Observation of glass synthesis by in-situ high temperature ESEM

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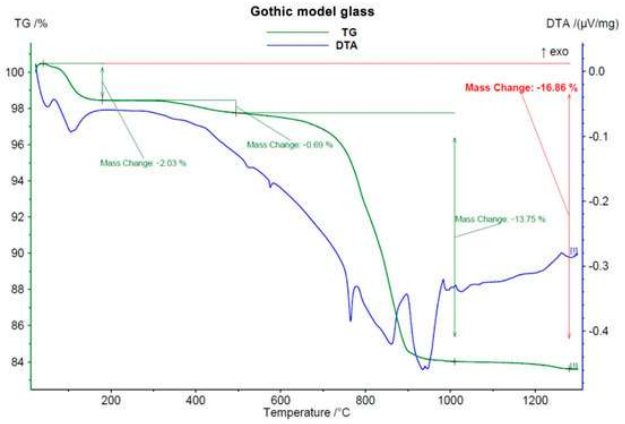
Introduction

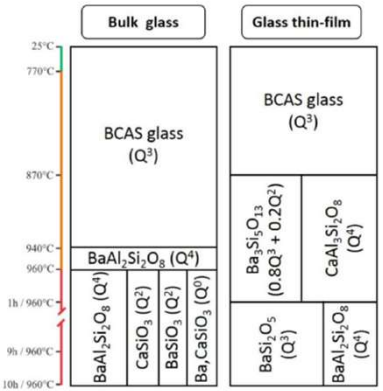
→ Necessity to understand the formation mechanisms of melts from primary compounds

→ A technique often used is to heat treat samples at different temperatures, soak them at RT and identify the phases formed by XRD, SEM, etc.

Increasing temperature →

→ Use of global techniques (such as DTA-TGA or HT-XRD)



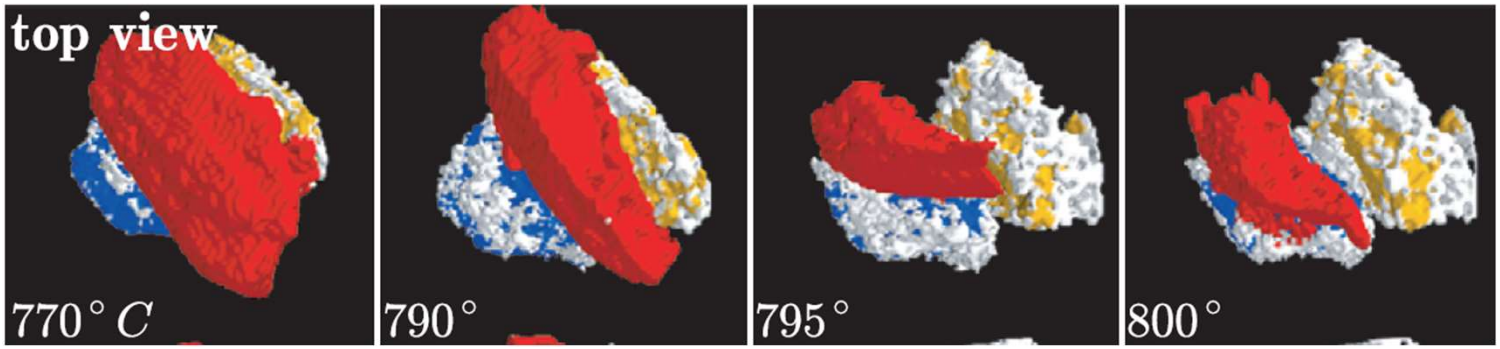


- Global information on the system
- Time consuming
- Possible biases that are linked to the sample quenching (crystallization of molten phases at high temperature, amorphous phases that are not identified by XRD…
- Choice of the quenching temperatures (some rapid transformations or those taking place in a narrow temperature range may not be identified).

Introduction

→ To overcome these limitations, it is interesting to implement in-situ characterization techniques, where the analysis is carried out during the heat treatment.

- Use of in-situ techniques (tomography → synchrotron, Gouillart 2012)
  - Local informations regarding chemical reactivity
  - But very time consuming and not easy to implement

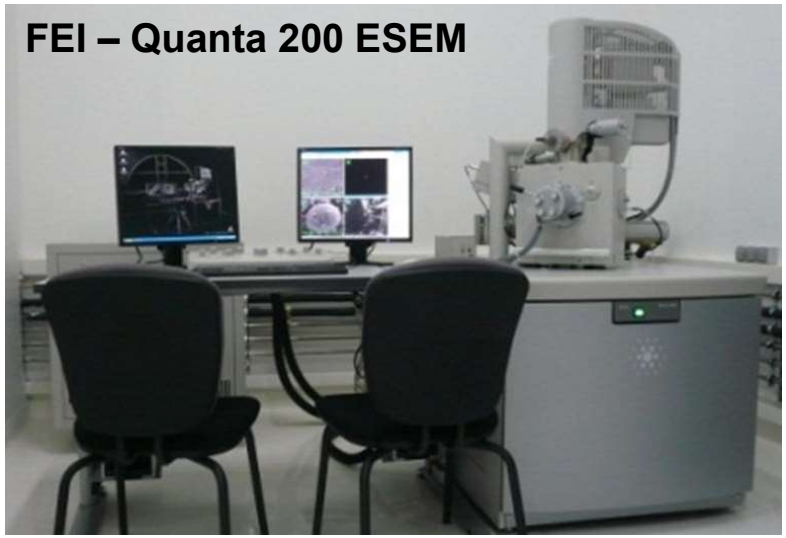


- Sodium carbonate grain
- Quartz grain 1
- Quartz grain 2
- Silicates (white)

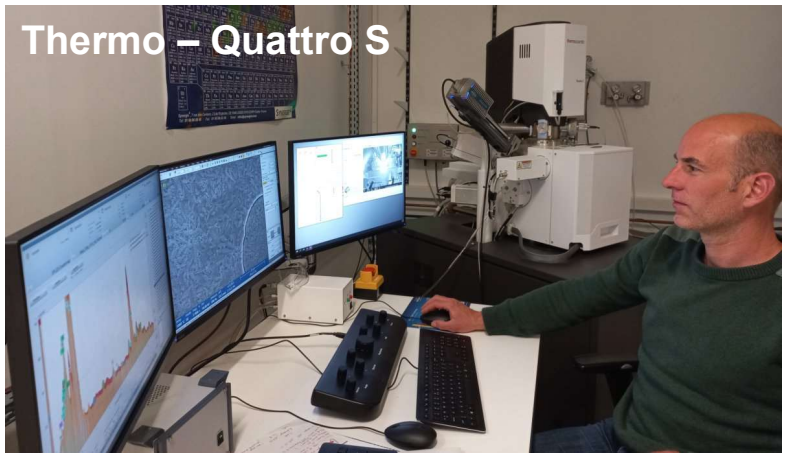
- In-situ High Temperature Environmental Scanning Electron Microscopy, HT-ESEM, possibly coupled with EDS analysis, is a particularly interesting technique for identifying the chemical reactions and various transformations taking place between the primary components and then between the different phases formed.

Gouillart et al., J. Am. Ceram. Soc., 95 [5] 1504–1507 (2012)

Materials and methods

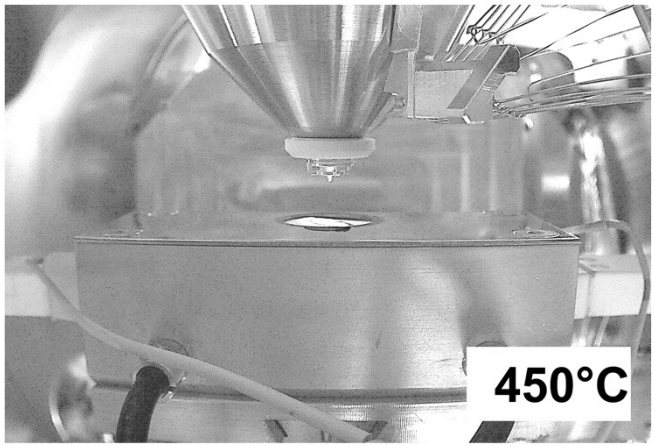


- Coupling the HT-ESEM mode with EDS
  - Detector
  - Methodologies for mapping and analyses
    - in-situ up to 500°C with an adequate furnace
    - After sample quenching at RT and adjustment of the analytical conditions
- Several issues / limits to (direct) X-ray collection
  - X-ray absorption in the gas
  - Sensitivity of the detector to light emission
  - Geometry of the furnace / EDS detector

