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: Deciphering the Formation Mechanism of Multiply Twinned Nanostructures by X-ray Scattering**	**Experiment number**: CH-6827
Beamline: ID02	**Date of experiment**: from: 01.09.23 to: 04.09.23	**Date of report**: 07.12.23
Shifts: 9	**Local contact(s)**: CHEVREMONT William	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report: Ligand-capped colloidal nanocrystals (NCs) derived from lead halide perovskites (LHP), particularly cesium lead halide (CsPbX3; X = Cl, Br, I), represent cutting-edge visible-light-emissive semiconductor NCs. These NCs, typically synthesized via rapid ionic coprecipitation, display remarkable traits such as nearly perfect photoluminescence efficiency and robustness against defects, even without surface passivation. They serve as promising single-photon emitters and exhibit aggregated emissive states, attracting attention across diverse applications like light-emitting diodes, downconversion displays, scintillators, photodetectors, and security tags. Despite their swift integration into practical applications, the ongoing synthesis literature continues expanding with varied protocols differing in precursors, ligand chemistry, solvents, surface treatments, and post-synthesis steps. These synthesis endeavors primarily aim to address the challenges posed by the delicate nature of these ionic semiconductors.

Understanding the formation mechanism of colloidal LHP nanocrystals is crucial for designing new nanostructures, yet reliable data on the pathways from molecular precursors to these structures are scarce. Employing synchrotron-based time-resolved in situ small and wide-angle X-ray scattering, we monitored the process of $CsPbCl_3$, $CsPbBr_3$, $CsPbI_3$ quantum dot formation in solution via precursors heated in octadecene to a varialble target temperature depending on the halide stoitometry. This investigation provided a comprehensive visualization of the evolution from precursor self-assembly to quantum dot creation.

During the allocated beamtime, we tracked the in situ transitions from the colloidal suspension to the nanocrystals nucleation and growth using a combination of SAXS and WAXS. In a single experiment, approximately 50 µl of the colloidal precursor suspension was loaded in quartz capilaryand heated to desired anneling temperature.

The experimental parameters of the beamline were as follows. The energy of the incident X-ray beam was set to 12.23 keV and the beam size was 25 x 25 μm^2. The SAXS data were recorded by the Eiger2 4M detector at

the sample-to-detector distance of 1.52 m. Images were collected with exposure times of 0.2 - 0.5 seconds. For the chosen exposure times no beam damage of the sample was observed.

Monodisperse lead halide perovskite precursors were produced at the KU Leuven by a hot-injection method and stabilized by oleic acid / oleylamine ligands. We studied the effect of the NC chemical composition ($CsPbCl_3$, $CsPbBr_3$, CsPbI3), size, as well as shape (cubic or hexagonal particles) on their formation kinetics during the provided beamtime.

The representative SAXS data revealing a transition from the colloidal precursor suspension into the colloidal quantum dots - visible by the appearance of Bragg reflections - as a function of high-temperature annealing are shown in Figure 1. Starting from seed, the nucleation and growth of LHPs follow a different pathway depending upon the choce of halide ions, which are the subject of the ongoing analysis.

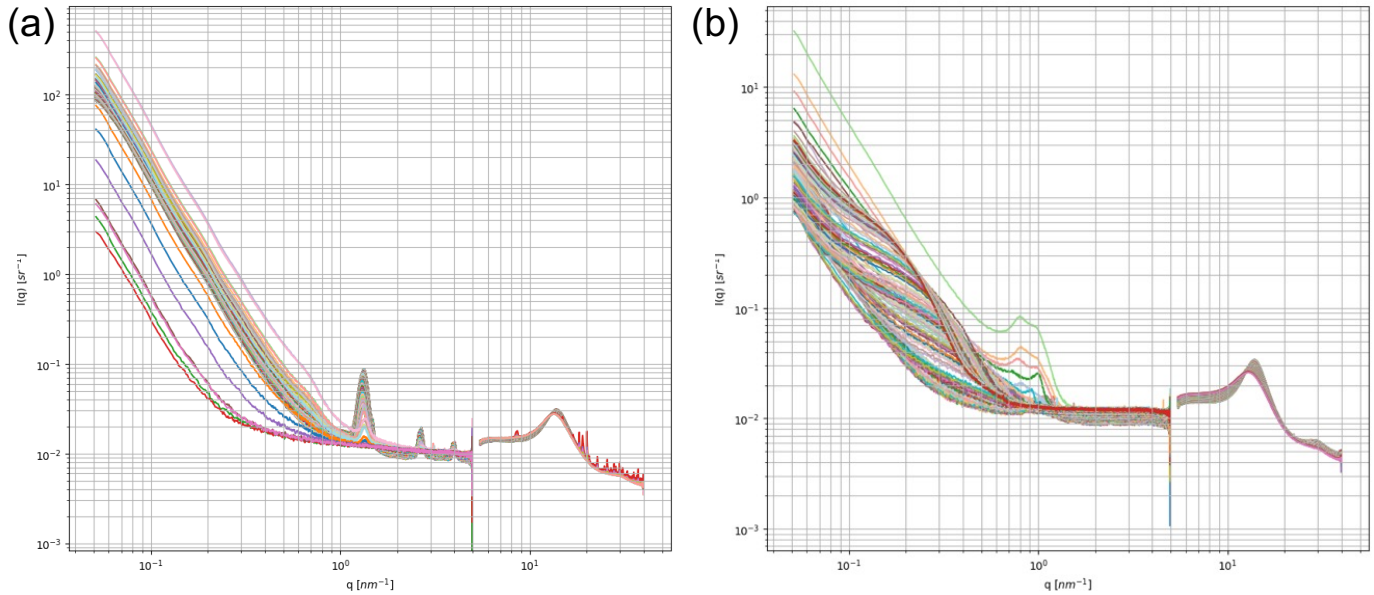

Figure 1. In-situ SAXS and WAXS of (a) $CsPbI_3$ and (b) $CsPbCl_3$ nanocrystals showing a different nulceation and growth evolution kinetics.