ESRF	**Experiment title:** Structural study of glassy and levitated liquid MO-Al_2O_3 and MO-Al_2O_3-Y_2O_3 (M=Sr, Ba)	**Experiment number**: HD-610
Beamline: ID11	**Date of experiment**: from: 23/01/2013 to: 29/01/2013	**Date of report**: 26/02/2016
Shifts: 18	**Local contact(s)**: Jon Wright	*Received at ESRF:*

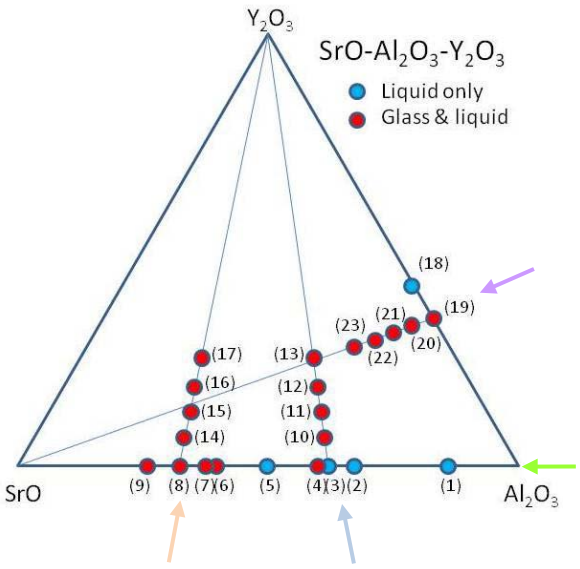
Names and affiliations of applicants (* indicates experimentalists):

Dr, A. BYTCHKOV, ESRF, Grenoble, France *
Dr M. LICHERON, CEMHTI, Orléans, France **
Dr L. HENNET, CEMHTI, Orléans, France **
Mrs S. BRASSAMIN, CEMHTI, Orléans, France
Dr D. ZANGHI, CEMHTI, Orléans, France **
Dr V. CRISTIGLIO, ILL, Grenoble, France **
Dr H. E FISCHER, ILL, Grenoble, France **

Report:

The aim of these X-ray diffraction experiments was to study the structure of various aluminate glasses $SrO-Al_2O_3$, $BaO-Al_2O_3$, $SrO-Al_2O_3-Y_2O_3$ at room temperatures and in the liquid state. The list of the studied compositions is given below and reported in the phase diagram for Sr based glasses and melts.

	SrO (mol%)	Al_2O_3 (mol%)	Y_2O_3 (mol%)	$SrO/(SrO+Al_2O_3)$	Liquid	Glass
1	14	86	0	0.14	X	
2	33	67	0	0.33	X	
3	38	62	0	0.38	X	
4	40	60	0	0.40	X	X
5	50	50	0	0.50	X	
6	60	40	0	0.60	X	X
7	62.5	37.5	0	0.625	X	X
8	67.5	32.5	0	0.675	X	X
9	75	25	0	0.75	X	X
10	35.62	58.13	6.25	0.38	X	X
11	33.25	54.25	12.5	0.38	X	X
12	30.87	50.38	18.75	0.38	X	X
13	28.5	46.5	25	0.38	X	X
14	63.28	30.47	6.25	0.675	X	X
15	59.06	28.44	12.5	0.675	X	X
16	54.84	26.41	18.75	0.675	X	X
17	50.63	24.37	25	0.675	X	X
	SrO (mol%)	**Al_2O_3 (mol%)**	**Y_2O_3 (mol%)**	**$Y_2O_3/(Y_2O_3+Al_2O_3)$**	**Liquid**	**Glass**
18		62.5	37.5	0.375	X	
19		70	30	0.3	X	X
20	6.25	65.63	28.12	0.3	X	X
21	12.5	61.25	26.25	0.3	X	X
22	18.75	56.88	24.37	0.3	X	X
23	25	52.5	22.5	0.3	X	X
	BaO (mol%)	**Al_2O_3 (mol%)**	**/**	**$BaO/(BaO+Al_2O_3)$**	**Liquid**	**Glass**
24	14	86		0.14	X	
25	33	67		0.33	X	X
26	67.5	32.5		0.675		X
27	70	30		0.7		X
28	75	25		0.75	X	X



The liquid state was achieved using an aerodynamic levitation system combined with laser heating. The setup includes a levitation chamber enabling XRD measurements in a transmission mode. The heating system is constituted by two CO_2 lasers and the temperature is measured using an optical pyrometer. Two gas cylinders containing oxygen and pure argon were connected together with mass flow controllers in order to vary the amount of oxygen from 20% down to pure argon.

