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Neutron diffraction of calcium aluminosilicate glasses and melts.

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Abstract

The combination of neutron diffraction with aerodynamic levitation and laser heating, pioneered by Neville Greaves and co-workers about 15 years ago, is an important tool for studying the structure of liquid melts. Since the first work on liquid Al_2O_3 published in 2001, the technique has been largely improved and experiments are now routinely performed at neutron sources, providing interesting structural information on various materials.

In this paper, the structure of glass-forming compounds in the system CaO-Al_2O_3-SiO_2 was measured by applying neutron diffraction with aerodynamic levitation. Results obtained in the liquid state above the melting point and from the glass at room temperatures are presented. Various compositions were studied by increasing the silica content and by changing the ratio CaO/Al_2O_3. As observed using other methods, the main structural changes relate to modification of the Al-O short range order.

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1 Introduction

Calcium aluminosilicate, CaO-Al$_2$O$_3$-SiO$_2$ (CAS), glasses and melts are of both technological and scientific interest. In particular their good optical and mechanical properties [1,2] and their refractory nature make them attractive for a wide range of industrial applications, including the production of concrete [3,4]. CAS melts are also the main components of slags produced in furnaces in coal and steel industries. In geosciences, they are of fundamental importance as they form a significant fraction of the composition of geological magmas [5,6,7].

The thermodynamic and dynamic properties of CAS show a strong dependence with the microscopic structure [8]. It is, therefore, important to study in detail the high temperature properties of the melts. In order to study the liquid state, we used the aerodynamic levitation technique combined with CO$_2$ laser heating. This technique was pioneered about 15 years ago by Neville Greaves with teams from the University of Aberystwyth (UK) and the CNRS-CEMHTI in Orléans (France) [9,10].

In this paper, we present results obtained from various CAS glass compositions at both room temperature and in the liquid state. Some of these glass compositions have already been studied by x-ray diffraction at room temperature [11,12] but only a few have been analyzed by neutron diffraction, in particular along the join R=1.57 [11,13]. Here and in the following, the R value is defined as the ratio CaO/Al$_2$O$_3$. In the liquid state only the compositions without silica have been studied extensively [14,15]. Our first results obtained for CAS liquids with low silica content have been reported recently in combination with Molecular Dynamics (MD) simulations. [16]. A recent work is also devoted to the study of CAS slags with other compositions [17]. The objective of the present investigation is to complete these previous works by extending the range of CAS compositions studied by neutron diffraction in

order to better understand the structure of the glasses and melts, in relation with the observed properties.

2 Technical details

2.1 Sample preparation

The samples were prepared from high purity crystalline $CaCO_3$, Al_2O_3 and SiO_2 powders. The appropriate quantities of powders were melted at 1600°C for 4 hours in a platinum crucible and then quenched to room temperature. The resulting materials were grinded and re-melted several times in order to ensure a good homogeneity of the glasses. A full description of the sample preparation is described in Neuville et al. [18]. The required quantity of material for each sample was then levitated in air using an argon-oxygen (~3%) gas flow and melted by laser heating. Rapid quenching, achieved by switching off the laser power, resulted in the formation, on cooling, of solid spherical samples with diameters of 4 mm (for the glass measurements) and 2.7 mm (to investigate the liquid state under levitation). The samples studied are listed in Table I. As in previous works, we employ the notation Cax.y, where x and y refer to the molar concentration of SiO_2 and Al_2O_3, respectively, and 1-x-y is the CaO molar content. The precise molar compositions of the glasses are reported in Neuville et al [7,19].

