Experimental report

17/02/2016

Proposal:	**6-03-432**	**Council:**	4/2014
Title:	Structural study of strontium aluminosilicate glasses and melts		
Research area:	Materials		

This proposal is a new proposal

Main proposer:	**Louis HENNET**
Experimental team:	Henry FISCHER Viviana CRISTIGLIO Didier ZANGHI DANIEL NEUVILLE Louis HENNET Alexey NOVIKOV Margarita FOMINA
Local contacts:	Henry FISCHER

Samples: SrO-Al2O3-SiO2

Instrument	Requested days	Allocated days	From	To
D4	6	5	05/12/2014	10/12/2014

Abstract:

The aim of this proposal is to study the structure of strontium aluminosilicates SrO-Al2O3-SiO2 (SAS) in both the glassy and liquid states. This study will extend the previous work performed at the ILL on the CaO-Al2O3-SiO2 system and will help to better understand the formation of aluminosilicates glasses, widely used in the glass industry.

In particular, 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

Understanding the structure and dynamics of aluminosilicate glasses and melts with alkaline earth elements is of great interest for various technological applications: fabrication of glasses or glass ceramics, etc. In a previous experiment, we studied in details the structure of several calcium aluminosilicate (CAS) glasses at room temperature and in the liquid state (Exp. 6-05-816) [1]. In this work, we replaced Ca by Sr and we studied various compositions along the joins *R*=1 and 3 (*R*= SrO/Al_2O_3) in the ternary phase diagram $SrO-Al_2O_3-SiO_2$ (SAS). This leads to compounds with the general formula: $(SiO_2)_X(Al_2O_3)_Y(SrO)_{100-X-Y}$ referenced as SAX.Y. The compositions of all studied samples are summarized in Table I.

Sample	*R*	Glass	Melt	SiO_2 (mol%)	Al_2O_3 (mol%)	CaO (mol%)
SA0.50	1		X (2000°C)	0.0	50.0	50.0
SA20.40	1	X	X (1750°C)	20.0	40.0	40.0
SA33.33	1	X	X (1750°C)	33.3	33.3	33.3
SA42.29	1	X	X (1850°C)	42.0	29.0	29.0
SA50.25	1	X		50.0	25.0	25.0
SA57.21	1	X		57.0	21.5	21.5
SA63.18	1	X		63.0	18.5	18.5
SA76.12	1	X		76.0	12.0	12.0
SA0.25	3	X	X (1950°C)	0.0	25.0	7.0
SA20.20	3		X (2050°C)	20.0	20.0	60.0
SA33.17	3	X	X (1750°C)	33.0	17.0	50.0
SA42.14	3	X		42.0	14.0	44.0
SA50.12	3	X		50.0	12.5	37.5
SA60.10	3	X		60.0	10.0	30.0

Table I. SAS 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 0.3–23.5 $Å^{-1}$.
For all compositions, measurements were performed on the glass at room temperature (RT) and/or on the melt. For the high temperature measurements, we used the aerodynamic levitation setup specifically designed for neutron diffraction at D4c and well described by Hennet et al. [2]. The temperature of the sample is reported in table I for each studied melt.

-II- Glasses at Room Temperature

The total structure factors *S*(*Q*) of the SAS glasses (RT) along the joins *R*=1 and 3 are presented in Figures 1 and 3 respectively. In both cases, by increasing the SiO_2 concentration the main visible differences concern the first peak which shifts towards lower *Q* values with a corresponding increase in intensity. This shows that the structure becomes more ordered with increasing silica concentration. A similar behaviour was observed with CAS glasses [1]. It was attributed to an increase of the ring size from 4 to 6 members for low and high silica content [3].

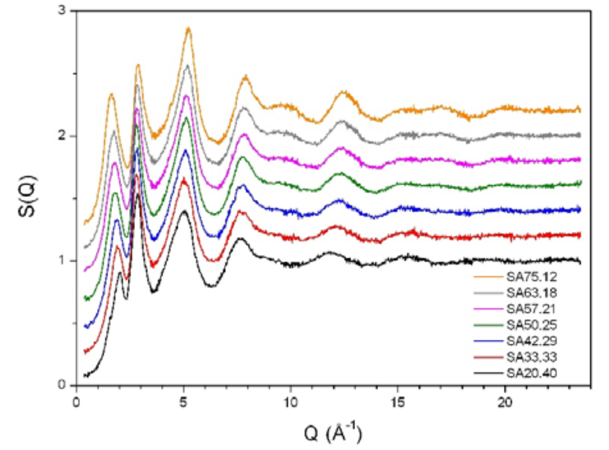

Figure 1. Total structure factors *S*(*Q*) for the SAS glasses (RT) along the join *R*=1 obtained from neutron diffraction.