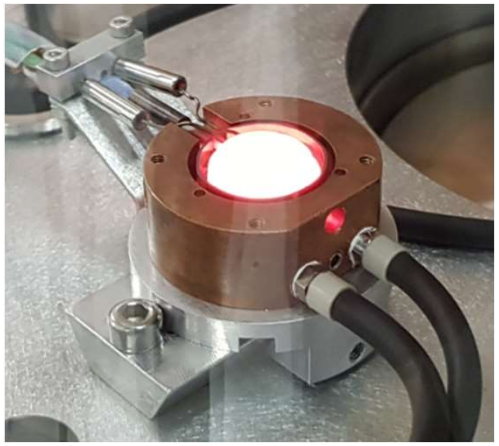


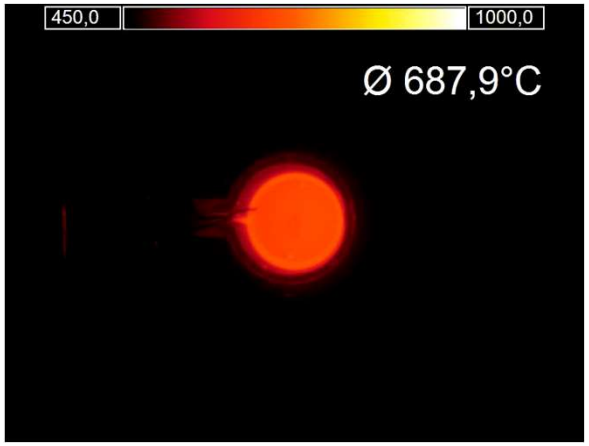
Materials and methods

- High temperature furnaces
  - FEI 1400

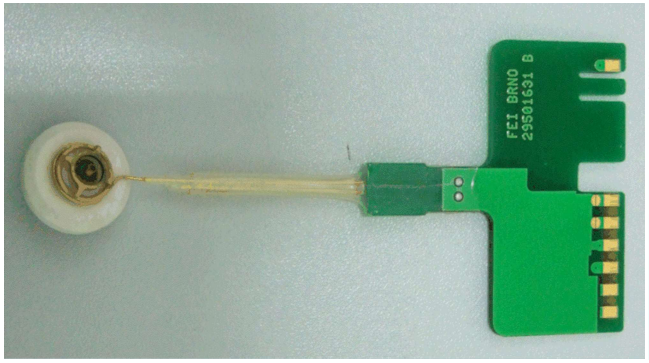


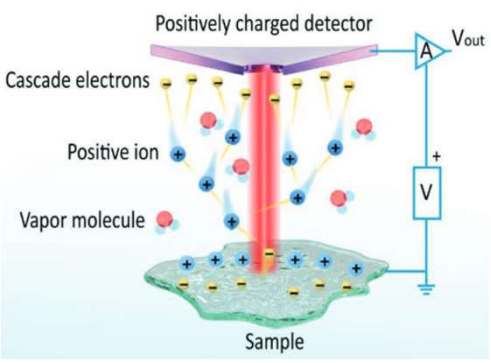
  - FurnaSEM 1300 (NewTEC Company – Nîmes)



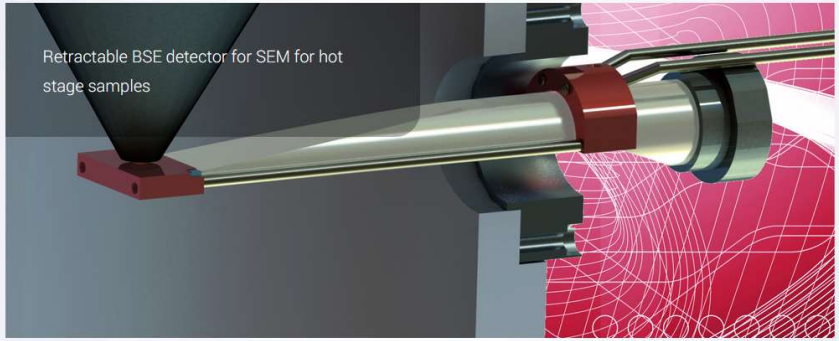


- Electron detectors (under gaseous environments)
  - SE → GSED up to 1350°C



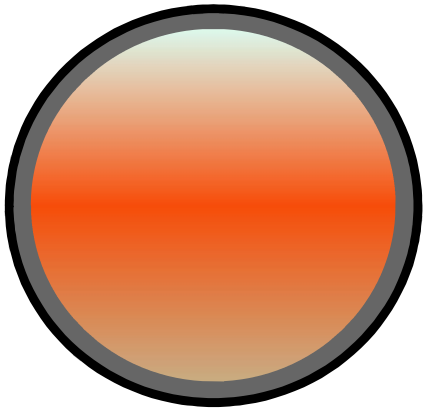


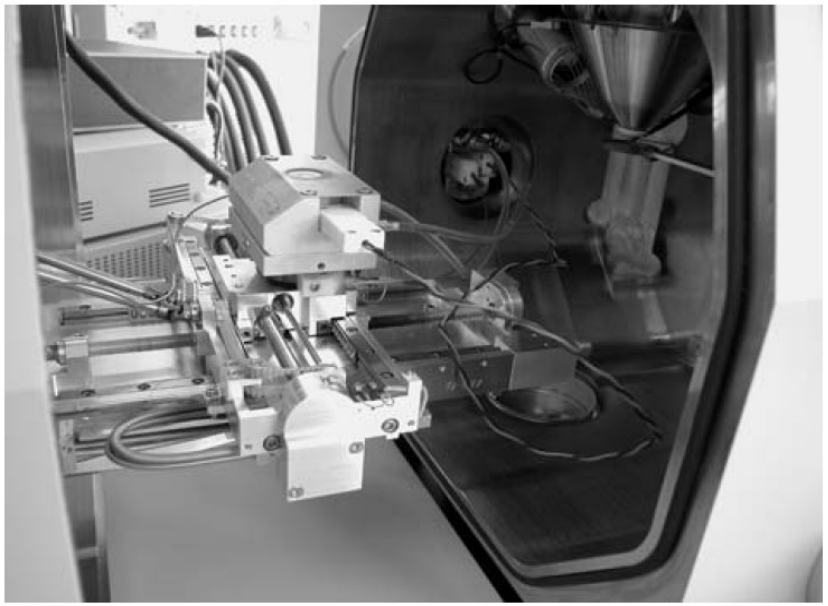
  - BSE → Karmen up to 1000°C (Crytur company)



Materials and methods

Platinum crucible





→ Heating rate = 0.5°C/min to 100°C/min
→ Temperature : 25°C – 1350°C
→ Gas pressure : 10 - 750 Pa (H_2O, air, O_2, N_2…)

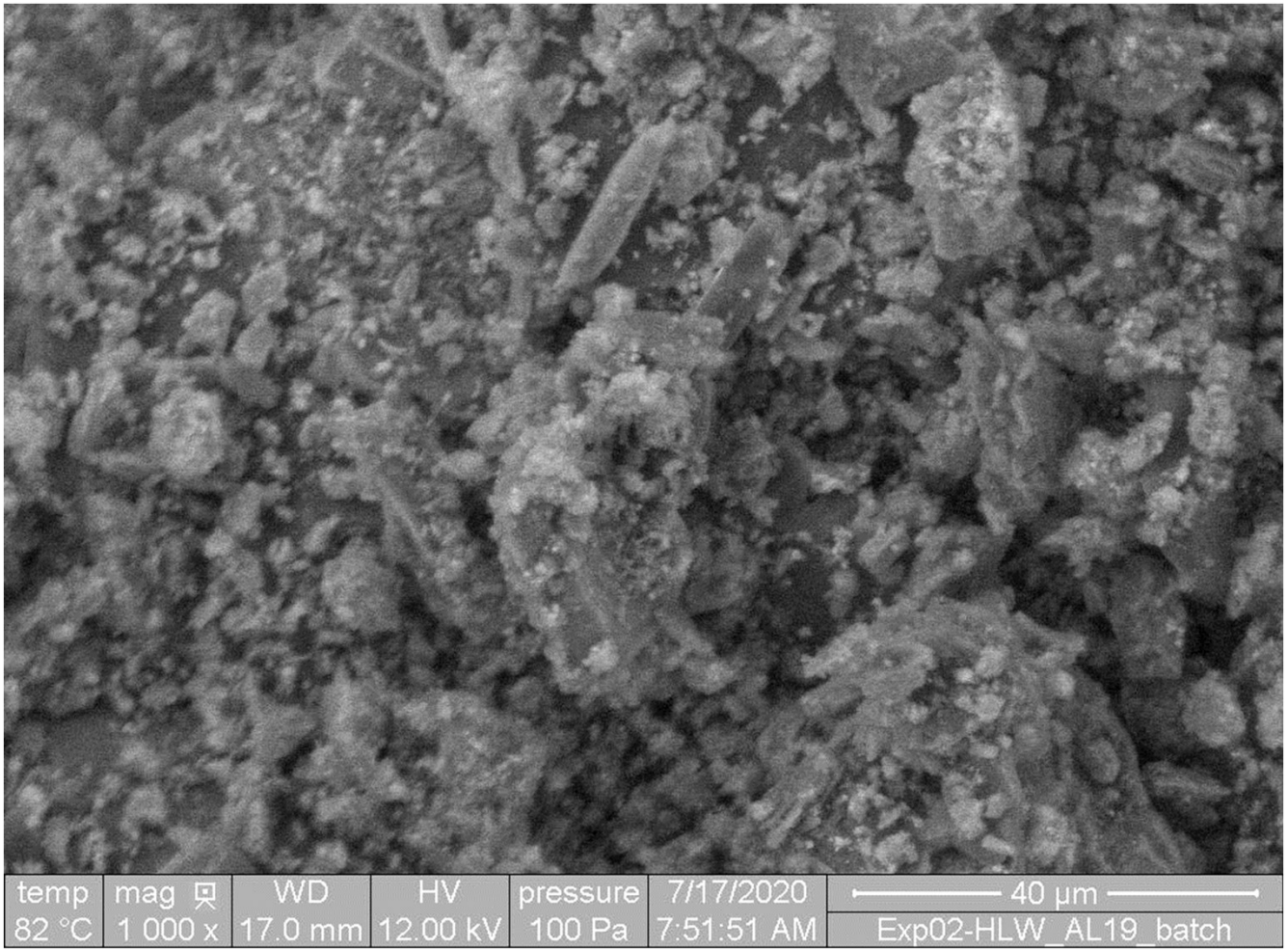
Strategy of the experiments

- To define the problem to be studied
  - **Glass elaboration / chemical reactivity**
- To determine the conditions for image recording
  - **25°C to 1000°C, 10°C/min, 120 Pa air**
- To record image series at different magnifications, under several conditions…
  - **X250 → X4000 + EDS analyses**
- Image processing (alignments, segmentation, measurements…)
  - **OK**
- To extract meaningful data
  - **To propose a chemical reactivity pathway**

Podor et al. Materials Characterization (2019) 151, 15-26.