Diffraction experiments were carried out using the Frelon 2D-detector available at the beamline and enabling the use of relatively short counting times. In order to derive structure factors with a wide *Q* range, we worked at an energy of about 100 keV. This configuration gave a $Q_{max} \sim 25 Å^{-1}$.

Figure 1 shows the structure factors *S(Q)* obtained with some $SrO\text{-}Al_2O_3$ compounds in the liquid state at 1900°C (samples 5 and 9) and in the glassy state at room temperature (samples 4 and 9). It shows strong evolutions with the composition (compare S9 and S5 liquids or S4 and S9 glasses). The differences observed between the *S(Q)*s of $(SrO)_{75}(Al_2O_3)_{25}$ at room and high temperatures is mainly due to thermal effects.

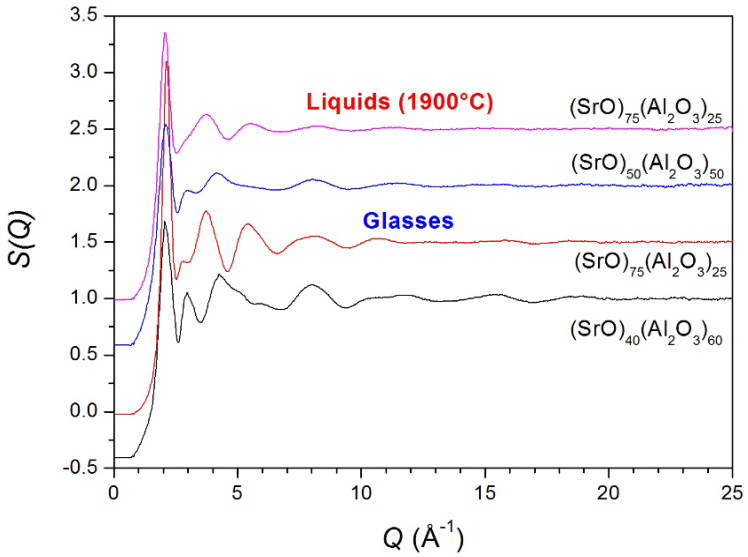


Figure 1. Structure factors S(Q) obtained with:

- Sample 5: $(SrO)_{50}(Al_2O_3)_{50}$ at 1900°C
- Sample 9: $(SrO)_{75}(Al_2O_3)_{25}$ at 1900°C & RT
- Sample 4: $(SrO)_{40}(Al_2O_3)_{60}$ at RT

Figure 2 shows the corresponding pair distribution function *g(r)* obtained with a Fourier transform of *S(Q)*.

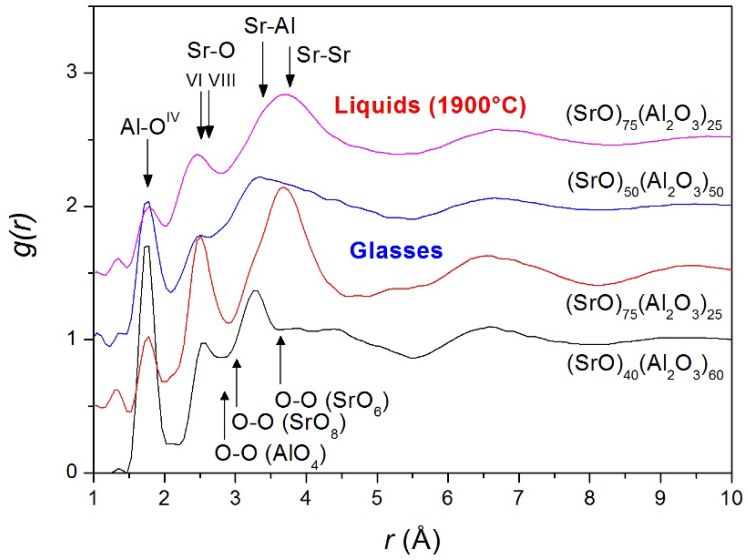


Figure 2. Pair distribution functions *g(r)* obtained with:

- Sample 5: $(SrO)_{50}(Al_2O_3)_{50}$ at 1900°C
- Sample 9: $(SrO)_{75}(Al_2O_3)_{25}$ at 1900°C & RT
- Sample 4: $(SrO)_{40}(Al_2O_3)_{60}$ at RT

For all samples, 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. Then O-O correlations coming from the AlO_4 tetrahedra should give rise to a peak at *r*~2.82 Å (overlapped by other contributions). The next peak at *r*~2.5 Å corresponds to Sr-O correlations. With the glass samples, we observe a decrease of the position from 2.57 Å (40% of SrO) down to 2.53 Å (75% of SrO) Å. This effect could be attributed to a decrease of the Sr-O coordination number from about 7 down to 6. A precise fit of the data is necessary to conclude.

