

# Study of the crystallization of new (vitro-)ceramics via a coupled in situ TEM/XRD approach at temperature

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## Summary

This PhD thesis focuses on the study of crystallization mechanisms in novel non-equilibrium materials obtained by crystallizing glass or undercooled melts at high temperatures. It will allow the selected candidate to acquire expertise in (vitro)ceramics and glass crystallization mechanisms, and will train them in the characterization of new crystalline materials with diverse properties (optical, ionic conductivity, magnetic, etc.). The approach will combine innovative synthesis methods (a new synthesis bench using aerodynamic levitation and laser heating), powder crystallography, high-resolution imaging by transmission electron microscopy (MACLE campus platform), and in-situ temperature experiments (laboratory XRD and TEM on the MACLE platform). The project benefits from established national (ANR CHATOFOR) and international collaborations for measuring specific physical properties, advanced diffraction, and particular synthesis techniques.

## Project Background

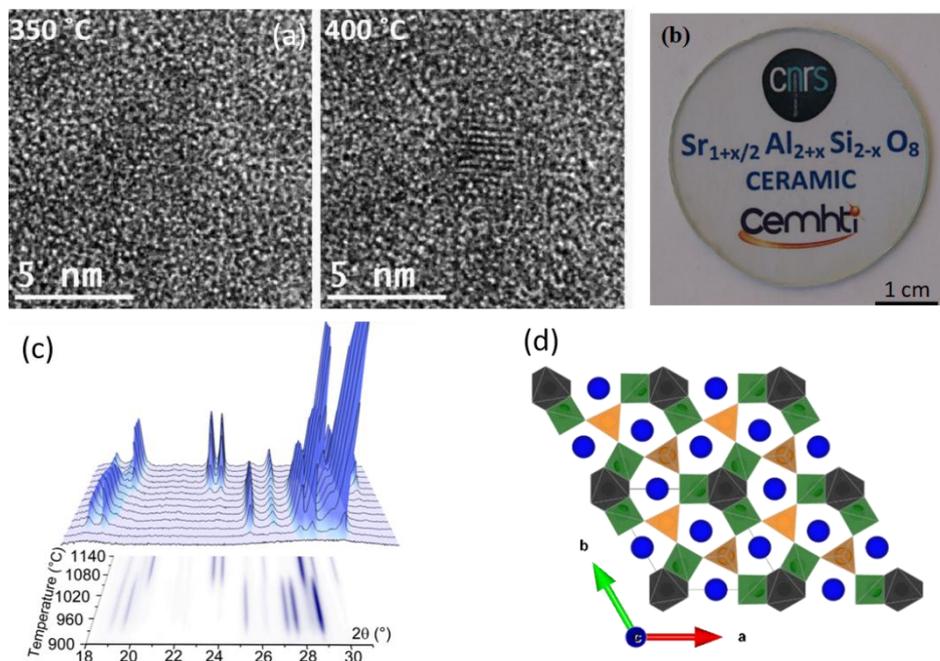
Solid-state synthesis by crystallization from glass or a molten liquid allows access to new functional inorganic materials that cannot be isolated by conventional methods (solid-state reaction). At the CEMHTI laboratory, precursor glasses and melts of various compositions can be synthesized using an original aerodynamic levitation device (ADL method) coupled with CO<sub>2</sub> laser heating. These precursors are then crystallized to create very dense oxide ceramics with new crystalline structures and/or microstructures that exhibit optical and/or transport properties (ionic conductivity) (for example, see <https://www.youtube.com/watch?v=IVpsMoQF0lg>).

This approach has recently been applied to the development of transparent polycrystalline ceramics, which constitute an emerging class of photonic materials competing with single-crystal technology in a wide range of optical applications such as laser materials, scintillators, optical lenses, and transparent armor. Understanding the mechanisms involved during synthesis is essential for controlling the final microstructures obtained. Recently, we have been exploring a high-temperature in situ approach in the TEM (up to 1200°C) to monitor and characterize the crystallization mechanisms and ordering phenomena in real time. Promising initial studies have focused on the crystallization of TiO<sub>2</sub> nanocrystals in a SiO<sub>2</sub> glass matrix (10.1021/acs.cgd.3c00300), as well as on the homogeneous crystallization of a YAG glass. The project aims to develop this approach by combining in situ temperature experiments in TEM and XRD to explore new mechanisms. Furthermore, the synthesis of new phases via glass crystallization lead to unreferenced structures whose structure must be determined, as is the case, for example, with high-entropy oxides. In this project, a multi-technique approach is envisioned, coupling X-ray diffraction and Rietveld refinement with high-resolution analytical transmission electron microscopy. HAADF-STEM imaging and atomic-scale STEM-EDS mapping offer the possibility of directly visualizing the cationic occupations of multi-element crystallographic sites and their disorder. The project also plans to develop a more quantitative approach through HAADF-STEM image simulation and by further refining the STEM-EDS mapping quantification methodology, building upon our recent work on 2D fitting as developed for the characterization of Zn/Ga/Ge langasites (10.1021/acs.inorgchem.2c01173). In addition, consideration is being given to exploring the 3D-ED (electron diffraction) approach, which would complement the information provided by X-ray diffraction but in a more local way.

