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Report:

The local structure of iron-containing melts has been the subject of numerous studies. However, most of these works consider only quenched glasses from melts. At high temperatures, only a few studies using *in situ* x-ray absorption spectroscopy (XAS) have been performed. In this diffraction work, we have studied several compounds including usual basaltic compositions but also refractory compositions such as komatite or chondritic glasses which have never been studied nor in the melted neither in the glassy phase.

In this report we present some results obtained with an oxide glass close to enstatite chondrite compositions ($\text{Si}_{24}\text{AlFe}_5\text{Mg}_{22}\text{Ca}_{16}\text{O}_{46}$). In conventional cooling, these glasses are difficult to obtain from the melt. In order to obtain rapid quench necessary for the glass formation, we employed a levitation technique combined with laser heating [1].

For these experiments, samples were levitated using a mixture of argon and oxygen (3%) and heated using two 125 W CO_2 lasers from the top and from the bottom to avoid temperature gradients and access a deep supercooling. Both laser beams were focused onto the sample using several mirrors. The temperature was measured from the upper part of the sample, at the point illuminated by the X-ray beam by means of optical pyrometers operating in the spectral range 1.45 - 1.8 μm . The absolute temperature scale of the pyrometers was checked by comparing the freezing point of the same sample with the known melting point. This was measured using a low cooling rate that led to the crystallization of the sample.

The structural evolution during the glass transition can be studied by time-resolved diffraction measurements. This requires short counting times with good statistics over a wide Q-range since the process occurs within a few seconds. For that, we used high energy x-rays (100 keV) with the ESRF Frelon 2D CCD camera. To perform the time-resolved measurements, the detector was configured in frame transfer mode giving an overall exposure/readout time of 30 ms. For the static conditions a normal, full frame mode with 60 seconds exposure time, was used.

We studied the structural evolution of the molten glass as it cooled down from the stable liquid phase well above the melting point T_m (~1390 °C) down to the cold glass below T_g (~980 °C).

Figure 1 compares the total structure factor $S(Q)$ for the sample in the glassy state at room temperature taken with acquisition times of 1 min and 30 ms. It can be seen that even with 30 ms the signal to noise ratio

is very good. The corresponding $g(r)$'s are presented in the inset of figure 1. The broadening of the first peak in the time-resolved measurement is due to the smaller Q-range used for the Fourier Transform.

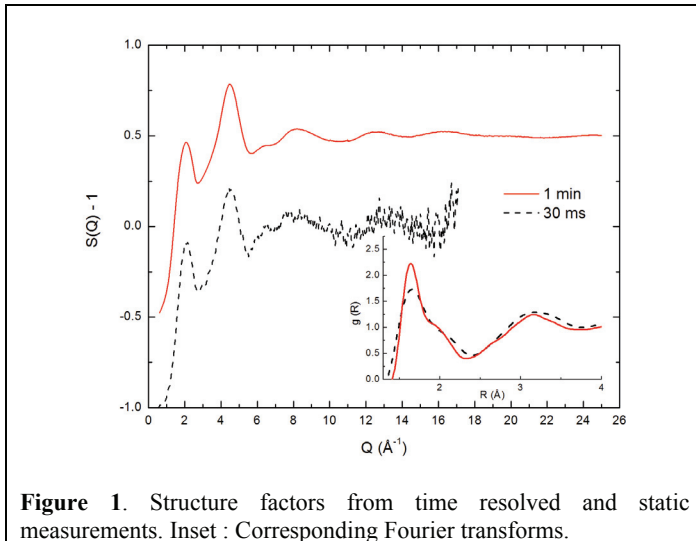


Figure 1. Structure factors from time resolved and static measurements. Inset : Corresponding Fourier transforms.