2.2 Neutron diffraction

The neutron diffraction (ND) measurements were made using the aerodynamic levitation and laser heating device installed on the D4C diffractometer [20] at the Institut Laue–Langevin (Grenoble, France), as described in ref [21]. Diffraction measurements were taken for the liquid samples at temperatures above the melting point for all studied compositions, for the empty levitation device inside the diffraction chamber, and for vanadium samples with the aim of making an absolute normalization of the scattering intensity to barns.st^{-1}.atom^{-1}. The neutron wavelength and zero-angle shift were determined by

3

fitting the positions of the Bragg peaks obtained from a reference nickel sample. The neutron wavelength used during the experiment was 0.4969 Å, giving a scattering vector Q-range of 0.3-23.6 Å^{-1}. The data processing was performed using the program CORRECT [22] which corrects the data for attenuation, background, multiple scattering and inelasticity (Placzek) effects. Since, for various technical reasons, there can be appreciable uncertainties with respect to the relative beam-illuminated volumes of the vanadium samples compared to the CAS samples using the levitation technique, we found it more accurate and reliable to perform an auto-normalization of the scattered intensity from the CAS samples. Specifically, the high-Q asymptote of the sample's intensity (after accounting for the Placzek inelasticity effect) was scaled so as to be equal to the theoretical self-scattering that depends only on the known composition of the sample. We then also confirmed that the atomic number density required for accurate normalization of the r-space function $G(r)$ (see equation in section 3.2) was equal to the theoretical atomic number density, thereby acting as an r-space consistency check of our auto-normalization performed in Q-space.

3   Experimental results

3.1   Structure factors

The total structure factors $S(Q)$ of all studied samples at room temperature and in the liquid state are presented in figure 1. For all compositions, room and high temperature measurements are very similar with only a few differences due principally to thermal effects which increase the structural disorder. This means that the short range order is very close in the glasses and melts. As observed for the compositions along the composition lines R=1 and 3, by increasing the SiO$_2$ content, the first peak (FSDP) in $S(Q)$ shifts towards lower Q values with a higher intensity. This shows that the degree of intermediate-range order, higher in the glassy state, is improved by incorporating silica into the structure. Although the FSDPs

are less visible in the liquid state, they seem to be at the same positions found for the glasses

and the same Q shift is observed with increasing SiO_2 content.

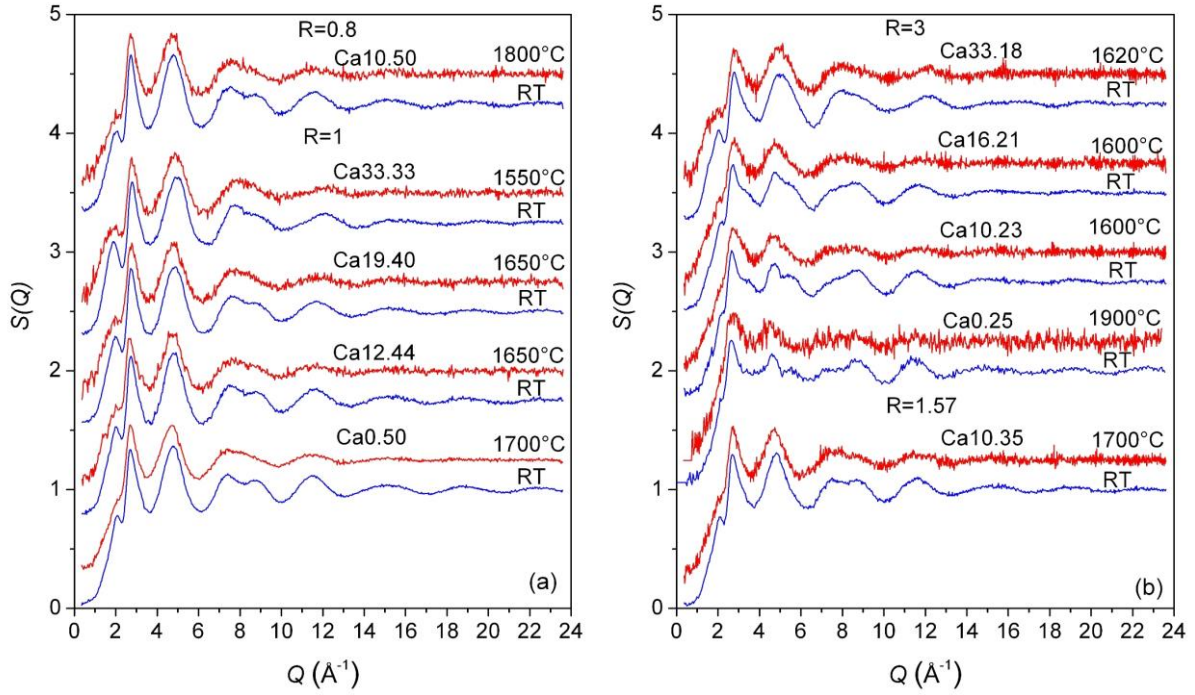Figure 1. Total structure factors $S(Q)$ of the CAS glasses and liquids for R=0.8 and 1 (a) and R=1.57 and 3 (b). The liquid temperatures are reported in the figure.

