PREMILINARY REPORT

Proposal MA 3028 : Relaxation of densified silica glasses, toward a better understanding of polyamorphism

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The aim of this proposal was to perform SAXS and WAXS experiments during the annealing of pre-densified oxide glasses (silica and silica based glasses). The measurements obtained during the relaxation from the densified to pre-densified state are currently analysed, and compared to previous Raman results. This should provide a proper image of the structural changes involved in this transformation and permit to asses or not the fundamental concept of polyamorphism in silica based glasses.

The data exposed here concern only silica. Several problems such as detector and furnace breakdown, or beam breakdown at critical time didn't allow us to perform about 50% of the work planned. The support of the Dubble team was very effective to overcome all the difficulties encountered. A special cover was specially designed for our experiment. Despite these unfortunate breakdowns, we could check that the line was fully adapted to the planned experiments.
In glasses, SAXS and WAXS experiments provide critical information on the system. The extrapolation of the SAXS at q = 0 nm^{-1} allows to quantify the density (and concentration) fluctuations, with the knowledge of the longitudinal modulus. From previous Raman measurements, these fluctuations are supposed to drive the relaxation. The WAXS signal present the characteristic First Sharp Diffraction Peak (FSDP), which mirrors the largest organized units present in glasses, which identification is still debated.

Silica samples from 3 densified precursors were annealed at different temperatures for a total of height reliable experiments. In addition, similar work on a binary sodosilicate glass at four different annealing temperatures. All the successful shifts are reported in table I.

Table 1 - The different sample studied, with their densification and annealing parameters. The succesfull experiments are also indicated.

Chemical compostion	Pressure of densification	Compression temperature	Annealing temperature	SAXS	WAXS
SiO_2	5 GPa	1020°C	700°C	Yes	Yes
			800°C	Yes	Yes
			850°C	Yes	Yes
			950°C	Yes	Yes
		750°C	850°C	Yes	Yes
			950°C	Yes	Yes
			1000°C	Yes	No
		425°C	850°C	Yes	Yes
$0.9SiO_2$-$0.1Na_2O$	5 GPa	300°C	300°C	Yes	Yes
			400°C	Yes	Yes
			500°C	Yes	Yes
			700°C	Yes	Yes

For the extrapolation of the SAXS intensity, a first and accurate overview can be assessed when following the intensity at small q during the relaxation. The intensities at q = 1, 2 and 5 nm^{-1} for the D750R850 relaxation (densified at 750°C, relaxed at 850°C) are presented versus in figure 1. The evolution of the intensity shows three different regions, demonstrating that the density fluctuations are associated to different structural changes during the different stages of the transformation.
Thus the SAXS measurements performed were successful.

