Experimental Report

15/02/2014

Proposal: **6-03-431** **Council:** 10/2012

Title: Structural study of glassy and levitated liquid MO-Al2O3 (M=Sr, Ba)

This proposal is resubmission of: 6-03-423

Researh Area: Materials

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Samples:
$(SrO)_x-(Al_2O_3)_{1-x}$
$(BaO)_x-(Al_2O_3)_{1-x}$

Instrument	Req. Days	All. Days	From	To
D4	5	5	29/04/2013	01/05/2013

Abstract:

The aim of this proposal is to study the structure of alkaline-earth aluminates MO-Al2O3 (M= Sr and Ba) in both the glassy and liquid states. This study will extend the previous work performed at the ILL on the CaO-Al2O3 system. In particular, it will be possible to study the structural evolution as a function of the size of the alkaline-earth cation.

Structural information derived from the pair-distribution functions (distances, coordination numbers) will be useful for understanding the mechanism of glass formation in these systems.

For this experiment, we will use the levitation setup developed by the CEMHTI (Orleans) and integrated into the D4c diffractometer.

These experiments will be complemented by X-ray diffraction and absorption (EXAFS) measurements, and Molecular Dynamics simulations will also be performed in collaboration with the ILL's computing group (C-lab).

-I- Introduction

To better understand the formation of alkaline earth aluminate glasses MO-Al_2O_3 (M= Sr and Ba), it is important to study the local environment around aluminium and M atoms. Therefore, the primary objective of this experiment was to study the structure of these glasses. As opposed to x-rays, neutron diffraction is less sensitive to cation-cation correlations but more sensitive to bonds involving oxygen. Thus, it gives important information about the Al-O, M-O and O-O environments.

Due to a delay with the restart of the reactor, the high temperature part of the experiment has been postponed and only the room temperature measurements have been done. Also, in order to optimize the beamtime, we only measured the vitreous SrO-Al_2O_3 (SA) compositions (listed in Table. 1).

Sample	SrO (mol%)	Al_2O_3 (mol%)	Density (g/cm^3)
S60	60.0	40.0	3.68
S62.5	62.5	37.5	3.70
S67.5	67.5	32.5	3.74
S72.5	72.5	27.5	3.78
S75	75.0	25	3.80

Table 1. Compositions studied in this work

The experiment was carried out at the D4c instrument at a working wavelength of ~0.5 Å. Diffraction measurements were performed over a 1.3–140 ° angular range giving a usable Q range of 0.3–24 Å^{-1}.

All samples were quasi-spherical with a diameter between 4 and 5 mm. They were mounted on the top of an open vanadium cylinder of diameter ~3 mm (smaller than the sample's diameter). In this way each sample was quickly mounted and dismounted from the same support. We used narrow vertical slits close to the sample to illuminate only a very little part of the vanadium with the beam.

-II- First results

The total structure factors $S(Q)$ of the studied SA glasses at room temperature are presented in Fig. 1. All curves are very similar. The main visible differences concern the more intense first peak at about 2.8 Å^{-1} which shifts towards lower Q values and becomes broader. This peak is mostly due to O-O correlations and its evolution should reflect the atomic rearrangements around the AlO and CaO polyhedra.

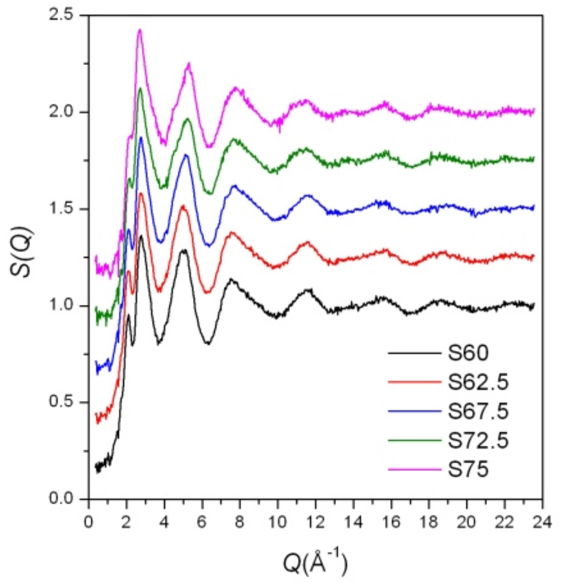

Fig.1. Total structure factors $S(Q)$ for the SA glasses at room temperature obtained from neutron diffraction.

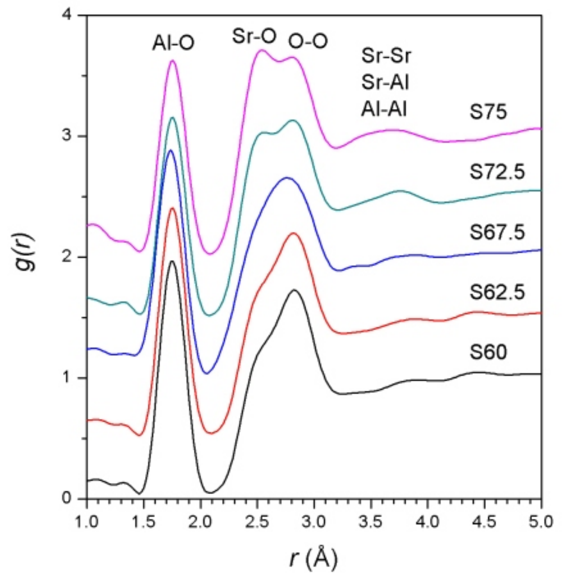

Fig. 2. Total pair distribution function $g(r)$ for the SA glasses (RT) as obtained by Fourier transforming the corresponding total $S(Q)$.

Fig. 2 shows the total pair distribution functions *g(r)* for all the compositions studied. For all, the first peak at ~1.75 Å arises from the contribution of the nearest neighbor Al-O correlations. Using a Gaussian fit to $T(r)=4\pi r\rho g(r)$, a coordination number between 4.2 and 4.4 is found for all compositions, showing that Al is mainly tetrahedrally coordinated.

The two grouped following peaks at ~2.5 and 2.8 Å are due to the Sr-O and O-O pairs. As expected, the intensity of the Sr-O correlations is higher after increasing the Sr-O content. The calculation of the coordination number is relatively difficult because the Sr-O contribution is not well resolved and the integration under the peak in T(r) is largely dependent on the O-O and all cation-cation correlations. Our first calculations seem to show that the coordination number is between 6 and 7.

Our recently performed XAS (X-ray Absorption Spectroscopy) analysis of these glasses will help to better define the Sr-O distance and coordination number as a function of the composition.

The broad contribution at ~3.7 Å corresponds to the cation-cation contributions (Sr-Sr, Sr-Al and Al-Al). Its amplitude increases when the Sr content is increased (higher coherent scattering cross section for Sr compared to Al).

-III- Conclusion

The objective of this first part of our neutron diffraction experiment was to examine the structure of various SA compositions in the vitreous domain of the phase diagram. If reliable results can be obtained about the Al-O pairs, it is more difficult to interpret the results around the Sr-O correlations. A XAS analysis has been performed recently and will give more precise information about these pairs. Results from x-ray diffraction experiments will give also additional structural information, in particular about the cation-cation pairs