3.2   Pair distribution functions

The total pair distribution function is calculated from the structure factor by the Fourier

transform:

$$G(r) - 1 = \frac{1}{2\pi^2 r \rho_0} \int_0^\infty [S(Q) - 1] Q \sin(Qr) \mathrm{d}Q \,,$$

where ρ_0 denotes the atomic number density. All values are listed in Table 1. For

glasses they were calculated using densities measured with the Archimedean method applying

toluene as immersion liquid [7,23]. For melts, they were derived from densities determined by
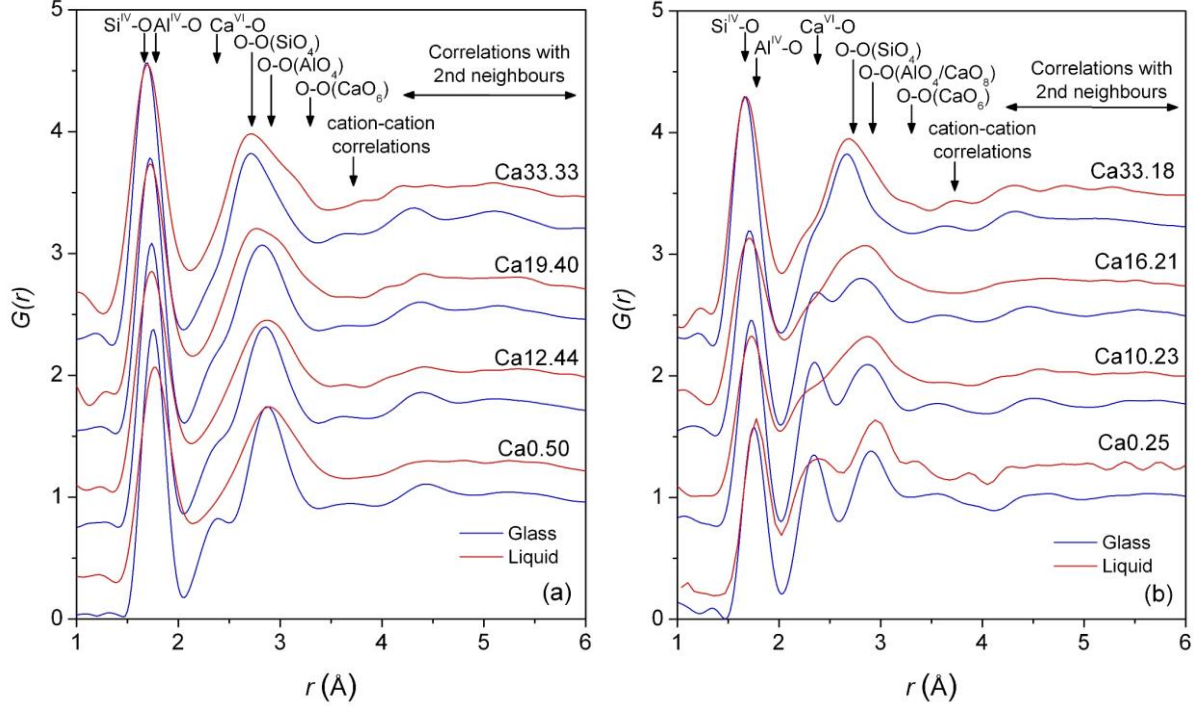
Courtial and Dingwell [24]..