Application to the study of glass elaboration

→ Elaboration of a glass melt from simple compounds : High-level waste (HLW) vitrification

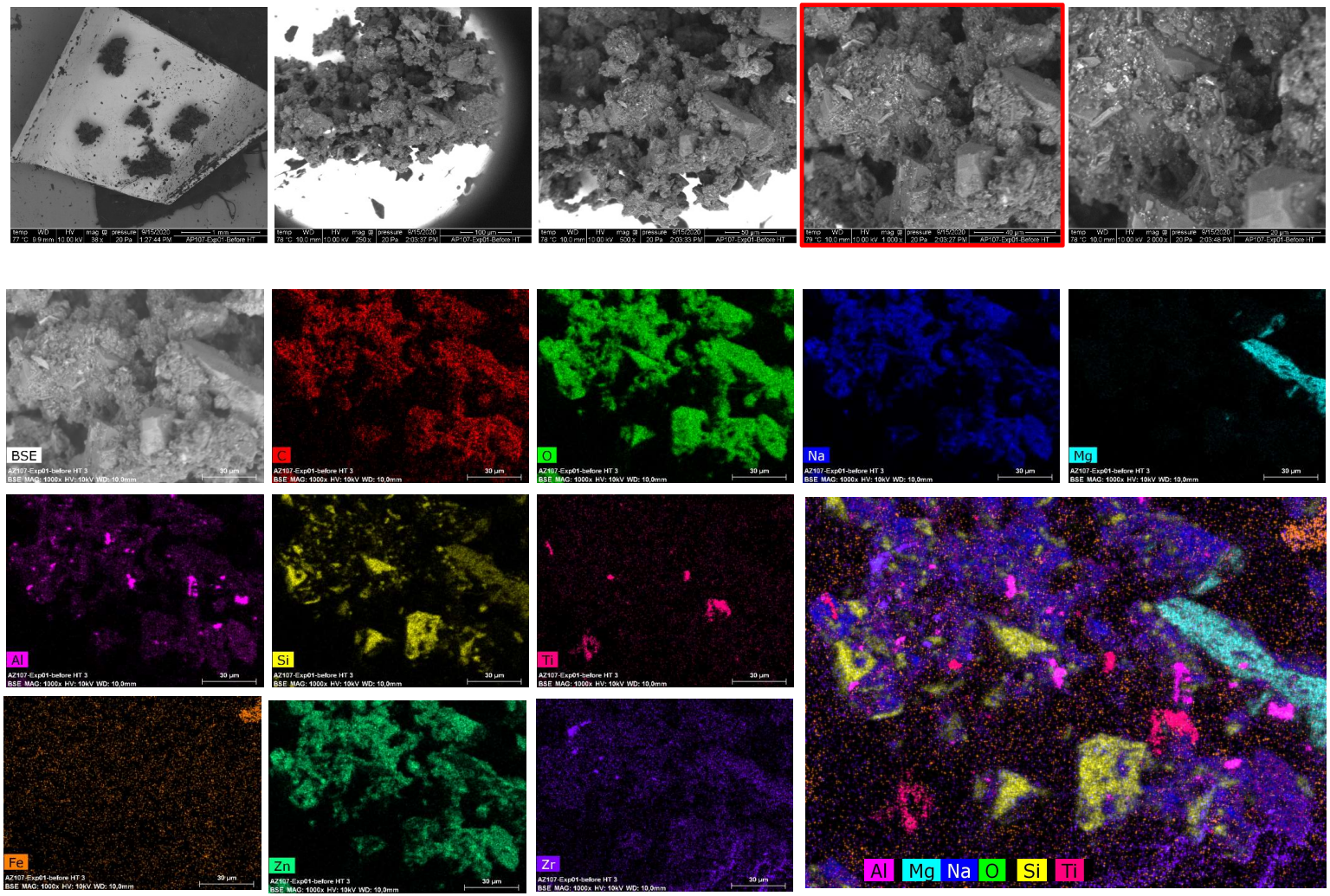


Pokorny et al. JACerS (2023)
DOI: 10.1111/jace.19361

Application to the study of glass elaboration

Elaboration of a glass melt from simple compounds

Vitrification of low-activity waste (LAW)



