Experimental report

13/02/2017

Proposal: 6-05-978 **Council:** 4/2016

Title: Reversibility window in Li-borate glasses and structural anomalies

Research area: Materials

This proposal is a new proposal

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Samples: x(Li2O).(1-x)(B2O3)

Instrument	Requested days	Allocated days	From	To
D4	8	8	13/12/2016	22/12/2016

Abstract:

Recent MD studies on a sodium silicate glass have shown the existence of a reversibility window (RW) related to the number of constraints of the topological glass and characterized by a negligible hysteresis loop and an anomalous behaviour of the FSDP. Alkali (in particular Li and Na) borates constitute an excellent system to confirm experimentally this unusual behaviour, as they have glass transition temperatures in the range 530-780 K. And due to the small atomic number of all its constituents they are well suited to Ab Initio MD simulations, which will complement the neutron diffraction data and provide additional insights into the structural changes related with the degree of stress of the glass. Therefore we propose to study by means of D4 the structure of ? Li-borate glasses of different composition at room temperature in order to correlate the changes observed in the FSDP with the rigidity properties of the glass, as well as the temperature dependence across Tg for two selected compositions (one inside the RW and one outside), in order to observe their different hysteresis loops.

Neutron scattering experiments have been carried out on four compositions in the xLi_2O-$(100-x)B_2O_3$ system, with x= 7, 14, 24 and 32. For each composition, two samples were measured, one enriched with ^6Li and the other one with ^7Li, in order to specifically determined the Li environment as a function of the Li_2O content.

The data were corrected with standard procedure (program Correct) from absorption, inelasticity and normalization with a vanadium standard.

Figures 1 and 2 compare the structure factors and the PDF(r)functions for the four compositions (7Li-enriched samples) at room temperature. A continuous evolution of the high Q part of the structure factors can be correlated with the progressive increase in the content of BO_4 units. This can also be seen in the real space by the shift towards high r values of the first B-O peak, since the mean B-O bond length is higher in the BO_4 units compared to the BO_3 units.
The first peak in the structure factors at ~1.54 $Å^{-1}$ will be studied in more details as it is an important feature to probe medium-range order and can show a possible relationships with the topological properties.

First difference functions giving Li-centered correlation pairs were successfully obtained for the glasses with 24 and 32 mol% Li_2O (Figures 3 and 4). The first peak around 2 Å is directly related to the Li-O bond length and the subsequent peaks to Li-B and farther Li-O distances.

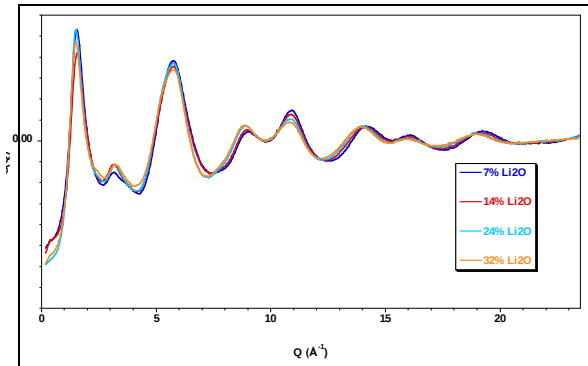

Figure 1: Structure factors for the four compositions with 7, 14, 24 and 32 mol% Li_2O.

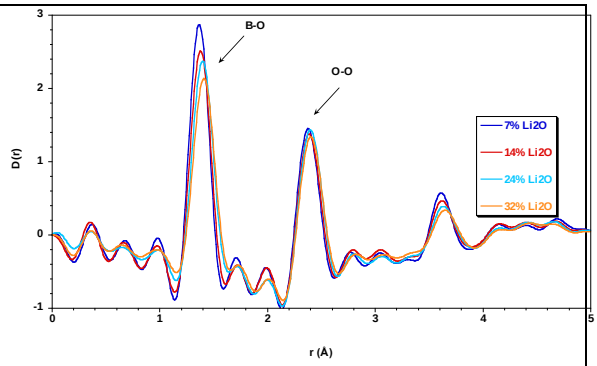

Figure 2: PDF(r) function corresponding to the obtained in figure 1 after Fourier transform up 23.4 $Å^{-1}$ without modification function.

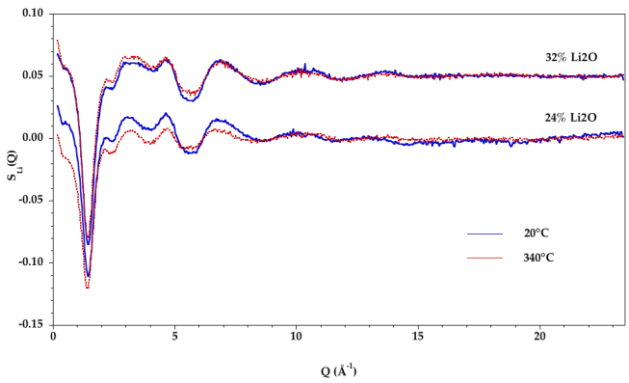

Figure 3: Lithium first order difference function for the two systems with 24 and 32 mol% Li_2O at ambient and high temperature.