Figure 2. Total pair distribution functions $G(r)$ for the CAS glasses and liquids along the composition lines R=1 (a) and R=3 (b). The positions of the various O-O correlations, as calculated assuming SiO_4 and AlO_4 tetrahedra and CaO_6 octahedra, are shown as a guide. The oscillations above r=4 Å arise from correlations between second neighbours.

Figure 2 shows the total pair distribution functions $G(r)$ for all the compositions studied along the joins 1 and 3.

The calcium aluminate compositions Ca0.50 and Ca0.25 have previously been studied in detail using neutron and x-ray scattering techniques in combination with MD and RMC simulations [14,25]. For these two compositions, the first peak found respectively at 1.76 and 1.74Å in the glass arises purely from the contribution of the nearest neighbour Al-O correlations. On melting, the observed shift of its position towards higher values is characteristic of an increase of the proportion of AlO_5 units in the structure (see data reported in Table I). In all G(r)s, the peak at around 2.3-2.35 Å arises from Ca-O bonds and is less resolved in the melt. In particular, the Ca-O peak broadens in the Ca0.25 composition and becomes barely resolvable from the next O-O correlations in the Ca0.50 melt, thus complicating the structural analysis. Further measurements of the Ca0.50 glass and melt have been made by applying the method of neutron diffraction with isotopic substitution (NDIS)

[26], which combined with the use of MD simulations, provides much more detailed structural information on the Ca-O coordination environment.

With the introduction of silica, the first peak corresponds to an overlapped contribution from both the Al-O and the Si-O nearest neighbour pairs. Its position moves gradually toward the Si-O bond distance as the SiO_2 content is increased. It becomes more difficult to determine the respective contributions of the Si-O and Al-O bonds, and the Ca-O correlations are also affected by the associated increase of the O-O contribution from SiO_4 tetrahedra that largely overlaps the peak and make the analysis more difficult. For composition along the join R=1.57, a detailed structural study have been made using x-ray and neutron diffraction experiment [13] and with Reverse Monte Carlo and MD simulations [27].

NMR experiments performed on all these glass compositions show that Al is 4-fold coordinated along the join R=3 up to 20% silica content and with small amounts of AlO5 units above and along the join R=1 (values are reported in table I for all compositions) [19]. For all liquids, only a small enlargement is observed on the high *r* side of the first peak. This is in accordance with an increase of the number of the AlO_5 units observed to elongate the Al-O distance in the Ca0.50 melt [26]. With CAS compounds, cation-cation correlations contribute much less to the total $G(r)$ than cation-O bonds and give rise only to small features found around 3.5 Å.

The determination of the coordination numbers and bond distances is performed using a Gaussian fit to the correlation function *T(r)=4πrρ₀g(r)* as described in Hannon and Parker [28]. Results of the fits are presented in figure 3 for glasses (a) and melts (b). In each case, only the two extreme compositions along the lines R= 1 and 3 are presented. The complete results are summarized in table I.

For the silicate samples, the Gaussian fit was performed by fixing the coordination number of the Si-O bond around 4 leading to a Si-O bond length of 1.62 Å in the glasses and

1.65 Å in the liquid state. For all samples, the average coordination numbers of Al–O bonds are found to be around 4 in accordance with NMR results [19]. Assuming perfect tetrahedra (angle of 109.47), it is possible to estimate the O-O bond length for SiO_4 and AlO_4 as 2.62 and 2.83 Å, respectively, in the glass. The Ca-O distance found around 2.32 Å is characteristic of 6-fold coordinated Ca as found in previous works [13,14,**16**,30]. Considering perfect CaO6 octahedra, an O-O distance of 3.28 Å is calculated (2.32 x √2). The positions of these three calculated O-O bond distances are indicated in figure 2. This shows that the shape of the wide O-O correlations which give distances between 2.5 and 3.5 Å can be reasonably described by the contribution of these 3 pairs. However, higher coordinated Ca found in previous works [13,29] would give rise to O-O correlations at positions between those for AlO_4 and CaO_6 polyhedra and cannot be excluded. Indeed, the Ca-O correlations for 7- and 8-fold coordinated Ca are expected around 2.4 and 2.5 Å and if present they are thus difficult to resolve.

