typical XRF spectrum, the insert shows the relevant peaks with fitting. **b)** 10x10 μm^2 map of the Pb XRF signal; the insert shows the map of the Au XRF signal in the same region and the electrodes edge is drawn with black lines. **c)** XBIC map acquired in the same region; the electrodes edge is drawn with black lines. **d)** Top view of the sample for the out-of-plane measurements. **e)** Rotatory sample holder used for the out-of-plane measurement with a sample mounted on it, the picture shows the lateral view, i.e. the X-ray beam arrives perpendicular to the page. **f**) Line profile of the XBIC intensity of the out of plane measurement. The blue vertical line indicates the position of the electrodes. The signal on the left is due to small misalignments of the sample, while the exponential decay on the right is given by the charge transport in the crystal, perpendicular to the crystallographic planes.