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# Diffraction study of calcium aluminate glasses and melts: I. High energy x-ray and neutron diffraction on glasses around the eutectic composition

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## Abstract

A series of four  $(\text{CaO})_x \cdot (\text{Al}_2\text{O}_3)_{(1-x)}$  glasses over the narrow compositional range  $x = 57.1\text{--}66.7$  have been studied using high energy x-ray and neutron diffraction. The coordination number of oxygen around aluminum was determined as 4 at all compositions. The coordination number of oxygen around calcium was extracted using a first-order difference method and found to be in the range of 5.2–5.5 up to a distance of 2.75 Å for all compositions, with the possibility of additional correlations at higher distances. The results are in good agreement with two recent molecular dynamics simulations and confirm an asymmetric distribution of CaO correlations in the glass structure.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Binary calcium aluminates  $\text{CaO}\text{--}\text{Al}_2\text{O}_3$  (CA) are abundant in nature and have considerable technological value as optical and structural materials. From a structural viewpoint CA glasses are of interest since they do not contain any of the traditional glass network forming oxides [1]. The CA phase diagram has been reported by Nurse *et al* [2] and there are 13 crystalline CA phases (see compilation by Ampian *et al* [3]), 3 of which lie within the narrow compositional range of this study; C4A3, C5A3 and C12A7. Many of these are of interest from the geological standpoint and are common components of hydraulic cements [4]. CA materials are promising as cold electron emitters, thermionic power generators and refrigeration devices. The crystalline C12A7 (Mayenite) phase can be modified to produce an electrically

conducting phase with delocalized electrons [5, 6]. CA-based glasses exhibit infrared transmission to ca 5500 nm and have potential applications as infrared optics and windows, laser hosts [7], high strength optical fibers, and photomemory materials [8–12].

CA liquids are relatively good glass formers only in a narrow composition range [13] although a wider range can be obtained by splat cooling or containerless methods. Wallenberger *et al* produced CA glass fibers containing 13.8 wt% barium oxide [14]. Pilkington electro-optic materials produced large plates (15 cm × 15 cm × 0.8 cm) of an infrared transparent CA-based glass containing barium and magnesium oxides<sup>6</sup>. McMillan and Piriou [15] carried out Raman spectroscopy on several CA glasses and crystals and interpreted the 50% CaO glass spectrum in terms of a fully polymerized network of tetrahedral aluminate units. The glass network is depolymerized by the addition of CaO and

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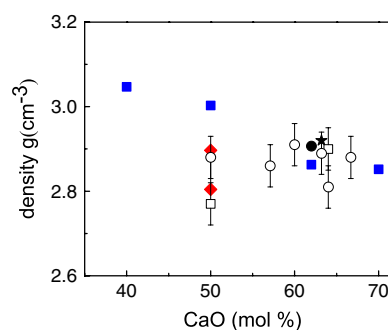
<sup>6</sup> Pilkington Type BS39B calcium aluminate glass specification.

it was suggested that between 60 and 70% CaO there is a ‘transition region’ between structures signified by a loss of Raman band structure. McMillan [13] also carried out  $^{27}\text{Al}$  MAS-NMR measurements on glasses along the CaO– $\text{Al}_2\text{O}_3$  join, prepared by fast (splat) quench techniques and slow cooling in levitation experiments. Fast-quenched glasses with >50%  $\text{Al}_2\text{O}_3$  contained Al coordinated by five and six oxygens, in addition to the dominant fourfold coordinated species. However for glasses with <50%  $\text{Al}_2\text{O}_3$  only four-coordinated aluminum was found. McMillan has also suggested that  $\text{OAl}_3$  triclusters i.e. three tetrahedral Al atoms each sharing the same oxygen, may break up upon quenching these glasses from the melt [16]. High-resolution solid-state NMR has been used to determine the fraction of oxygen triclusters in CA glass and it is found that there is 5% of tricluster both from the O and Al signature [17].