As seen previously, accurate information about the Ca-O local structure is difficult to obtain due to large overlapping contributions from the O-O correlations and temperature effects which broaden the peaks. This precludes the determination of Ca-O coordination number from our total structure measurements. By comparison to XANES experiments at the Ca-Kedge, Ca was estimated to be in regular 6-fold coordination in C3A glass (Ca0.25), 7-fold coordination in CA (Ca50.00) with localized 6- to 7-fold coordination sites in CAS glasses [18,30]. A recent NDIS study of the Ca50.00 composition found a Ca coordination number of 6.2 in the liquid state and around 6.4 in the glass [26]. This shows that the use of more selective techniques than conventional ND are important in order to more precisely determine the atomic arrangement around Ca atoms. Recently, NDIS experiments have been made to investigate the structure of liquid Ca0.25 [31].
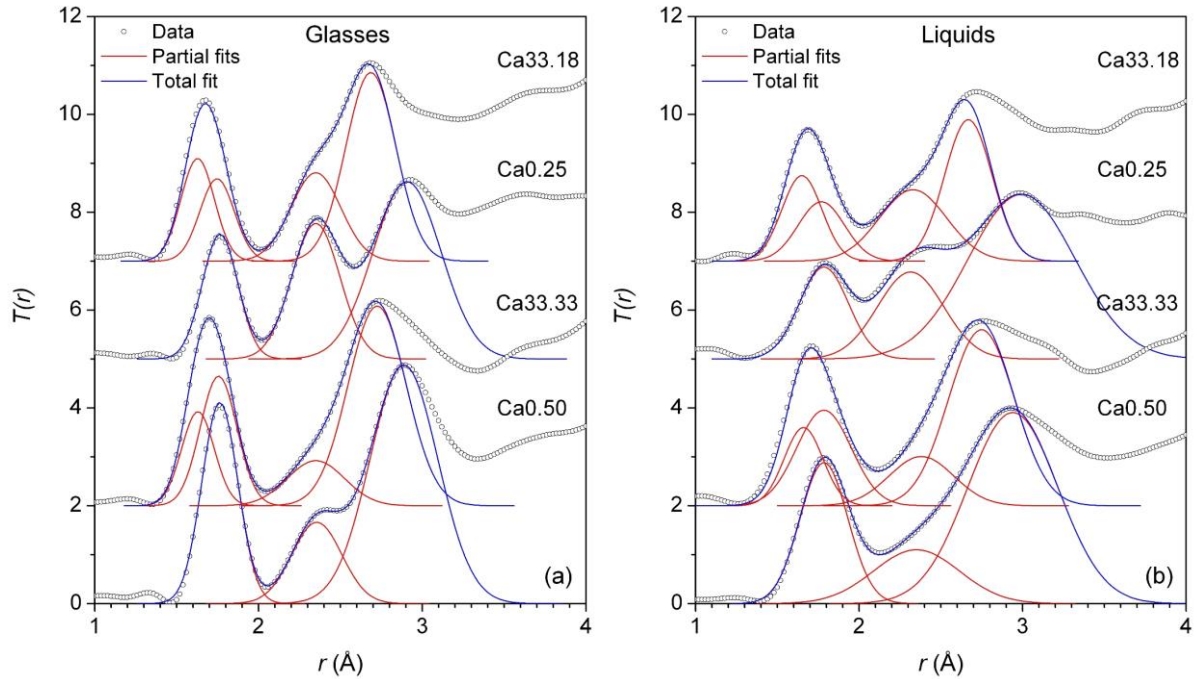
Figure 3. Total correlation function $T(r)$ for the compositions bearing 0 or 33% of SiO_2 along the joins R=1 and 3 for glasses (a) and melts (b). The partial fits and the final result are compared with the experimental data.