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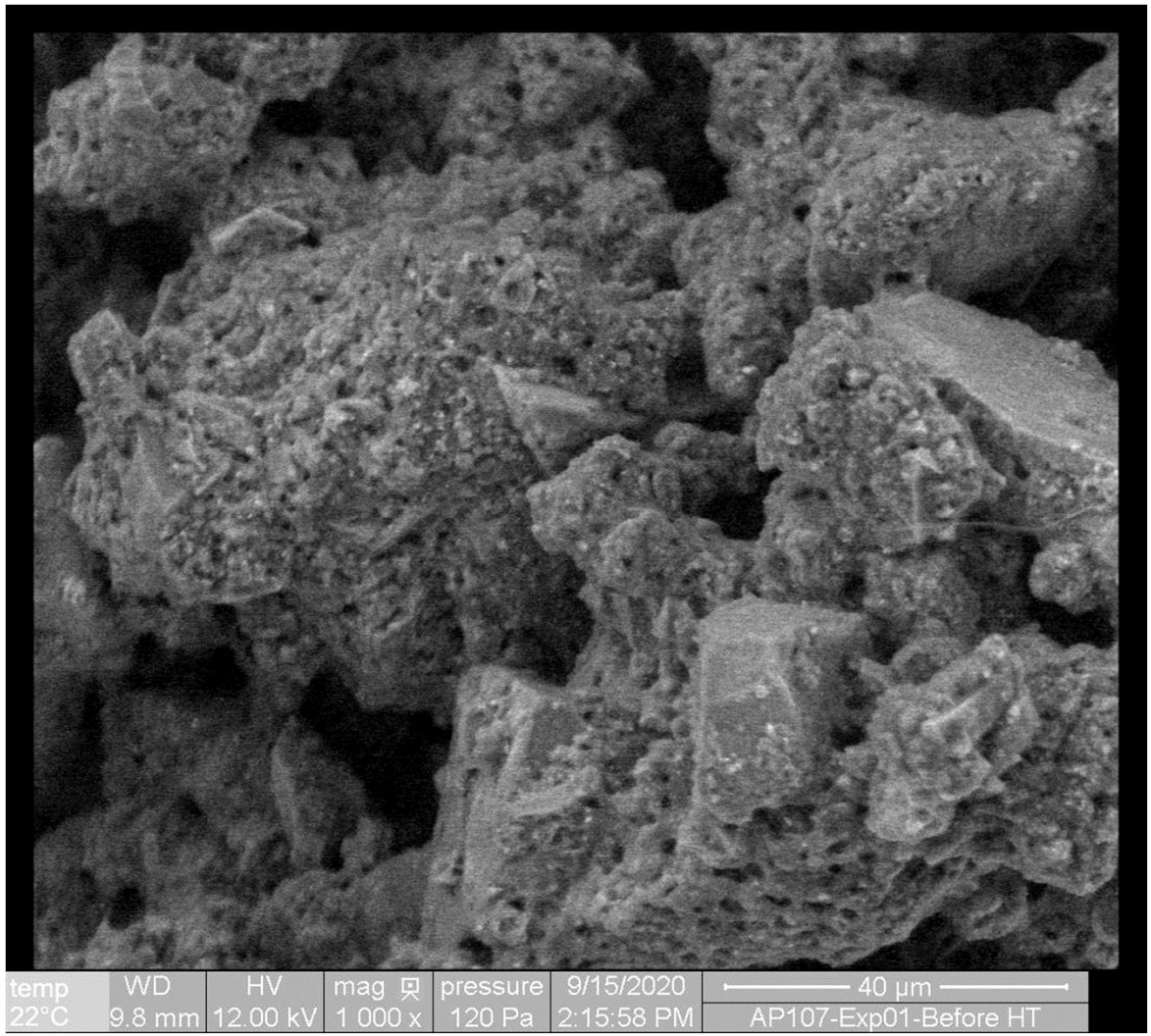
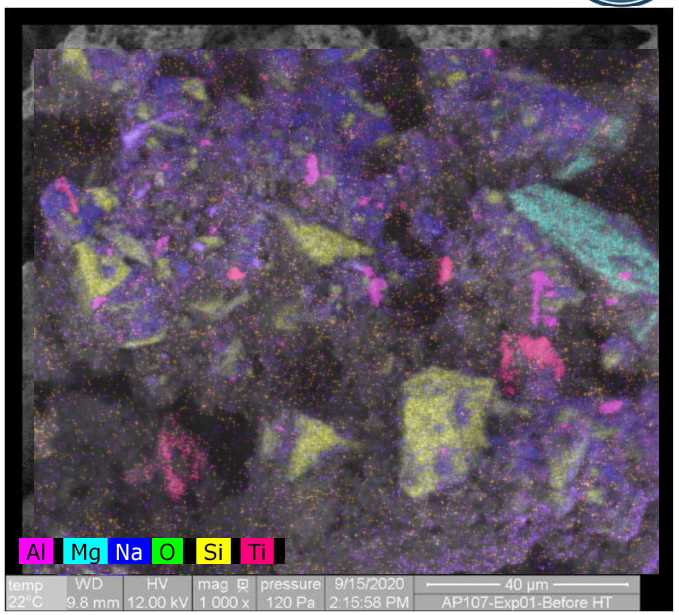
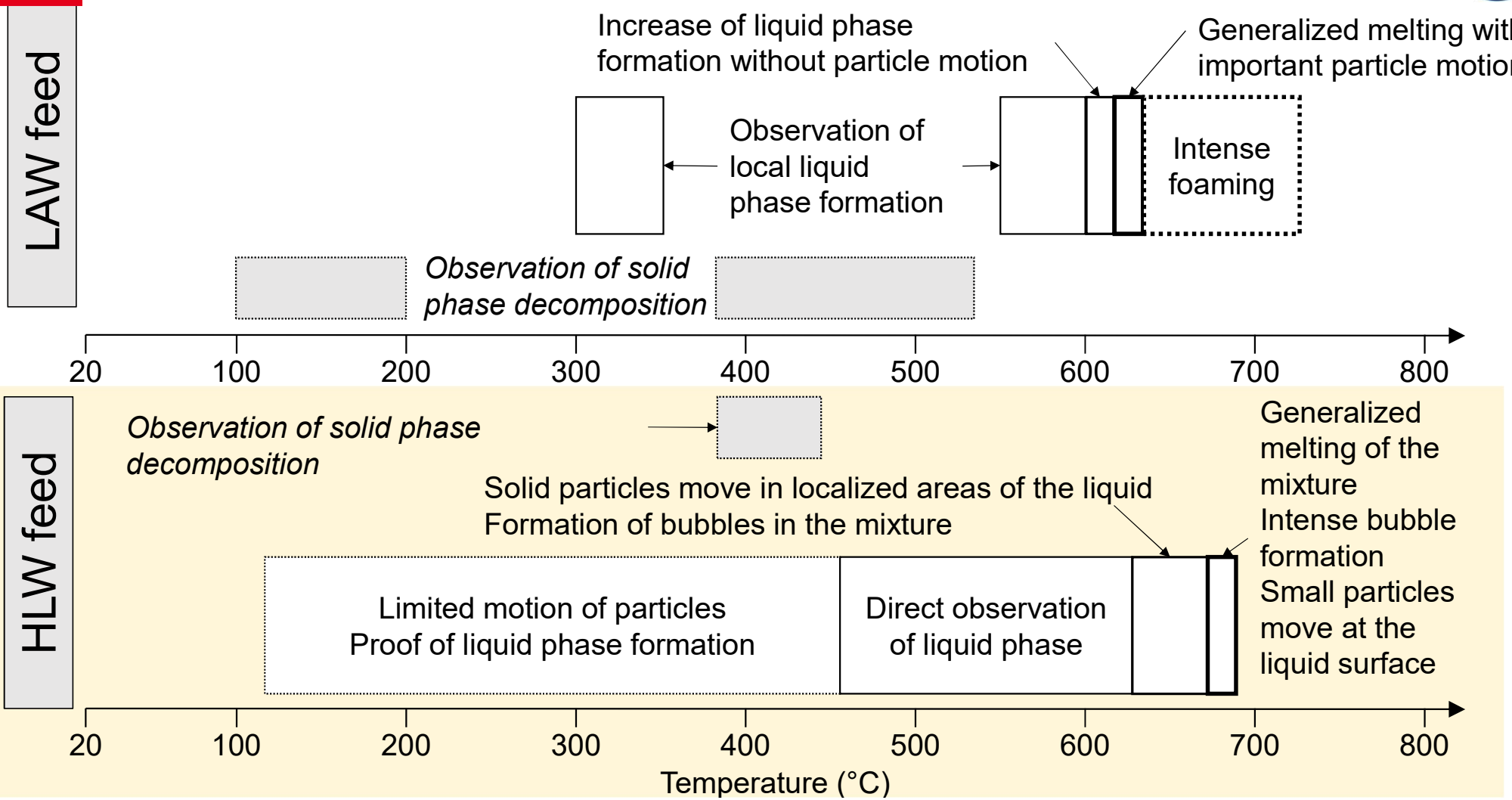


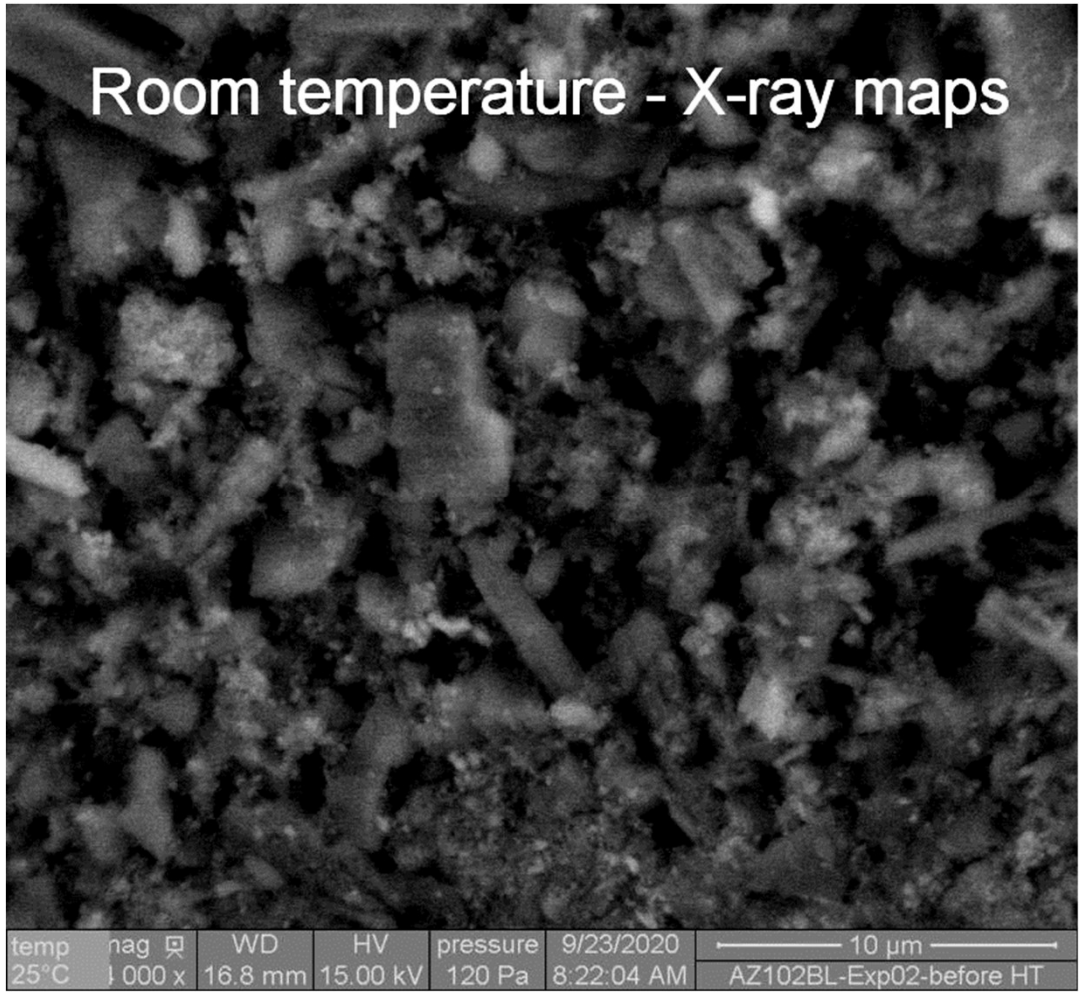


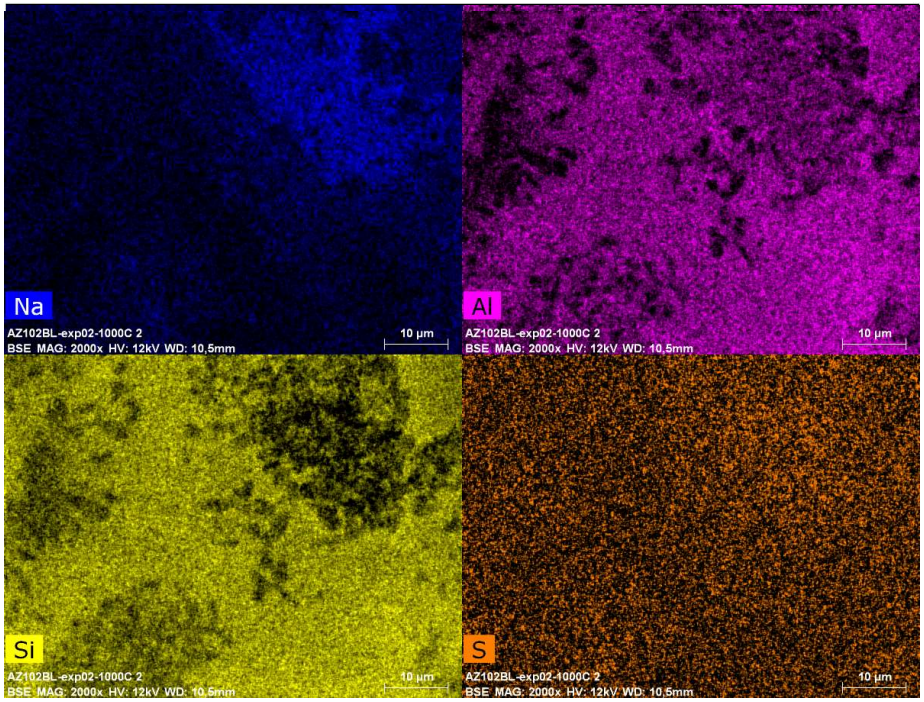
- 350°C: Decomposition of Na compound
- 350°C: Increase of volume of SiO_2
- 570°C: Formation of a complex transient phase (Na_2O, SiO_2, Al_2O_3)
- 577°C: Incorporation of Al_2O_3
- 600°C: Beginning of complete melting
- 620-700°C: Foaming
- 650°C → 1000°C: Formation of floating compounds