## Objectives and realisation

The doctoral research will initially consist of an experimental and methodological phase aimed at synthesizing new glass compositions that, through congruent crystallization, yield interesting (vitro-)ceramics. To achieve this, the candidate will use an original synthesis method developed at the CEMHTI laboratory, enabling the vitrification of relatively refractory compositions: aerodynamic levitation combined with CO<sub>2</sub> laser heating (a new levitation setup is currently under development at the laboratory).

The second phase of the research will focus on the real-time characterization of different types of crystallization mechanisms involved in the synthesis of these new (vitro-)ceramics using a multi-technique approach combining DSC, X-ray diffraction, and in situ temperature-controlled transmission electron microscopy. This will require developing the methodology and data processing for high-temperature in situ experiments conducted in the TEM. This approach is entirely original in the field of obtaining (glass-)ceramics by crystallizing a parent glass. Furthermore, this synthesis route often leads to the production of new, unreferenced crystalline phases, for which it is necessary (i) to determine the structure by X-ray, neutron, and/or electron diffraction and (ii) to study the nature and morphology of the crystals, grain boundaries, or the presence of residual/secondary phases by electron microscopy (TEM and EBSD SEM). The CEMHTI laboratory possesses extensive expertise and a wide range of multiscale characterization techniques usable in situ at temperature (XRD, SEM, TEM, etc.) and numerous spectroscopic methods (NMR, Raman, EXAFS) to determine the fine structure of the synthesized ceramics. We also have access to synchrotron and neutron facilities to carry out these detailed structural characterizations.



**Figure.** (a) In situ TEM image showing crystallization in the SiO<sub>2</sub> - TiO<sub>2</sub> system ;(b) A fully-crystallised transparent ceramic disc of type  $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$ ; (c) In situ XRD acquisition showing the crystallization of a glass of composition 35 BaO - 65 Al<sub>2</sub>O<sub>3</sub>; (d) Crystalline lattice of a langasite  $Ca_3GaZn_{0.5}Ge_{4.5}O_{14}$ .

### **Facilities and Equipment**

The CEMHTI laboratory has excellent equipment for the synthesis, structural and physical characterization of ceramic materials, as well as access to the instruments of the MACLE-CVL platform. These include:

- Aerodynamic levitation coupled with CO<sub>2</sub> laser heating.
- Powder X-ray diffraction equipped for in situ measurements up to 2000 °C.
- Scanning electron microscopy (FEG-EMS coupled with EBSD).
- Transmission electron microscopy with ultimate resolution (in situ up to 1200 °C).
- High-temperature infrared and Raman spectroscopies.
- High-field, high-temperature solid-state NMR spectroscopy.
- High temperature AC impedance measurements.

### **External collaborations :**

The project will benefit from national and international collaborations with the following institutes:

- ISCR (Rennes), ANR CHATOFOR project for development of new chalcogenides for infrared applications
- Use of synchrotrons APS (Argonne - USA) and SOLEIL (Gif-sur-Yvette – France) ; French and European neutron sources ILL (Grenoble), ESS (Sweden) et ISIS (UK).
- ICMS (Seville, Spain): characterization of optical properties of new oxides.

### **The Candidate:**

Required skills:

Master's degree in chemistry, materials science or physics with a foundation in physics of matter or physical chemistry.

Essential knowledge of the structure and microstructure of crystalline and amorphous oxides, and experience in their development.

Knowledge of microscopy, XRD, and thermal analysis techniques.

Expected understanding of crystallization, diffusion, and phase transformation mechanisms, as well as (vitro-)ceramics in general.

Desired qualities:

Enthusiasm for experimentation

Rigorous and meticulous in experimental work and data processing

Ability to work independently

Analytical and synthesis skills, ability to present findings clearly, and to work effectively in a team

Fluency in written and spoken English

Project management and work planning skills

Written and oral communication skills in French

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