

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://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: Study of liquid silicates during zeolite formation	Experiment number: A26-2-956
Beamline:	Date of experiment: 14/02/23 – 19/02/23	Date of report: 24/02/2023
Shifts:	Local contact(s): Dmitry Chernyshov	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Prof Christine EA Kirschhock (KU Leuven) Dr. Eric Breynaert (KU Leuven)* Dr Karel Asselman (KU Leuven)* Dries Vandenabeele (KU Leuven)		

Report:

Despite decades of intensive research, the molecular mechanism behind zeolite formation is not fully understood. This is especially troublesome given the societal impact of these materials. The main barrier impeding a better understanding of zeolite crystallization is their conventional synthesis method, which is based on the hydrothermal conversion of an aluminosilicate gel. Gels are inherently complex due to their multiphasic nature and complicate proper data collection and interpretation, as solid fractions involved in early stages of crystallization are difficult to distinguish from the bulk. As a consequence, in-situ crystallization studies on zeolites using X-rays are scarce, and usually require complex, dedicated sample environments with limited experimental and instrumental flexibility. [1,2]

Our syntheses start from hydrated silicate ionic liquids. These homogeneous, optically clear precursor mixtures consist initially only of soluble (alumino)silicate oligomers, readily crystallizing in 15+ zeolite topologies, depending on cation type, batch composition and temperature. [3,4]. HSILs have already proven to be a model system for characterization of the liquid-state speciation through NMR spectroscopy, as well as monitoring crystallization progress via conductometry [5]. In-situ X-ray scattering is required for the description of all stages during crystallization: from initial amorphous (alumino)silicate aggregation, nucleation, and crystal growth through coarsening and Ostwald ripening in the final stages. The crucial steps for ubiquitous phenomena such as zeolite phase changes with temperature, and the competition between different frameworks in early stages of crystallization typically occur on time scales that are hard to probe via ex-situ studies.

During experiment A26-2-956, the potential and versatility of the synthesis protocol for in-situ X-ray analysis was evaluated using a simple setup: a crystallization environment consisting of a sealed quartz capillary, rotated to prevent sedimentation, and heated in a cryostreamTM (Fig. 1). The crystallization of two zeolite topologies, GIS and ANA, was successfully monitored in situ, at crystallization temperatures between 90-200°C with excellent signal-to-noise and detection of minute crystal fractions (Fig. 2). The precursor compositions were 0.5 SiO₂: 0-0.025 Al(OH)₃:1 MOH: 4-9 H₂O (M = Na, K, Cs).

The precursor liquids do not display hints of long-range order prior to heating, despite their concentrated nature. Upon heating, however, a small angle contribution appears of which only the tail fell within the q-range of the measurement (Fig. 2). Onset of opacity for Cs-based mixtures (Fig. 3), or even formation of visible gel-

aggregates for Na-based mixtures, happens rapidly upon heating. These optical changes did not initially coincide with significant evolutions of the recorded scattering patterns or appearance of a diffraction pattern. Relevant processes during this ‘induction phase’ are therefore occurring at length scales not reached in the current experiment ($Q < 0.2 \text{ \AA}^{-1}$). An earlier study, probing solution conductivity in situ during crystallization in analogous mixtures [5], observed a conductivity increase during this induction phase which is indistinguishable from subsequent crystallization. This shows that, while (alumino)silicate condensation and densification processes are already occurring during the induction phase, the initially formed particulates or aggregates lack sufficient long-range order to diffract.

Figure 2 displays examples of collected data of zeolite crystallization. At a synthesis temperature of 120°C , synthesis performed at home demonstrated that Na-ANA is the stable end-member for the examined batch composition, but here a competing Na-GIS crystallized initially (Fig. 2). Arrows in figure 2 indicate the emerging Na-ANA reflections, which appear later, but prior to completion of Na-GIS crystallization. Further monitoring of the recrystallization was interrupted due to corrosion of the quartz capillary. In the analogous Cs-based mixture at 170°C , the stable end-member (Cs-ANA) is the first and only phase observed, and no initial metastable phases are formed at this synthesis temperature.

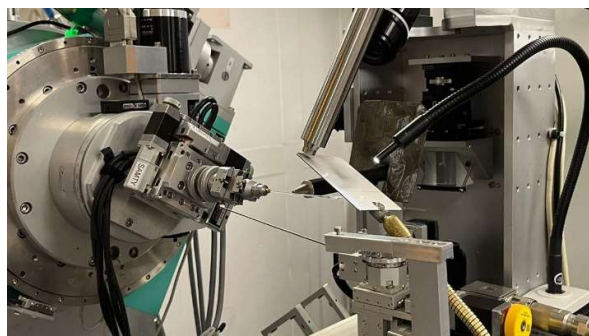


Figure 1: The sample environment for crystallization consists of a sealed quartz capillary, mounted on a regular goniometer head and heated with a cryostreamTM.