Application to the study of glass elaboration



Application to the study of glass elaboration

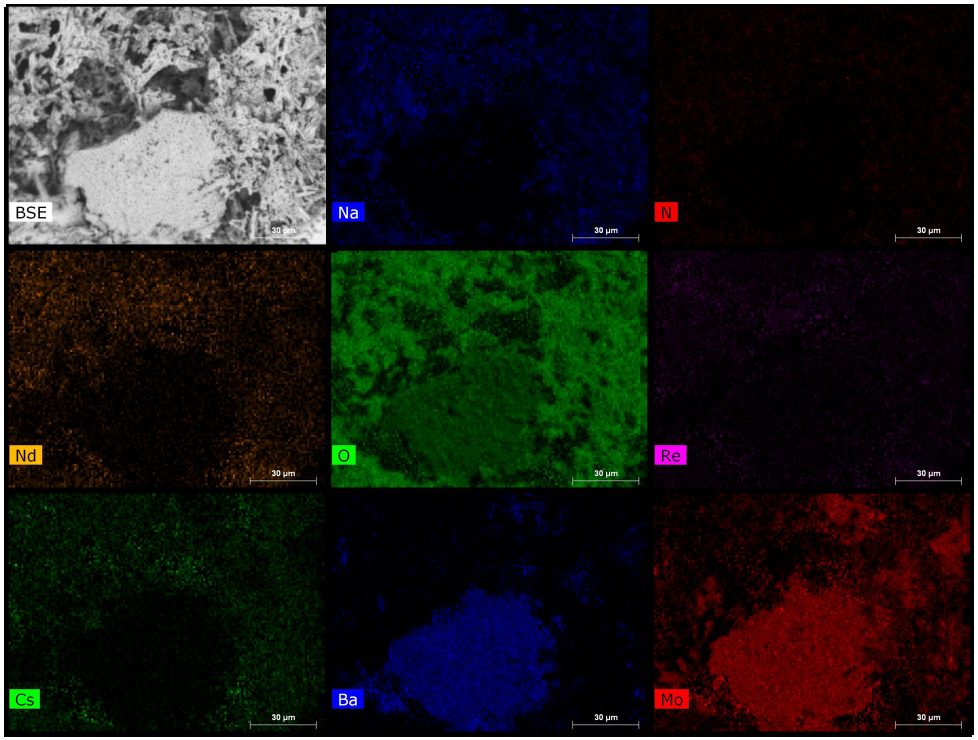


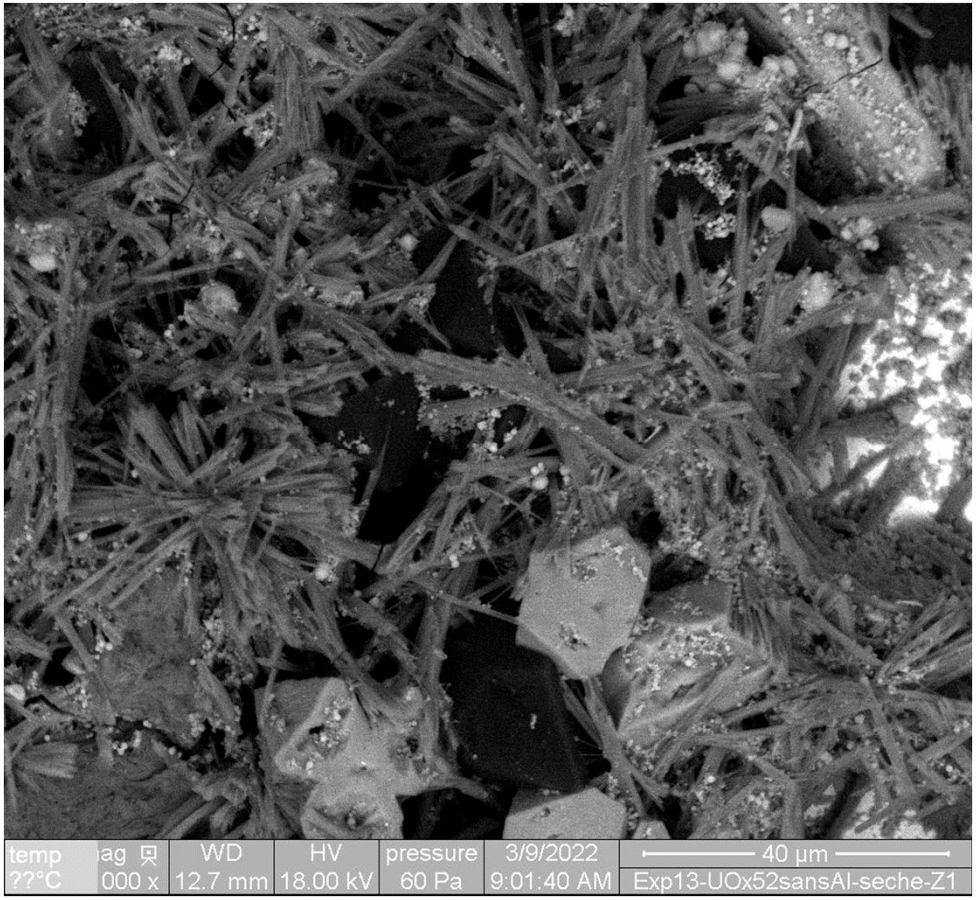


- Correlation between images and analyses
  - Formation of phase formed at the µm scale
  - Time consuming
- Coupled analyses at HT → next step !

Application to the study of glass elaboration

- SIVIT project = direct incorporation of radwastes in the glass from a liquid (see Nabyl et al., poster)
- **Behaviour of the dried solution containing precursors alone (up to 600°C)**