4 Discussion

As shown in various papers [26,29,30], the Ca0.25 glass (R=3) has a structure composed by tetrahedraly coordinated Al, Q^2 species with 2 bridging (BO) and 2 non-bridging (NBO) oxygen atoms, and Ca in a regular six fold coordination. With increasing the Al_2O_3 content, Al changes from Q^2 to a mixture of Q^3 and Q^4 species for Ca0.39 (R=1.57) [27] and Q^4 in the Ca0.50 glass (R=1) associated to some proportion of AlO5 units to ensure the cationic mobility as shown in [19,30]. This change in the Q species distribution implies a decrease of the number of NBO leading to the observed increase of the viscosity with the Al_2O_3 content [30].

With adding silica along the join R = 3, the distribution of Al into Q species increases also from Q^2 to Q^4 for the Ca23.21 (not studied in this paper) as shown in Al NMR, Raman spectroscopy and XANES at the Al K-edge [19]. In this case, the increase of the SiO_2 content, produces an increase of the polymerization of Al from Q^2 to Q^4 because Si atoms are in Q^0

species and concentrate all NBOs around them. For the Ca33.18 composition, the Q species of Si increase from Q^0 to Q^1 whereas Al Q species stay in Q^4 and some AlO5 units appears.

Along the join $R=1$, which is the charge compensation line, the glasses are then fully polymerised and by using XANES experiments at the Ca absorption edge, Neuville *et al* explained the evolution of the FSDP by an increase of the ring size from 4 to 5 members for low and high silica content [18]. When R is increased, Ca atoms play the role of network modifiers with the creation of NBOs leading to less ordered structure.

In the silicate glasses, the first peak in $G(r)$ is a weighted sum of the Si-O and Al-O correlations. By fixing the tetrahedral configuration of the SiO_4 units during the fit to $T(r)$, it is possible to derive reasonable Al-O bond lengths of 1.74-1.76 Å and 1.76-1.78 Å in the glasses and melts, respectively. The Al-O coordination numbers are slightly higher in the melts, reflecting an increased proportion of AlO_5 units for most of the compositions. It can be noted that with an error bar of $\pm$ 0.5 neutron scattering technique is not sensitive enough to reproduce the evolution of the coordination numbers determined with NMR at room temperature (see table I). For Ca0.25, if the distance Al-O at room temperature found at 1.74 Å is characteristic of purely 4-fold coordinated Al in accordance with the amount of AlO5 (Table1), the found coordination number of 4.2 is a bit high, although it is within the error bar of ± 0.5. This could be explained with a possible small influence of the Ca-O correlation (highest concentration) but more probably by an overestimation of the density, measured on a sample using a different cooling rate. New density measurements will be performed directly on the measured sample and ongoing x-ray scattering experiment on theses glass compositions will also enable to conclude. At high temperatures, there is no precise determination of the AlO5 content and the main results come from MD simulation (some of them are reported in Table I). For C3A, one can see that different values can be obtained, depending on the calculation method.

The study of Ca-O correlations is more difficult due to large overlapping O-O contributions. From a simple Gaussian fit, it seems that the bond distances (summarized in Table I) and thus the coordination number, doesn't change by increasing the silica content along the joins R=1 and 3. Depending on the temperature and the composition, the Ca-O coordination number is then expected to be between 6 and 7 by comparison with a previous study [26,30]. However, a more sophisticated fit including all contributions is needed to get more accurate information on the Ca-O correlation and take into account existing Ca with higher coordination.

The small effect of the increase of the silica content was also observed by Cormier et al along the join R=1.57 [13,27]. They found that even at low silica contents, silicon becomes part of the aluminate network and thus attributed the changes observed on the dynamics to structural rearrangements at medium range order.