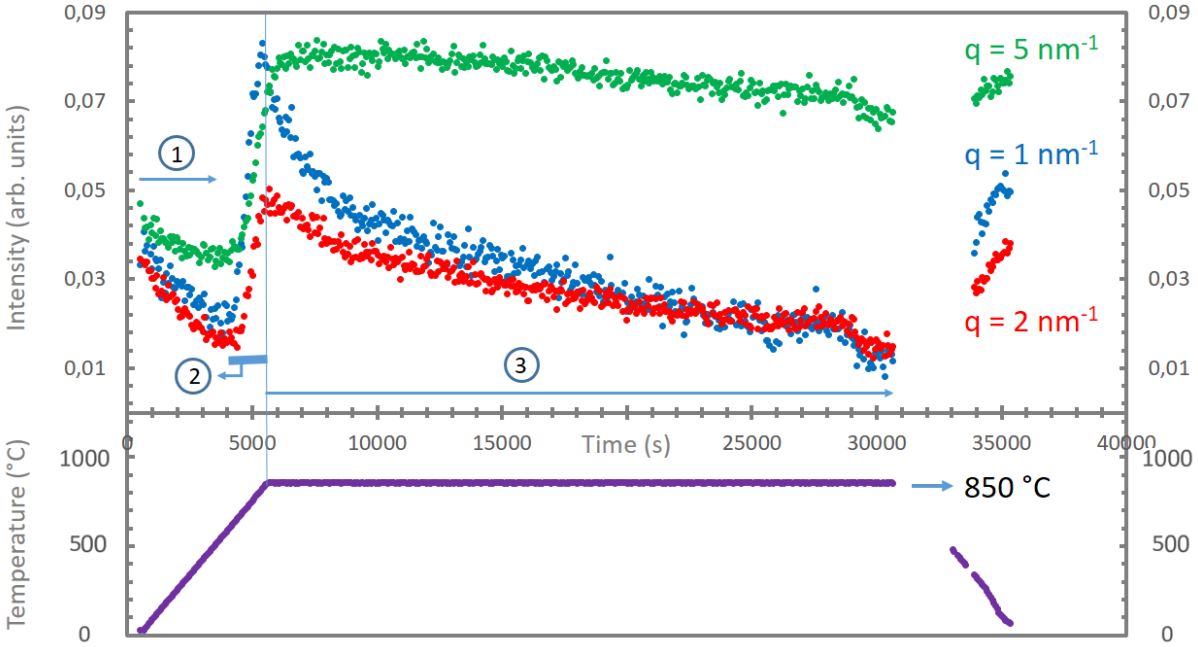

Figure 1 - Evolution of the SAXS intensity at q = 1,2, 5 nm-1 (up) and the temperature (down) against the time for the d750r850 (up).

The FSDP present on the WAXS signal was also tracked during the different experiments. The position of the maximum of the FSDP during the D1020R850 relaxation is presented below, in figure 2.

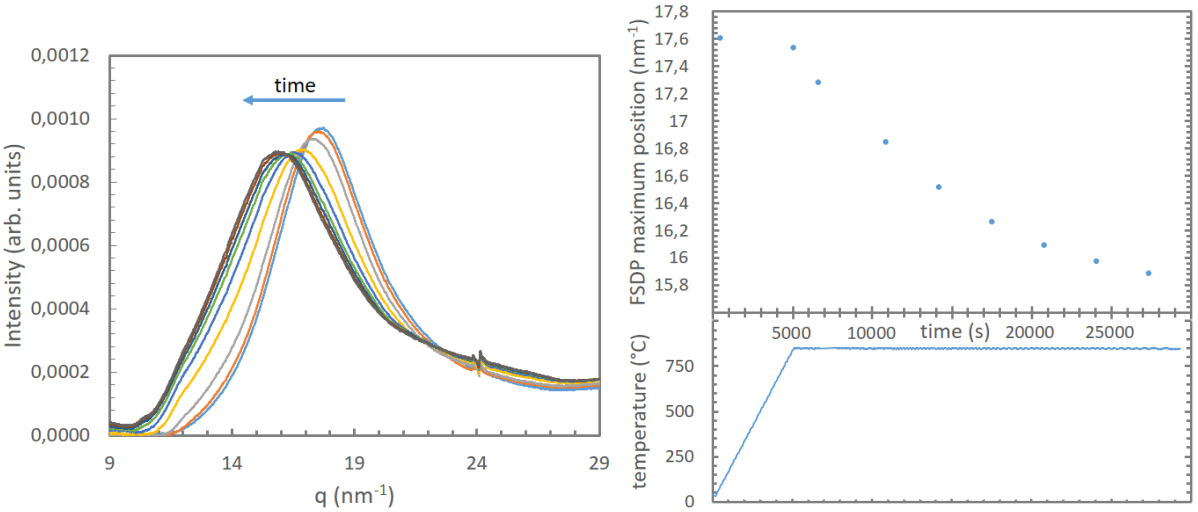

Figure 2 - Evolution of the FSDP for the d1020r850 (left). Evolution of the position of the maximum of the FSDP (right up) and the temperature (right down) against time for the d1020r850.

A very long annealing was performed on this sample in order to get the final fully relaxed state. Significant (>50%) of the total relaxation were followed for five of the eight samples studied. The different isothermal annealing showed a similar behavior for each starting densification, with different recovering rates. They allow us to extract activation energies, which differs significantly from them obtained with Raman spectroscopy. Moreover a cross comparison of the evolution of the degrees of transformation from Raman, SAXS and WAXS measurements show that these evolutions do not follow the same law, indicating different relaxation processes at the different characteristic length and different orders of the glassy structure.

The problems we encountered didn't allow us to perform a complete analysis of the binary silicates. Only one chemical composition has been studied. A change in the doping content and the nature of the alkali cation were planned to make a complete study of binary silicates glasses.