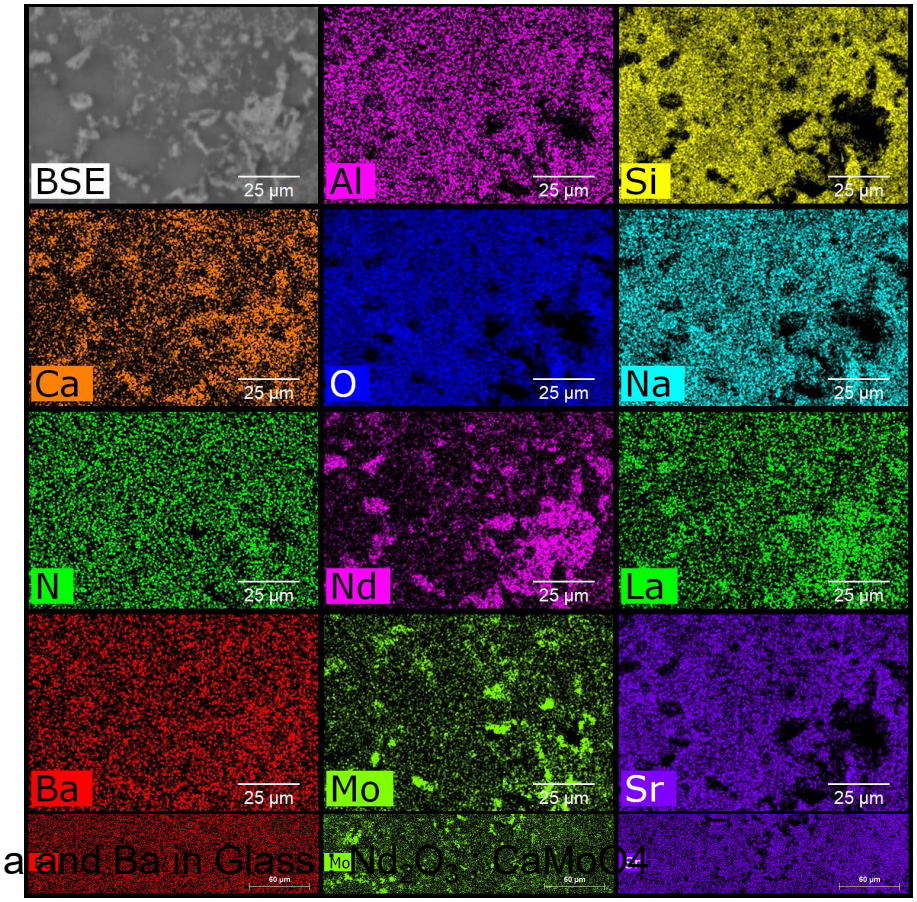




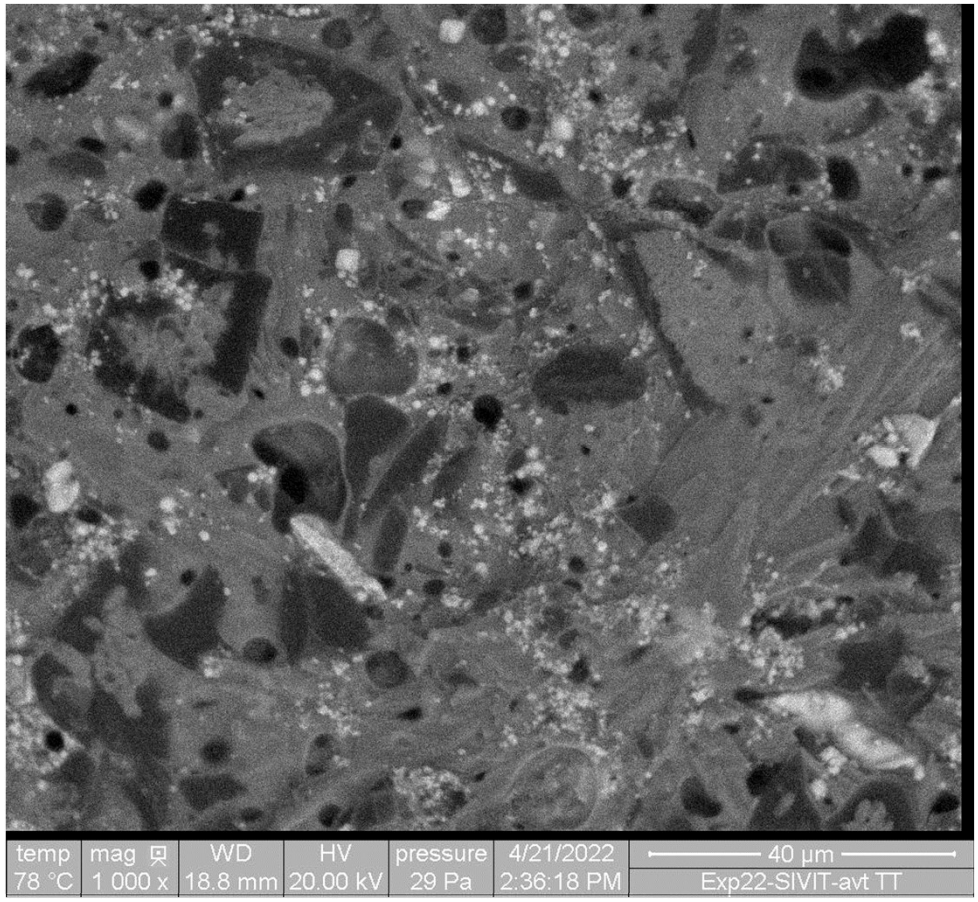
Nitrates : $NaNdNO_3(5H_2O) + NaNO_3 + Ba_{0.5}Sr_{0.5}(NO_3)_2$
Phosphomolyddate : $Mo_{14.4}O_{43}P$
Oxyde : $CsReO_4$

Application to the study of glass elaboration

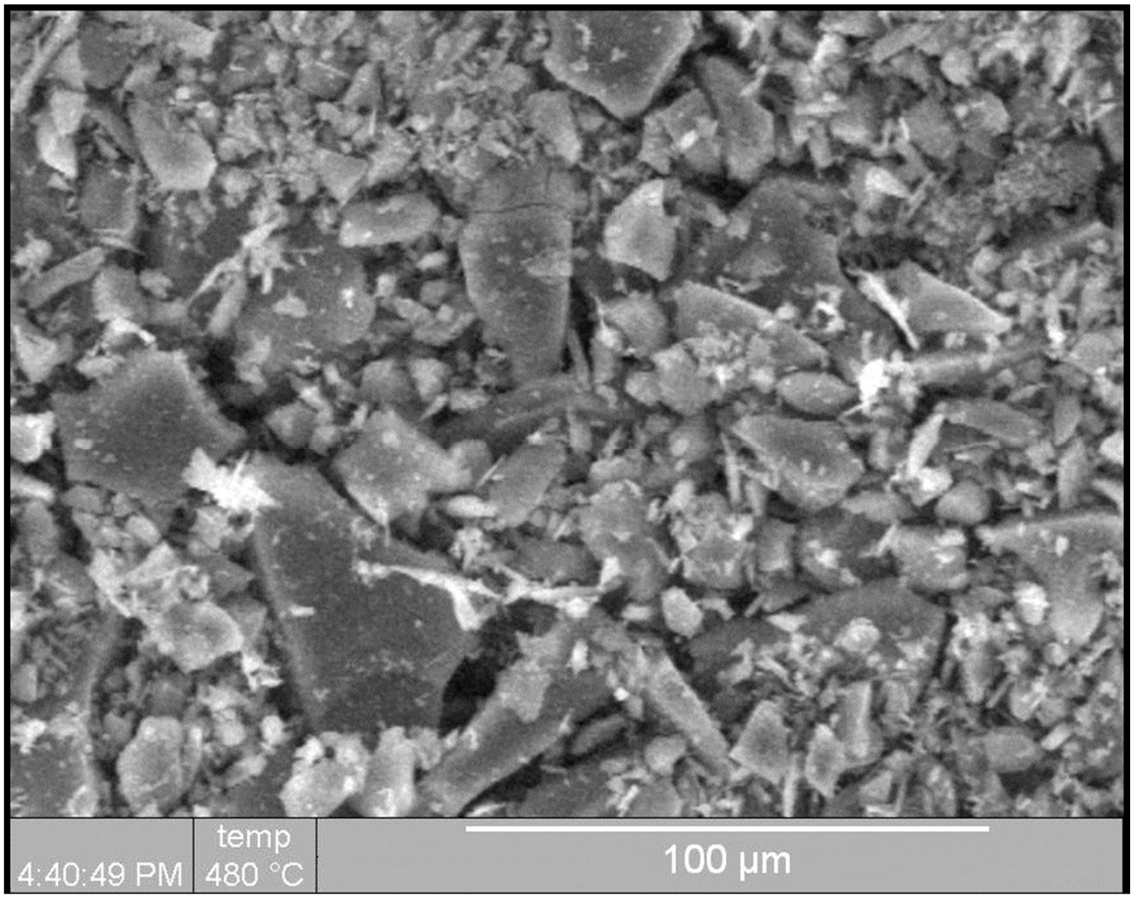
- SIVIT project = direct incorporation of radwastes in the glass from a liquid (see Nabyl et al., poster)
- **Behaviour of the mixture {dried solution containing precursors + glass frit}**