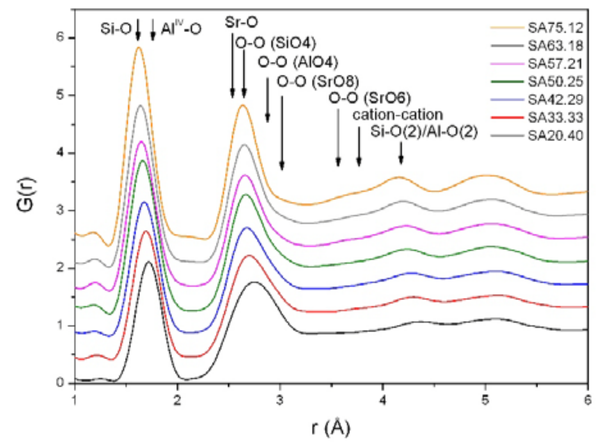

Figure 2. Total pair distribution function *G(r)* for the SAS glasses (RT) as obtained by Fourier transforming the corresponding total *S*(*Q*) (*R*=1).

Figures 2 and 4 show the corresponding total pair distribution functions *G(r)*. For SA0.25 (Figure 4), the first peak arises purely from the contribution of the nearest neighbor Al-O correlations. Its position found at about 1.76 Å is characteristic of 4-fold coordinated aluminium. This is in good agreement with results obtained with NMR and Raman spectroscopies which found Al in Q2 species [4]. The next peak at *r*~2.53 Å corresponds to Sr-O correlations and is partially overlapped by the peak at *r*~2.82 Å corresponding to the O-O bond distance in AlO_4 tetrahedra. For the join *R*=3, by increasing the SiO_2 content, only a single peak is visible in *G(r)* at about 2.66 Å (figure 4). This peak is now an overlap of 3 main contributions. (i) the Sr-O correlations with a contribution decreasing from 37% (SA0.25) down to 18% (SA60.10), (ii) the increase in the O-O correlations coming from the SiO_4 tetrahedra which give rise to a peak at *r*=2.65 Å. (iii) the contribution of the O-O correlations coming from the AlO_4 tetrahedra whose intensity decreases also progressively by adding silica, due to the decrease of the Al content.

The distance found for the Sr-O bonds corresponds to an octahedral configuration which gives rise to O-O correlations at about 3.6 Å where a small peak is observed in figure 4.

The same observations can be made for the join *R*=1 (figure 2). However, an additional contribution is found at *r*~2.53 Å and could correspond to 8-fold coordinated Sr, difficult to evidence due to the large overlap of the Sr-O and O-O contributions.

The next peak at *r*~3.8 Å, weakly probed, could corresponds to the cation-cation correlations, Finally, the barely resolved peaks at *r*~4.3 and *r*~5.1 Å correspond to correlations with the second oxygen neighbors.

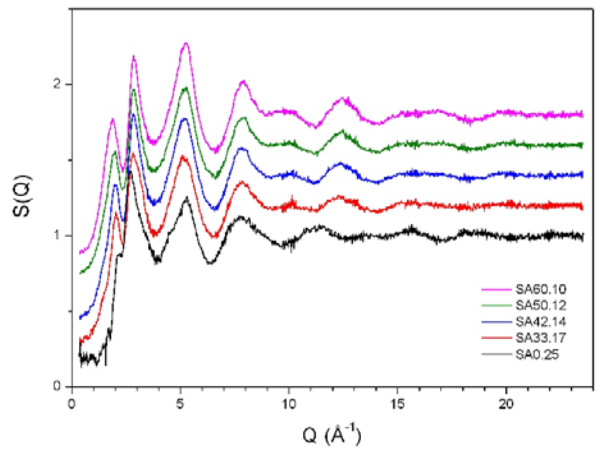

Figure 3. Total structure factors *S*(*Q*) for the SAS glasses (RT) along the join *R*=3 obtained from neutron diffraction.

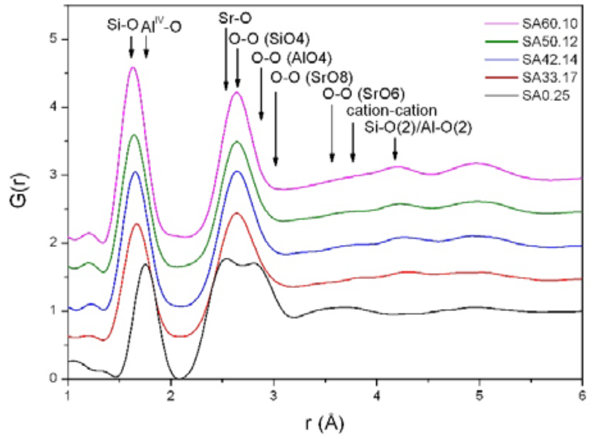

Figure 4. Total pair distribution function *G(r)* for the SAS glasses (RT) as obtained by Fourier transforming the corresponding total *S*(*Q*) (*R*=3).

