



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: Probing average and local structure in tin halide perovskites	Experiment number: CH-5879	
Beamline: ID11	Date of experiment: from: 04/05/2021 to: 07/05/2021	Date of report: 23/02/2022
Shifts: 6	Local contact(s): Eleanor Lawrence Bright Carlotta Giacobbe	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Rossella Chiara Mauro Coduri* Lorenzo Malavasi Marta Morana* Department of Chemistry, University of Pavia, Italy		

Report:

Scientific background

Metal halide perovskites (MHPs) are interesting materials for their manifold applications, from photovoltaics to photocatalysis. These compounds have general formula ABX_3 where A is a small organic cation, such as methylammonium= $CH_3NH_3^+$ (MA) and formamidinium= $HC(NH_2)^+_2$ (FA), or Cs; B is usually Pb, Sn or Ge, and X is a halide, like I, Br or Cl. Whereas the average structure and optical properties of MHP have been thoroughly characterized, their local structure has been only partially explored, despite its influence on the functional properties [1]. This is particularly true for tin halide perovskites [2], despite the huge interest in replacing highly toxic lead with other elements. During this experiment, we performed a systematic characterization of tin-based MHPs with compositions $ASnX_3$, where A= MA, FA, Cs and X= I, Br, at various temperatures by means of total scattering and X-ray pair distribution function (PDF) analysis.

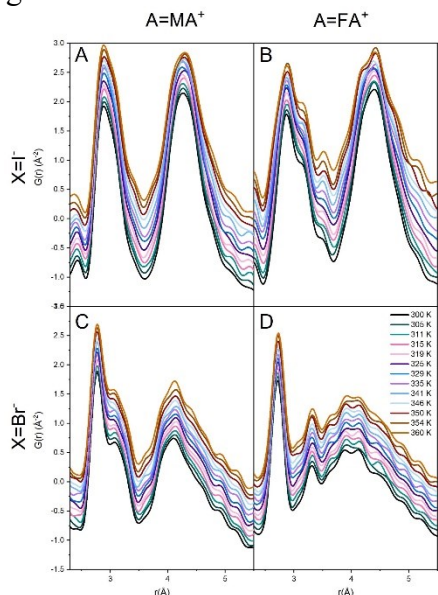
Experimental methods

X-ray PDF data were collected the material science ID11 beamline (exp number CH5879), at incident wavelength at incident wavelength 0.158135 \AA , using a Dectris Eiger2 X CdTe 4M detector placed 125 mm away from the sample. The distance was calibrated against a CeO_2 standard using the pyFAI package, which was used also to integrate the 2D images [3]. The powdered samples were packed into quartz capillaries (provided by Hilgenberg) with a 0.5 mm diameter and rotated during the data collection. A Cryostream was employed to collect low and high temperature data from 80 to 360 K.

Preliminary results

Rietveld refinement to assess the quality of the samples was performed using the software Topas [4] and the resulting crystals structure were consistent with previous literature reports for all samples. PDFs were obtained using PDFgetX3[5] with a Q_{max} of 23.5 \AA , and PDF modelling was carried out using PDFGui [6]. The instrumental parameters used in the PDF fit were $Q_{broad} = 0.03 \text{ \AA}$ and $Q_{damp} = 0.025 \text{ \AA}$, as determined from the CeO_2 standard.

In the entire temperature range the data suggest a trend of increasing distortion with increasing the size of the cation, from MA to FA, and the hardness of the anion. As a consequence, the bromide compositions show a larger distortion than the iodide counterparts. In the PDF data, the distortion appears as asymmetry and broadening in the peaks related to the Sn-X and X-X distances.



The observed effects agree with the hypothesis that these compounds are subject to a dynamic off-centering of the B cation that is thermally activated and thus enhanced by temperature. In order to understand the underlying distortion in the local structure of these materials different models were tested against the room temperature data (RT) to allow for octahedral tilting and octahedral distortion. For all the studied materials the local structure was found to be of lower symmetry with respect to the average one, which is cubic. The iodide compounds were well described by a rhombohedral model, whereas the bromide ones needed an orthorhombic distortion. A similar trend is also present at low temperature and a similar approach was applied to describe the local structure. Whilst the bromide compounds show large distortion and are described by an orthorhombic model, the iodide ones are consistent with a tetragonal model. The distortion is larger at low temperature and for the bromide compounds, whereas at room and higher temperature the local structure of tin iodide compounds seems to

be more affected by off-centering of B site cation due to the larger activity of the lone pair with respect to lead analogs[2].

The analysis of the data from the Cs-containing samples is in progress.

References

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