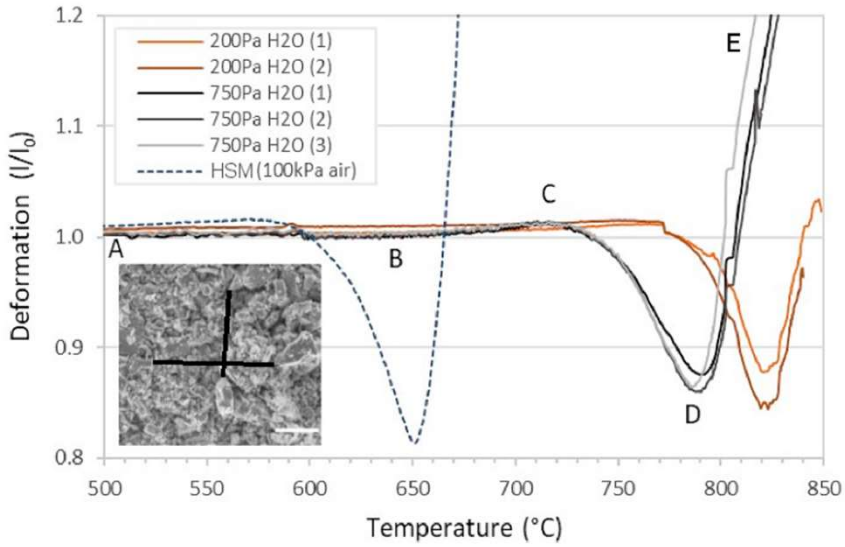


Na and Ba in Glass : Nd_2O_3 ; $CaMoO_4$



Other applications – Glass foam formation

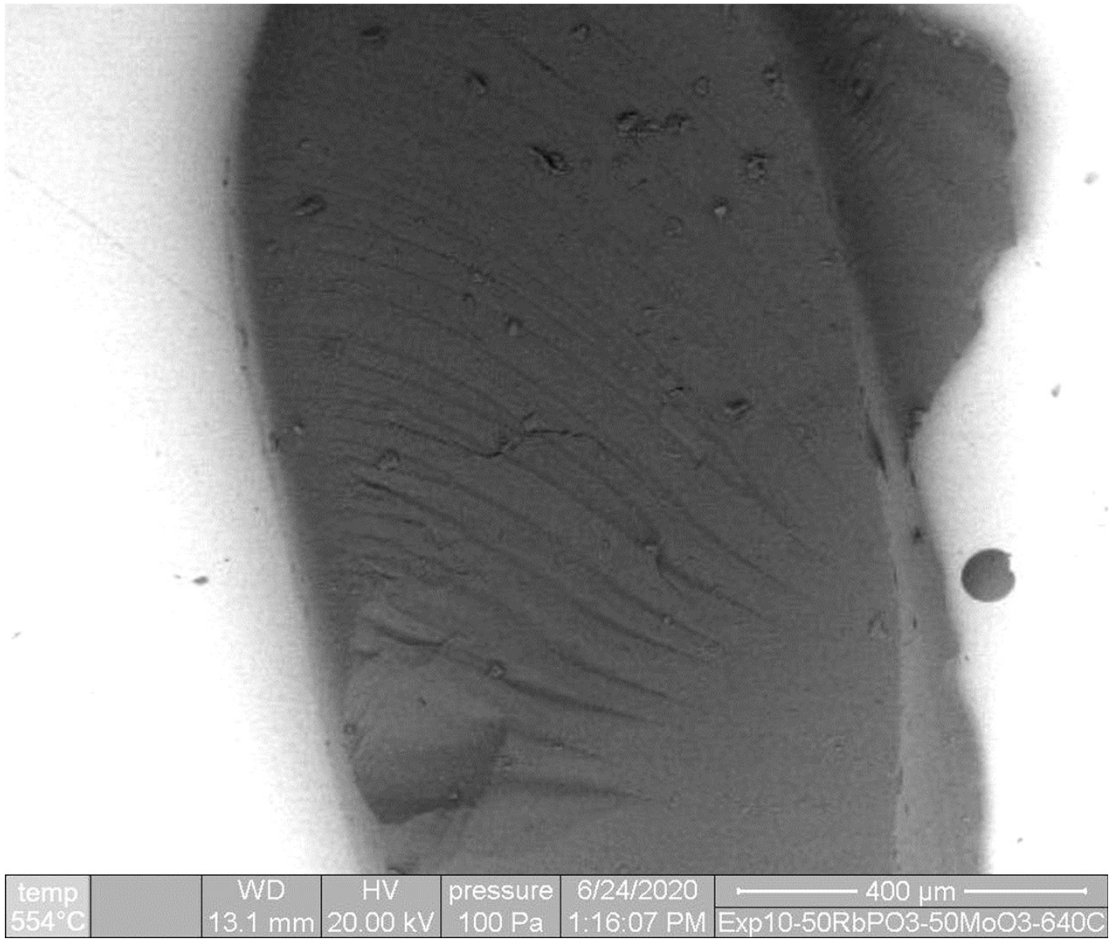


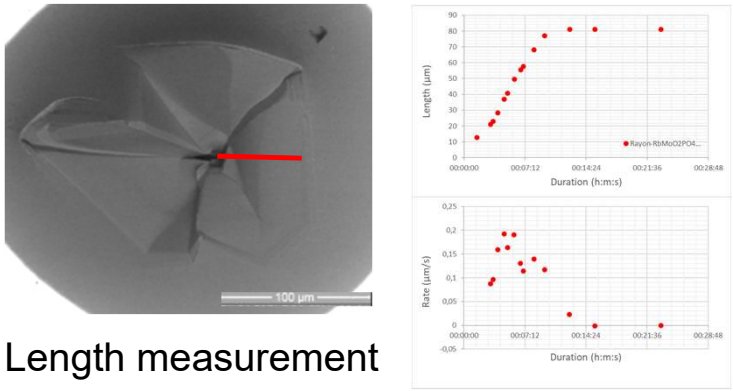


Méar et al., Ceram Int (2021) 47[18], 26042–26049

Other applications – Cristallisation in glasses

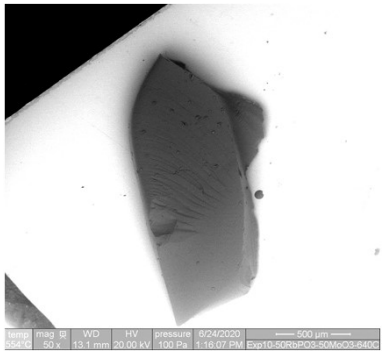
50 $RbPO_4$ – 50 MoO_3 glass





Length measurement

- Average growth rate of crystals = 0.25 ± 0.10 µm/s

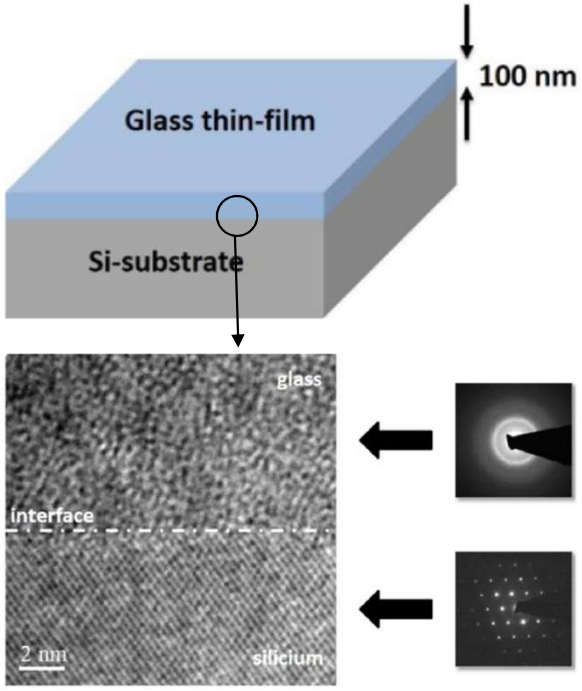


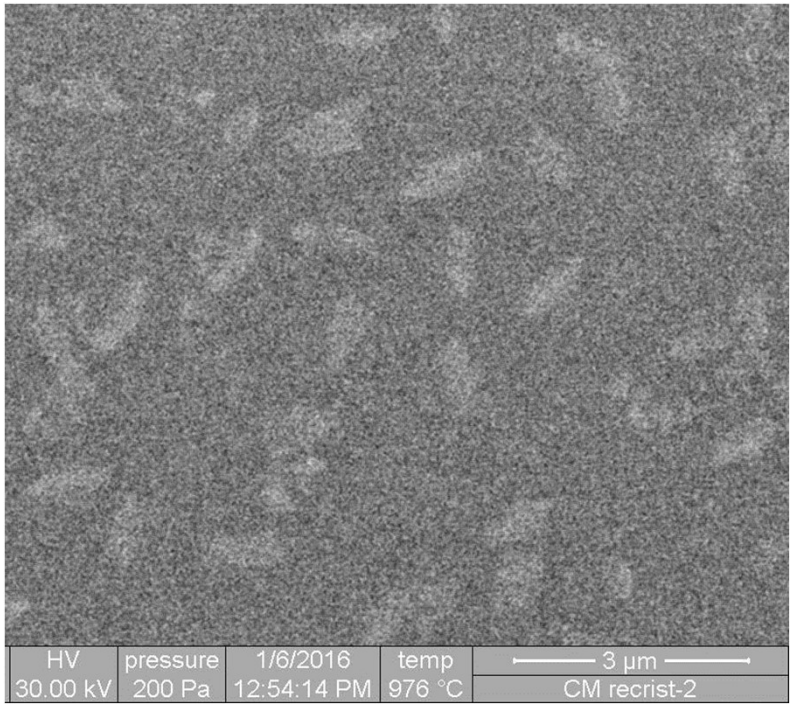
Bodiang et al., JNCS (2023) 606, 122193

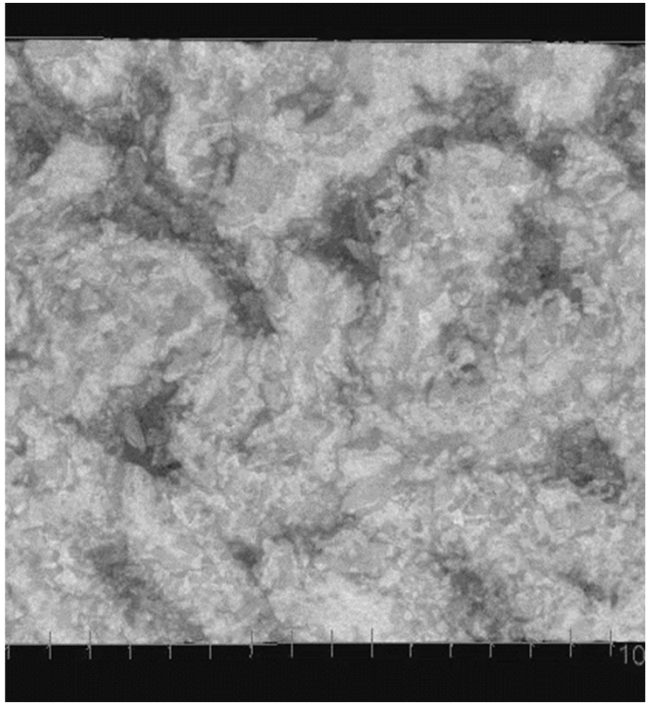
Other applications – Behaviour of thin films

Study of glass thin film crystallization at high temperature

- Recording image series showing crystal formation
- Image alignments, image segmentation and 3D representation (x, y, time)