-III- High temperature measurements

Various SAS compositions with Silica content up to 42% were measured in the liquid state at temperatures close to their respective melting points. The measurement acquisition time was the same as for room temperature measurements.

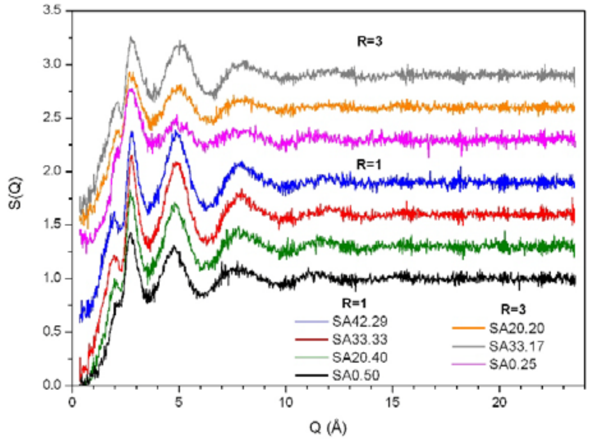

Figure 5. Total structure factors *S*(*Q*) for the SAS melts obtained from neutron diffraction.

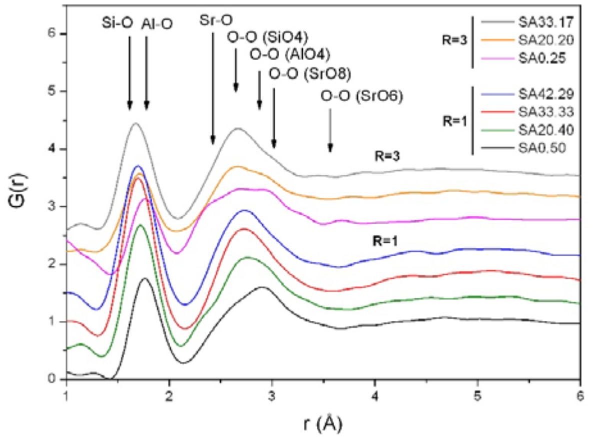

Figure 6. Total pair distribution function *G(r)* for the SAS melts as obtained by Fourier transforming the corresponding total structure factors.

Figure 5 shows the obtained static structure factors for the different compositions. Compared to the glasses, all liquid structure factors are noisier, notably due to the smaller sample volume exposed to the beam. The FSDP is almost at the same position, but its intensity is much lower than that for the glass. This is a signature of a less ordered system.

This increase in the structural disorder in the liquid is also detected in the pair distribution functions presented in Figure 6 where broader peaks are observed.

For the compositions without silica, Al-O correlations are found at a slightly higher distance of about 1.78 Å. This could suggest an increase of the number of AlO_5 units in the melt as observed with some Calcium aluminates [1]. Additional NMR experiment will give more details about coordination numbers.

The short range order around Sr, seems largely modified and shows a complex configuration. A first Sr-O contribution is present at distances shorter than 2.53 Å, meaning that Sr-O with coordination lower than 6 should be present. All pair distribution functions exhibit also a peak at about 3 Å corresponding to O-O distances in SrO_8 polyhedra. Finally some correlations observed between 3 and 3.6 Å could be attributed to O-O bonds for 7-fold coordinated Sr.

-IV- Conclusion

The objective of the neutron diffraction experiment was to study the short and medium range order of strontium aluminosilicates in the glassy and liquid states. The first analysis presented here shows interesting results in particular about the short range order around Sr atoms. Large overlaps with O-O bonds make the interpretation difficult and a precise data treatment has to be performed.

The comparison with x-ray diffraction and absorption experiments performed recently on the same compositions will be helpful to derive reliable structural information on these SAS glasses and melts.

-V-References

[1] L.Hennet, J.W.E.Drewitt, D.R.Neuville, V.Cristiglio, J.Kozaily, S.Brassamin, D.Zanghi, H.E.Fischer, submitted to J. Non-Cryst. Solids.

[2] L. Hennet, I. Pozdnyakova, A. Bytchkov, V. Cristiglio, P. Palleau, H. E. Fischer, G. J. Cuello, M. Johnson, P. Melin, D. Zanghi, S. Brassamin, J-F. Brun, D. L. Price and M-L. Saboungi, Rev. Sci. Instrum. 77 053903 (2006).

[3] D. R. Neuville, L. Cormier, A. M. Flank, V. Briois and D. Massiot, Chem. Geol. 213 (2004) 153-163

[4] M. Licheron, V. Montouillout, F. Millot, D.R. Neuville, J. Non-Cryst. Solids, 257, 2796-2801 (2011).