EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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:** Stabilization of low-density polymorphs by negative pressure	**Experiment number**: HC -4459
Beamline: BM26	**Date of experiment**: from: 25 January 2022 to: 28 January 2022	**Date of report**: 5/4/2023
Shifts: 6	**Local contact(s)**: Martin Rosethal, Daniel Hermida	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. Nico Dix, Dr. Martí Gich, Mr. Pierrick Merlin
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Daniel Hermida
ESRF

Report:

The combined SAXS-WAXS experiment allowed us to confirm the stabilization at room temperature of Rocksalt CsCl which was crystallized from the molten CsCl infiltrated within the SBA-15. In the experiment, we also investigated the possibility of stabilizing rocksalt CsBr and CsI within SBA-15 mesopores. The main findings reloated to WAXS and SAXS are reportedd below

Main Findings obtained from WAXS:

These temperature-dependent experiments yielded several unexpected results:

1) CsCl rocksalt was stabilized at room temperature, but two *Fm-3m* phases were present with significantly different lattice parameter (7.012 Å for smaller crystals (F1) formed within the channels *vs* the 6.982 Å of the larger crystals stabilized outside the channels (F2)) (see Fig. 1A).
2) Small nuclei of the rocksalt CsCl were already present above 320ºC, well below the 469ºC of the bulk transition. Since only a mix of CsCl+SBA-15 was investigated and not a capillary with only CsCl, it is not clear if such early nucleation is due to the presence of SBA-15 or common for CsCl (note that no reports exist on synchrotron XRD experiments on heating CsCl).
3) The infiltration of CsBr into SBA-1 did not occur (no diminution of the intensity of SAXS peaks observed, in contrast with the case of CsCl and CsBr) but in spite of that we observed the formation of Rocksalt CsBr at high temperature (between 600ºC and 530ºC, see Fig. 1B), not reported so far in heating-cooling experiments, but only in ultrathin epitaxial films[9] or in cluster beams in vacuum.[10] Here again, the lack of control experiment (heating a capillary with only CsBr) did not allow assessing the role of SBA-15 in the process.
4) The CsI infiltrated in SBA-15 did not crystallize in rocksalt on cooling. However, see Fig. 1C, the lattice parameter of the cubic primitive crystals formed within the pores (P1) is significantly larger than that of

the primitive crystals (P2) formed outside the silica channels (a_{F1}=4.698 Å, a_{F2}=4.664 Å), suggesting that the liquid is subjected to tensile strain upon cooling.

Besides confirming our previous findings, the aim of this proposal is getting further insights on the stabilization of rocksalt of Cs halides in nanoporous confinement, namely by addressing points 1)-4) discussed above.