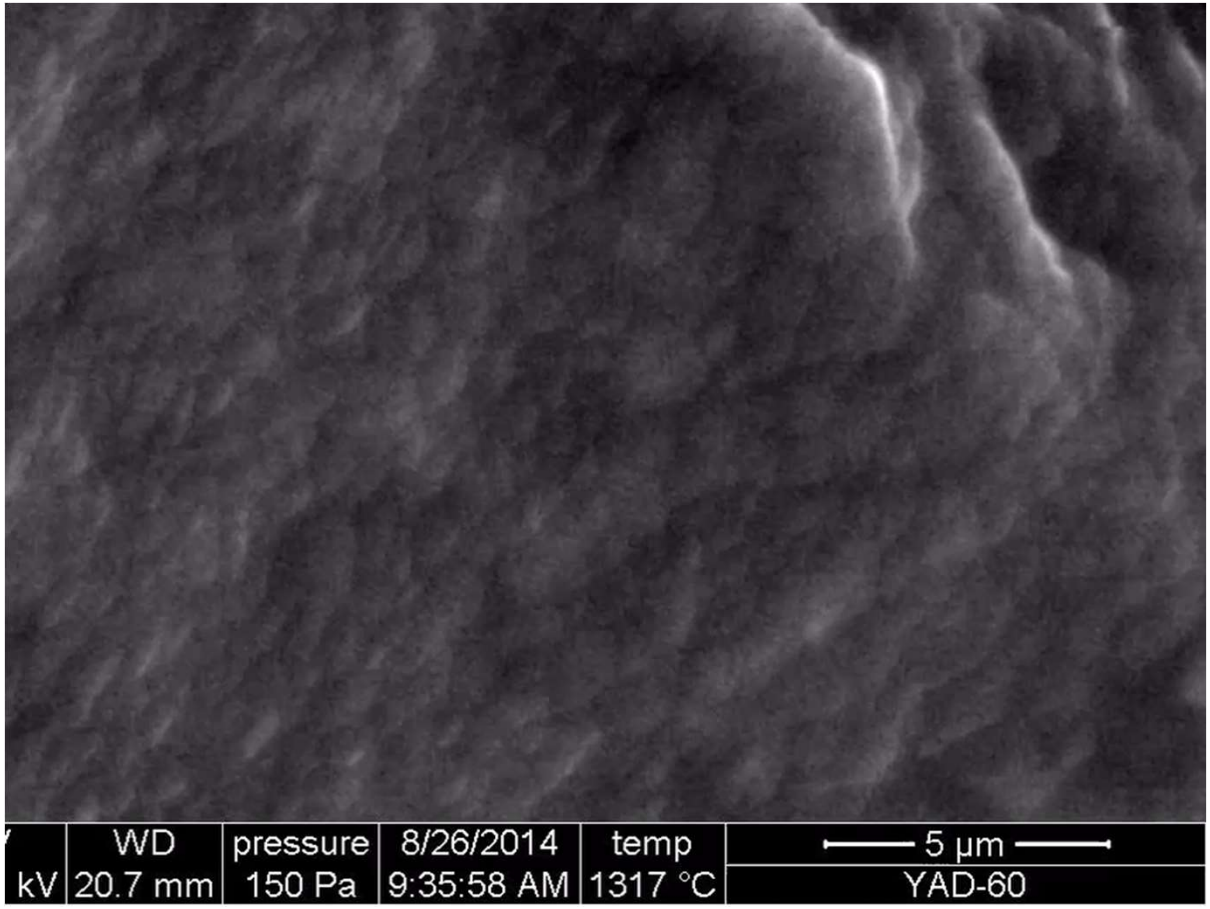


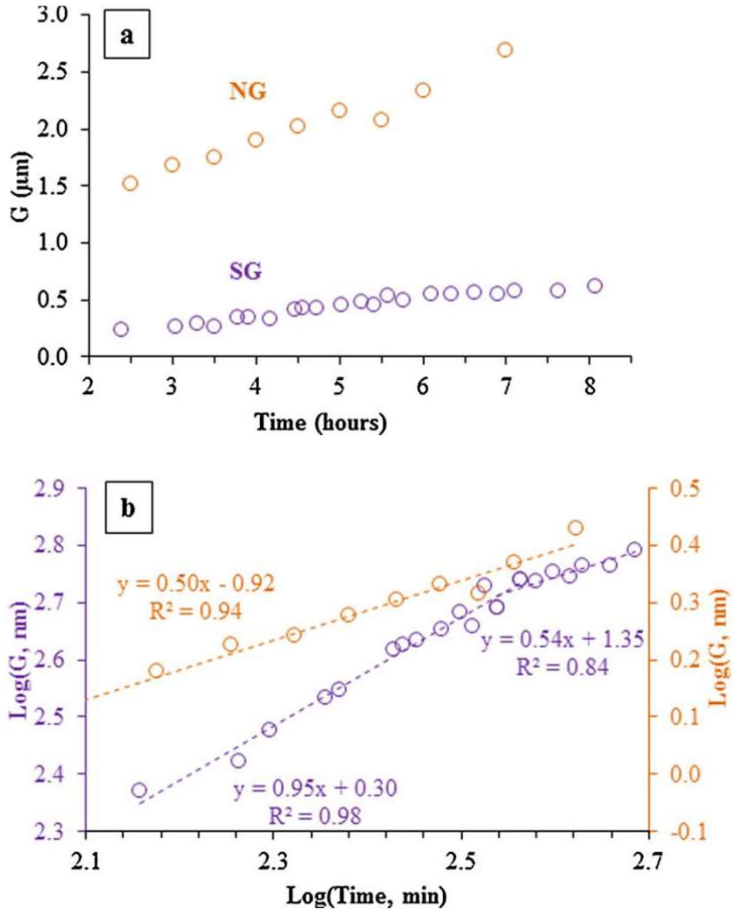




Carlier et al., JNCS (2021) 551, 120406

Other applications – Sintering of ceramics



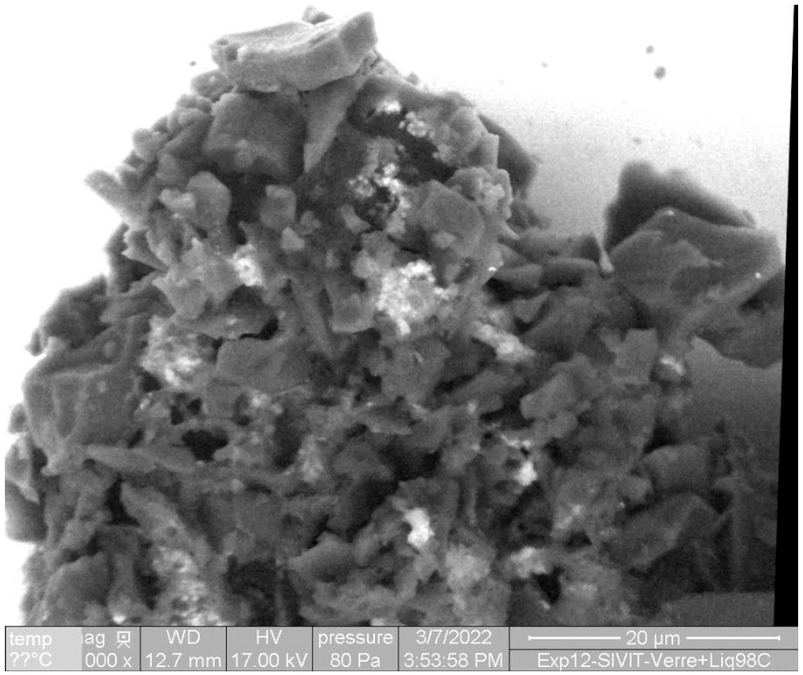


Arinicheva et al., JACerS (2018) 38 227-224

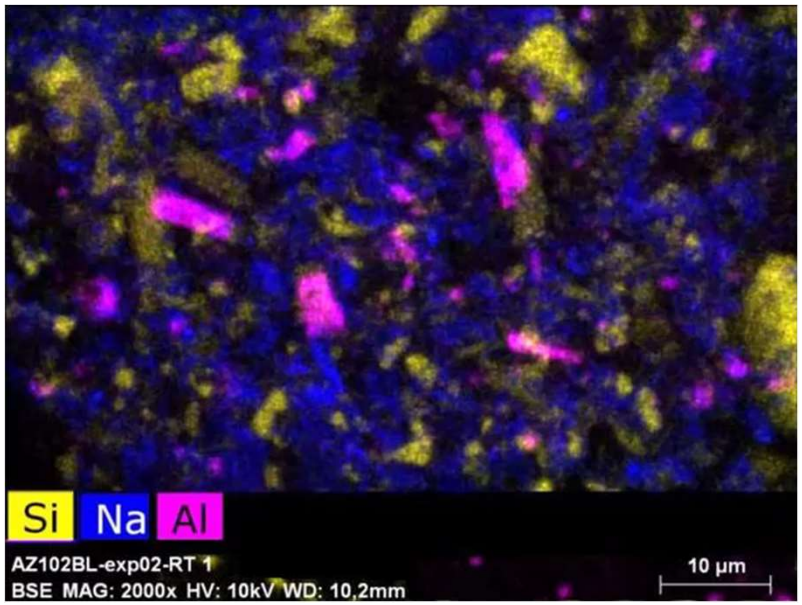
Conclusions

Conclusions

- **New opportunities of experiments are offered by in-situ high temperature Environmental Scanning Electron Microscopy (HT-ESEM)**
  - Glass synthesis
  - Glass reactivity with gases
  - Crystallization in glasses
  - Foaming…



- **Possible coupling of images with in-situ analyses (SEM-EDS)**
  - Direct observation and characterization of compounds formation
  - Possibility to evidence intermediary compounds
  - Possible description of the reaction mechanisms at the micrometer scale



Thank you very much for your attention !