As seen in table I, the weighing factor for the Sr-Sr correlations has the highest value (0.367) for $(SrO)_{75}(Al_2O_3)_{25}$. This means that the intense peak observed at 2.7 Å is mainly due to the Sr-Sr pairs. For the lowest Sr-O concentration (40%), the Sr-Sr contribution is largely reduced whereas the one from Sr-Al and Al-Al is increased. We can conclude that the shoulder in the left part of the Sr-Sr contribution can be due to Sr-Al pairs and that the peak at 3.28 Å, well visible with the sample 4 (40% SrO) is a contribution of both Al-Al and Sr-Sr correlations.

Atomic Pairs	$(SrO)_{40}(Al_2O_3)_{60}$	$(SrO)_{50}(Al_2O_3)_{50}$	$(SrO)_{75}(Al_2O_3)_{25}$
Al-O	0.235	0.181	0.071
Sr-O	0.228	0.264	0.310
O-O	0.133	0.111	0.065
Sr-Sr	0.098	0.156	0.367
Sr-Al	0.202	0.214	0.168
Al-Al	0.104	0.074	0.019

Table I. Weighting factors of atomics pairs for the 3 presented compositions.

The comparison with additional results obtained recently from neutron diffraction, more sensitive to the oxygen environment, will be helpful to have a better idea of the structure. We also performed recently EXAFS experiments that will provide specific information on the local order around Sr atoms.

Figure 3 shows the pair distribution function *g(r)* obtained with the $(MO)_{75}(Al_2O_3)_{25}$ (M=Sr or Ba) at room temperature. For both systems the local order is very similar. The visible differences are due to the longer ionic radius of Ba compared to Sr (+0.17 Å) which shifts the position of pairs containing Ba to the right. All pairs which not involve Ba or Sr (Al-O, O-O and Al-Al) stay at the same position.

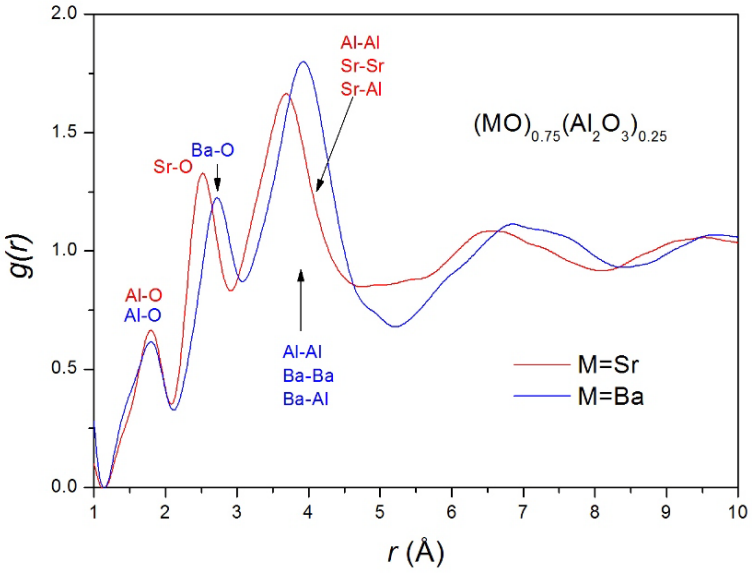


Figure 3. Pair distribution functions *g(r)* obtained with:

- Sample 9: $(SrO)_{75}(Al_2O_3)_{25}$ glass
- Sample 28: $(BaO)_{75}(Al_2O_3)_{25}$ glass

The data treatment of the ternary compounds is more difficult since the signal is now due to correlations coming from 10 atomic pairs. In addition, the Y-O contribution, expected around 2.3 Å, leads to large overlaps with the Sr-O correlations (found around 2.5 Å). Additional EXAFs measurements at the Y-K absorption n edge are needed to go further in the analysis.