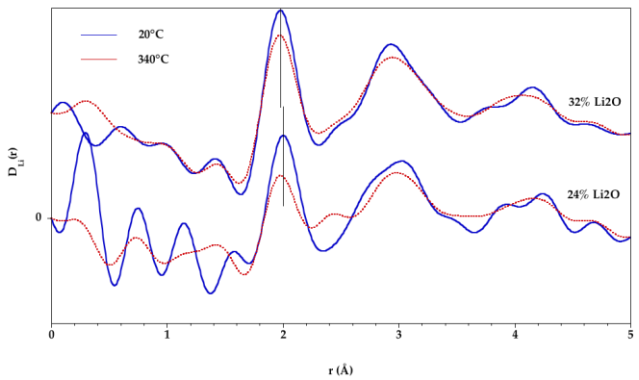

Figure 4: Lithium first order difference PDF(r) function for the two systems with 24 and 32 mol% Li_2O at ambient and high temperature.

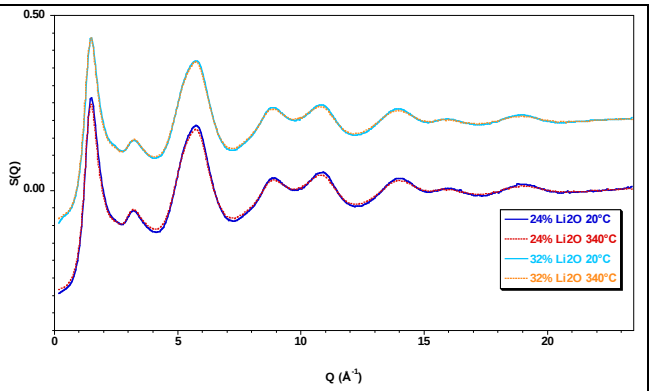

Figure 5: Structure factors for the samples with 24 and 32 mol% Li_2O at room temperature and 340°C.

Measurements were also obtained at high temperature using a vanadium furnace. Levitation is not possible for this system as high volatilization is expected. The high temperatures were chosen close to the glass transition temperatures Tg to assess structural relaxation. The results are presented in figure 5 and 6 for the 24 and 32 mol% Li_2O as the samples exhibiting significant changes. The structure factors show a small damping of the structural oscillations likely due to the thermal disordering with temperature. This results in a broadening of the contribution in real space (and a concomitant decrease in intensities). In particular the first peak near 1.4 Å, attributed to the B-O bond length, is not shifted, which indicate that no boron coordination change should occur just below Tg.

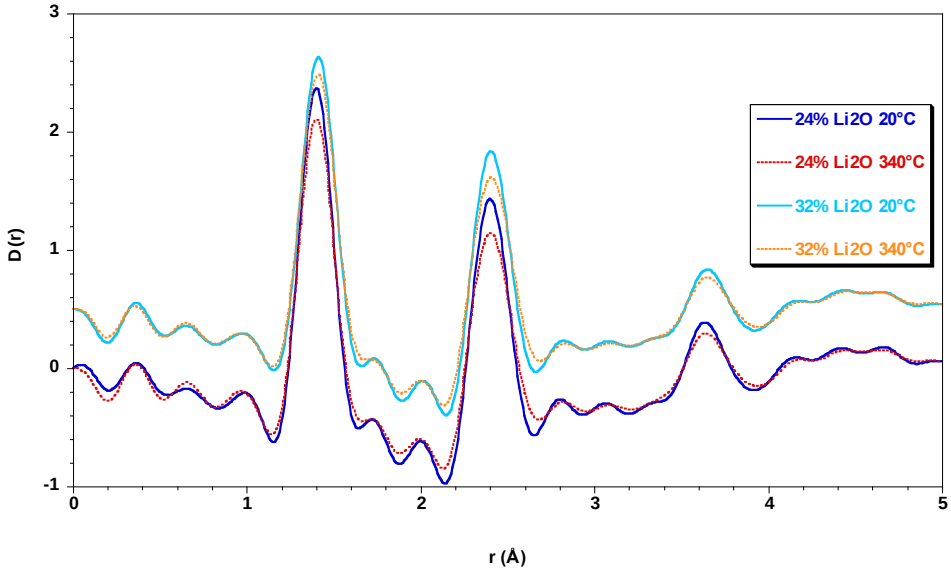

Figure 6: PDF(r) function corresponding to the data obtained in figure 5 after Fourier transform up to 23.4 $Å^{-1}$ without modification function.

These preliminary results indicate:

- a continuous evolution of the structure with the Li_2O content (Figure 1 and 2) but a fine sampling in composition is required to better assess the structure-topology relationships
- high temperature measurements are required to determine the structural changes with temperature and compare with Molecular Dynamics simulations which are being realized.

We have identified the technical issues to obtain high temperature measurements up to the liquid state. In order to prevent liquid flow and contamination, such experiments will be obtained with extruded vanadium cells, using the same vanadium furnace.