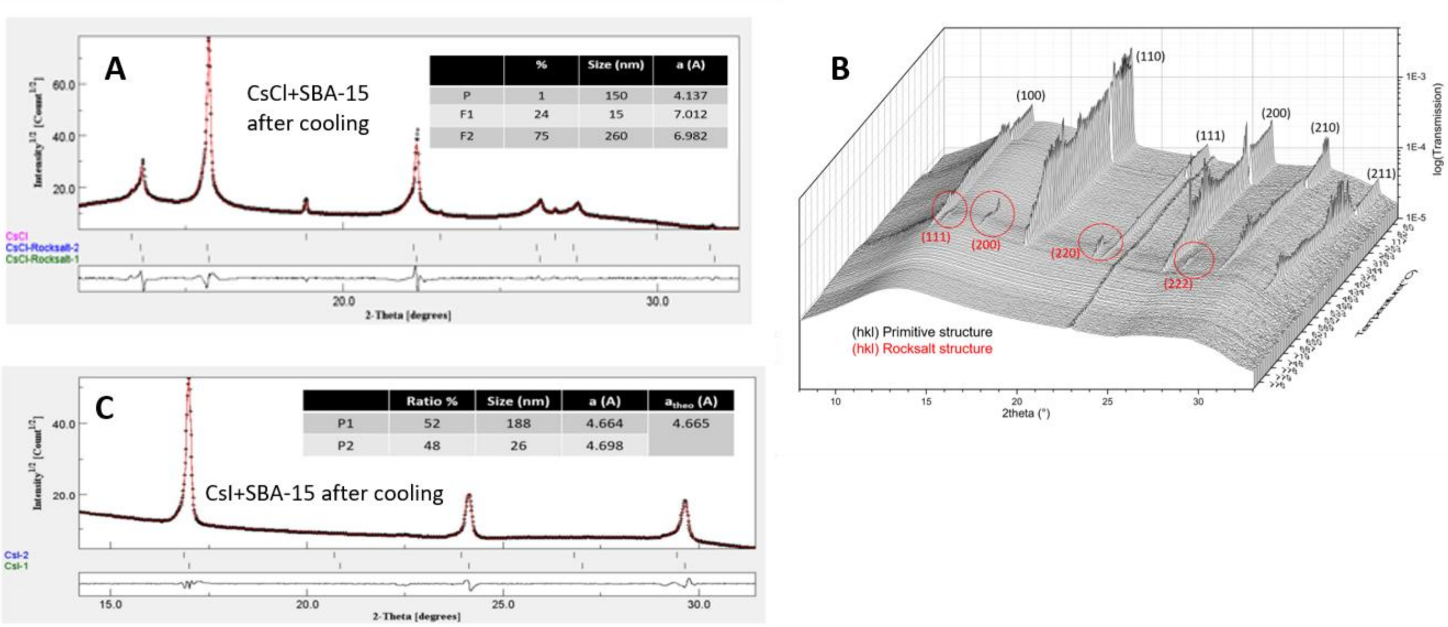

Figure 1. (**A, C**) Rietveld refinement of WAXS patterns acquired at BM26 ESRF (λ=0.9568 Å). (**B**) WAXS patterns of the cooling of CsBr showing the appearance of the Rocksalt phase (reflections indexed in red) at high temperatures (600ºC<*T*<530º).

An additional experiment to complete the WAXS results will take place in June 2023 at the MSPD beamline of ALBA synchrotron

Main Findings obtained from SAXS:

The temperature-dependent SAXS data is being analyzed by fitting experimental data using a home-made minimization procedure involving MINUIT [1] package program in collaboration with Alessandro Longo. Infinitely long cylinders are taken into account in the form factor P(q) and an hexagonal ordering is considered in the structure factor S(q) a Porod contribution has also been considered. Figure 2 presents the fits obtained for the sample before (A) and after (B) the heating experiment. The fits indicate that a fraction of the SBA-15 pores have been filled but that others have remained empty, while the hexagonal ordering is maintained. This confirms the findings obtained by TEM would indicate that the infiltration of molten CsCl does not destroy the ordering of mesopores.

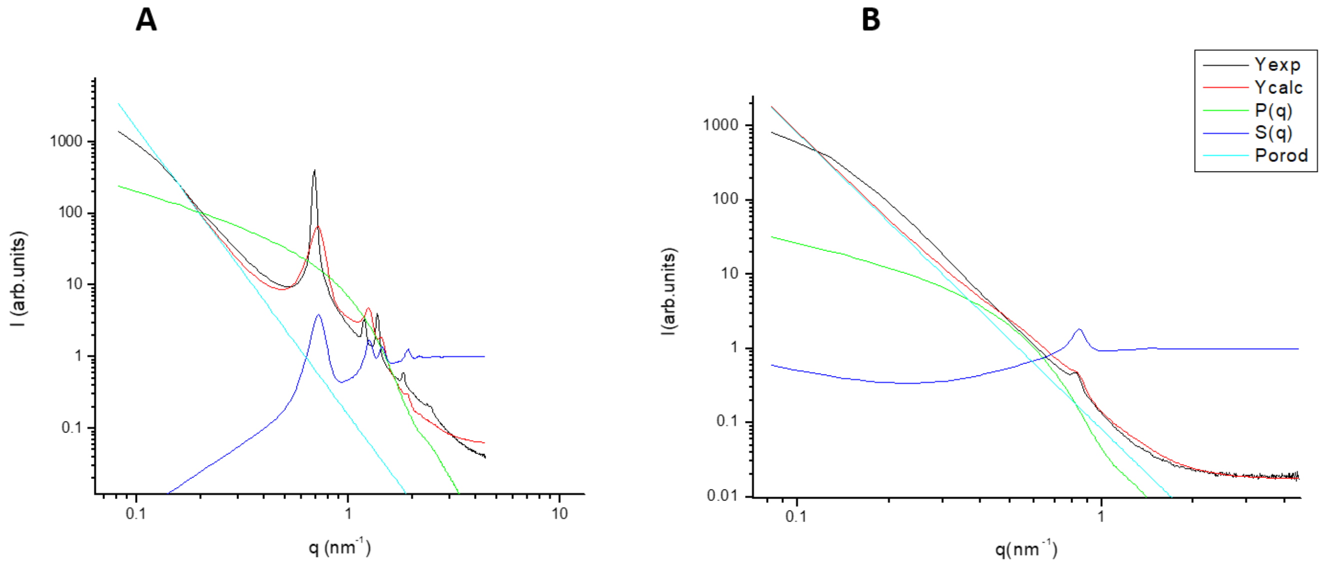

Figure 2. Preliminary analysis of SAXS patterns corresponding to the sample before (**A**) and after (**B**) the heating.

References

[1] MINUIT is a Python interface to the MINUIT2 C++ package (standard tool at CERN): https://indico.cern.ch/event/833895/contributions/3577808/attachments/1927550/3191336/iminuit_intro.html