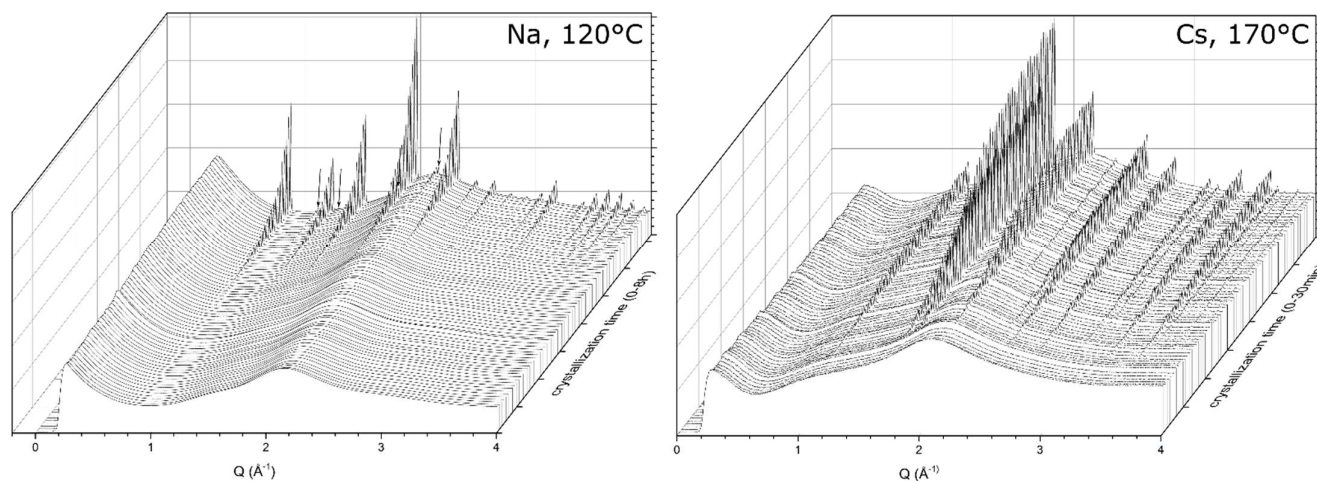


Figure 2: Crystallization of precursor mixtures with composition $0.5 \text{ SiO}_2 : 0.025 \text{ Al(OH)}_3 : 1 \text{ MOH} : 9 \text{ H}_2\text{O}$ ($M=\text{Na}, \text{Cs}$).

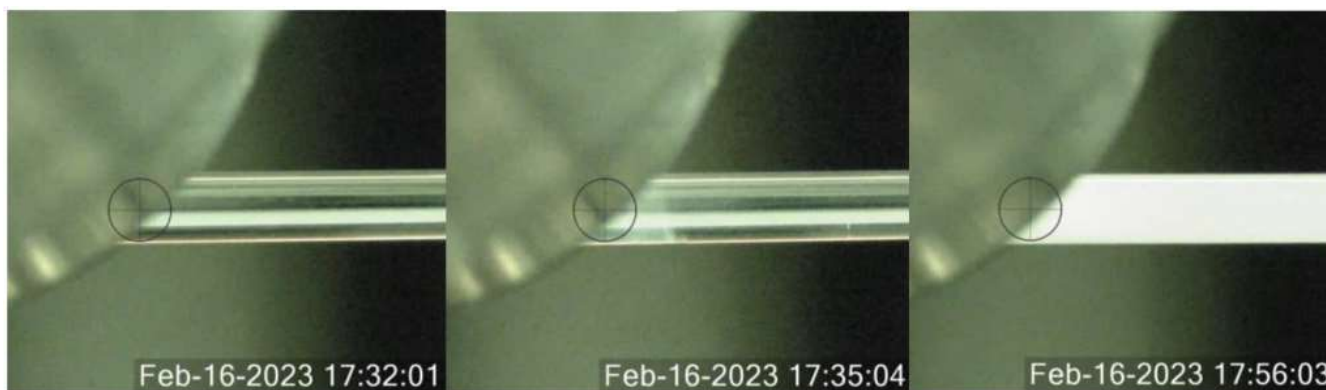


Figure 3: Optical changes in the synthesis solution ($0.5 \text{ SiO}_2 : 0.02 \text{ Al(OH)}_3 : 1 \text{ CsOH} : 9 \text{ H}_2\text{O}$) upon heating (170°C). Detection of a crystalline phase in the XRD pattern occurs is delayed after onset of opacity in the hot zone (center image). Initial condensation/aggregation of soluble aluminosilicate oligomers yield initially amorphous solids, which evolve into the crystalline end product (right image).

Detailed evaluation of the effect of cation type and batch composition on the relevant processes in the induction phase, growth kinetics and phase selection will benefit from acquisition of more data for a wider variety of batch composition and synthesis temperatures, and extension of the lower end q-range (combined SAXS/WAXS). During the current experiments, opportunities to improve the experimental protocol were identified allowing for a more stable setup with a wider reach of batch compositions and synthesis temperatures: (1) High alkalinities corrode the quartz capillary, causing them to fail before crystallization is complete. (2) Synthesis liquids are not homogeneously heated, resulting in temperature, and possibly chemical, gradients. (3) Employed temperatures sometimes exceed the boiling point of the liquids. These issues are readily resolved in a newly designed pressurized sapphire cell, as part of a new proposal linked to this experimental report.

[1] Fan, Wei, et al. "In situ small-angle and wide-angle X-ray scattering investigation on nucleation and crystal growth of nanosized zeolite A. " (2007), *Chemistry of Materials*, 19(8), 1906-1917.

[2] Minami, Ayano, et al. "Tracking Sub-Nano-Scale Structural Evolution in Zeolite Synthesis by in Situ High-Energy X-ray Total Scattering Measurement with Pair Distribution Function Analysis." (2022), *Journal of the American Chemical Society*, 144(51), 23313–23320

[3] Pellens, Nick, et al. "Nucleation of Porous Crystals from Ion-Paired Prenucleation Clusters." *Chemistry of Materials* 34.16 (2022): 7139-7149.

[4] Asselman, Karel, et al. "Ion-Pairs in Aluminosilicate-Alkali Synthesis Liquids Determine the Aluminum Content and Topology of Crystallizing Zeolites." *Chemistry of Materials* 34.16 (2022): 7150-7158.

[5] Pellens, Nick, et al. "A zeolite crystallisation model confirmed by in situ observation." *Faraday Discussions* 235 (2022): 162-182.