The large number of atomic pairs in the CAS system complicates the data analysis. In order to have a full description of the short range order for these compositions, additional high temperature EXAFS measurements at the Ca-K absorption edge would be useful. Indeed, existing works are limited to very few melt compositions [30]. Using diffraction, it is necessary to use more selective techniques. The Ca X-ray absorption edge at 4.038 keV precludes the use of anomalous scattering experiments as performed with liquid Y_2O_3 [32]. NDIS is then a good solution, despite the long counting times required due to the relatively small size of the levitated spheres.

In addition of these experimental techniques, interesting information can be also derived from MD and/or RMC simulations. Drewitt et al studied various calcium aluminate melts including Ca0.50 and Ca0.25 [14]. From these simulations, they derived information about the distribution of coordination numbers for Ca and Al and the various bond angle distributions provide insight into the connectivity of polyhedra. L. Cormier et al studied in details some glasses along the join R=1.57 [27] and in addition of the previous

informationthey got also information on the ring statistics, the distribution of the Q species, the number of NBOs, or the existence of triclusters. This interplay between triclusters, NbOs and AlO5 units was also studied by MD simulation for the low silica content composition along the join R=1 [16] enabling to derive also valuable information on the dynamics [33].

5   Conclusion

This study shows that the use of neutron diffraction combined with levitation techniques is an important tool for deriving structural information from liquid materials and to obtain useful information about coordination numbers and bond lengths.

In this work we showed that limited structural changes are observed by increasing the ratio CaO/Al_2O_3 or the SiO_2 content in CAS glasses. At high temperatures a small increase in the Al-O coordination number is observed. This is due to the presence of a larger fraction of AlO_5 units. The short range order around Ca remains almost unchanged over the whole composition range studied. These observations are in good agreement with previous results obtained with other techniques. The combination of these results with simulations will make it possible to derive reliable information in the liquid state and in particular about the dynamics.

	R	T (°C)	ρ_0 (Å⁻³)	r^{Si-O} ± 0.02 Å	r^{Al-O} ± 0.02 Å	r^{Ca-O} ± 0.05 Å	CN^{Si-O} ± 0.5	CN^{Al-O} ± 0.5	AlO5 units
Ca10.50	0.8	RT	0.0783	1.62	1.75	2.32	4.04	4.09	4.2%
		1800	0.0745	1.65	1.76	2.34	4.05	4.26	/
Ca0.50	1	RT	0.0773	/	1.75	2.35	/	4.05	3.5%
		1700	0.0734	/	1.78	2.32	/	4.20	15%,18% [14,25]
Ca12.44	1	RT	0.0772	1.62	1.76	2.34	4.02	4.07	4.5%
		1650	0.0737	1.65	1.77	2.32	4.05	4.18	10% [33]
Ca19.40	1	RT	0.0773	1.62	1.76	2.34	4.08	4.05	5.8%
		1650	0.0737	1.65	1.77	2.34	4.05	4.10	8% [33]
Ca33.33	1	RT	0.0770	1.62	1.75	2.34	4.05	4.06	8%
		1550	0.0735	1.65	1.77	2.36	4.05	4.23	/
Ca10.35	1.57	RT	0.0758	1.62	1.76	2.35	4.04	4.11	2.6%
		1700	0.0716	1.65	1.77	2.32	4.05	4.15	1.2 [27]
Ca0.25	3	RT	0.0723	/	1.74	2.34	/	4.20	0%
		1900	0.0632	/	1.77	2.32	/	4.20	5%;10% [14,34]
Ca10.23	3	RT	0.0736	1.62	1.75	2.34	4.02	4.05	0%
		1600	0.0684	1.65	1.77	2.30	4.05	4.18	/
Ca16.21	3	RT	0.0744	1.62	1.75	2.34	4.08	4.09	0%
		1600	0.0691	1.65	1.76	2.30	4.04	4.20	/
Ca33.18	3	RT	0.0759	1.62	1.74	2.34	4.05	4.12	7%
		1620	0.0703	1.65	1.76	2.32	4.05	4.19	/

Table I Summary of the structural parameters for all samples. The join composition is indicated as well as the proportion of AlO5 units in glasses determined by NMR [19] and melts from MD simulations.

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