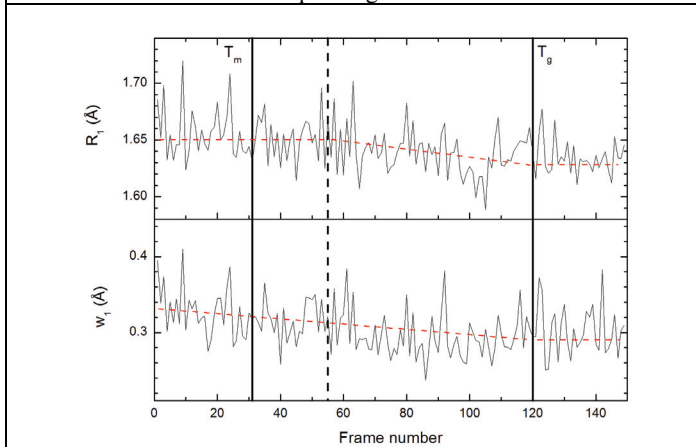


Figure 3. Real space evolution during cooling. R_1 and W_1 are respectively the position and width of the first peak

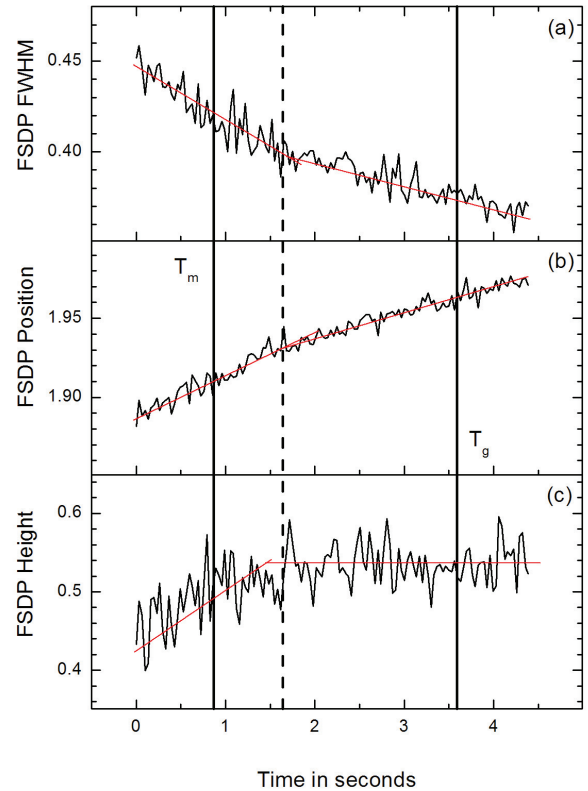


Figure 2. Evolution of the width (a), the position (b) and the first peak height (c) during the free cooling as a function of time. Solid horizontal lines represent the melting point T_m and the glass transition T_g temperatures. Dashed line shows the dynamic crossover temperature, conventionally taken as $1.2 T_g$

Figure 2 shows the profile analysis of the first peak in $S(Q)$ during the free cooling process as a function of time: width (a), position (b) and height (c). We observe a sharpening of the first peak with decreasing temperature down to about $1209\text{ }^\circ\text{C}$ ($\sim 1.24 T_g$) which is represented by the vertical dashed line. After that point the slope is a little bit lower. At the same time the intensity that starts to increase linearly at the beginning remains at a constant value beyond this temperature. This is consistent with an increased intermediate range order in the glass. We observe also an increase with the first peak position with decreasing the temperature. Similar behavior has been found in other liquids and glasses [2]. The onset of these structural changes is occurring close to the crossover temperature taken as $1.2 T_g$ for fragile liquids [3].

The structural evolution in the real space is presented in Figure 3. Contrary to the Q-space, there is very little changes with either the position (R_1) or the width (w_1) of the first peak. We observe a small decrease in the first neighbor position from the critical temperature down to T_g and a small decrease in the width over the entire temperature range. A possible reason could be the complicated chemical composition of the sample.

Since lot of atomic pairs contribute to the first peak it is very difficult to separate the individual contributions. Then, to complement this work, EXAFS measurements will be performed on the same samples at the Fe K absorption edge and Molecular Dynamics simulations will be also used to go further in the analysis.

[1] A. Bytchkov et al. , submitted to JSR (2010)

[2] S. C. Moss and D. L. Price, in *Physics of Disordered Materials*, edited by D. Adler, H. Fritzsche and S. R. Ovshinsky (Plenum, New York, 1985), pp. 77–95

[3] C. A. Angell, *J. Non-Cryst. Solids* **73**, 1 (1985)