The structure of CA glasses has been measured using x-ray and neutron diffraction techniques. The first study was reported by Morikawa *et al* [18] using conventional x-ray diffraction measurements on a 63.2 mol% CaO splat-quenched glass close to the eutectic composition. The data was interpreted in terms of three different crystalline models and pentacalcium trialuminate ( $\text{C}_5\text{A}_3$ ), which consists of a network of five membered rings of  $\text{AlO}_4$  tetrahedra, gave the best agreement with the measured radial distribution function. Hannon and Parker [19] studied the structure of splat-quenched calcium aluminate glasses containing 62 and 70 mol% CaO by high-resolution pulsed neutron diffraction. Their results confirmed the tetrahedral coordination of Al, and found a calcium coordination number of four with an average Ca–O bond length of 2.34 Å. It was proposed on the basis of bond valence calculations that more distant Ca–O correlations should be present and were obscured by the O–O correlations resulting in an effective coordination number of 6. Cormier *et al* [20] performed both neutron and x-ray diffraction measurements on a water-quenched glass containing 61 mol% CaO. Aluminum was found to be coordinated on average by 4.1 oxygens and calcium by 4.7 oxygens at a distance of 2.36 Å, however it was suggested that the Ca atoms resided in distorted (non-Gaussian) octahedral sites.

Benmore *et al* [21] performed pulsed neutron and high energy x-ray diffraction on CA glasses containing 50 and 64 mol% CaO. The samples were produced by the containerless cooling of liquid droplets heated by a laser beam and suspended in an aerodynamic levitator. The results show Al on average to be surrounded by 4.0 oxygen atoms and Ca to be surrounded by 5.6 oxygens in the 50% CaO glass. However, in the 64% CaO glass the average Al coordination number was observed to increase to  $\sim 4.8$  oxygens and the calcium coordination number found to fall to 3.9. By combining the neutron and x-ray data sets it was possible to remove the O–O correlations from the neutron diffraction spectra, but no additional Ca–O peaks could be observed up to 2.7 Å.

Recently two molecular dynamics simulations have been performed on calcium aluminate glasses. Kang *et al* [22] showed Al to be tetrahedrally coordinated by oxygen at 70% CaO, with the proportion of five and sixfold coordination increasing as the  $\text{Al}_2\text{O}_3$  content is increased, and a Ca



**Figure 1.** The density of calcium–aluminate glasses versus composition: this study with additional measurements on 50% and 64% CaO (open circles), Benmore *et al* [21] (open square), Hannon *et al* [19] (black solid circle), Morikawa *et al* [18] (black star), Kang *et al* [22] (simulation, blue squares). Also shown are two liquid density measurements on CA (with <1 mol%  $\text{Nd}_2\text{O}_3$ ) by Paradis *et al* [40] at 1560 and 2000 K (red diamonds).

coordination number ranging from 5.6 to 5.9. Thomas *et al* [23] also find a dominant tetrahedral network for a 62.5% CaO glass with an average of 6.2 oxygens around Ca. Both simulations suggest the low Ca coordination number observed in diffraction experiments may be explained by an additional asymmetric distribution of Ca–O correlations with a tail extending out to  $\sim 3.0$  Å. When considered in light of the crystal structures (see Ampian *et al* [3] and table 5 of Kang *et al* [22]) we note that although the Ca–O coordination number can vary between 4 and 12, the correlations do not extend beyond 2.7 Å for Ca–O coordination numbers <7. To gain a better understanding of the distorted Ca environment in the CA glass, we have performed high energy x-ray diffraction and neutron experiments on several CA glasses.

## 2. Experiments

The glass samples with the nominal compositions of 66.7, 63.2, 62.5 and 57.1 mol% CaO were made by the containerless melting and cooling of liquid droplets suspended in an aerodynamic levitator. Application of the levitator has been reported in our previous work on aluminate liquids [24, 25]. Samples were made from high purity mixtures of calcium carbonate and aluminum oxide powder, which were milled, fused and milled again to achieve homogenization of the mixture. Portions of this mixture were then fused in to ca 3 mm diameter spheroids using a  $\text{CO}_2$  laser beam [26]. Approximately 40 glass spheroids were synthesized to provide about 2 g of glass material. The densities of the glasses were measured using a pycnometer with distilled water as the immersion fluid which was corrected for any temperature variation. The measured densities in this work are compared with previously reported values in figure 1.

During the x-ray data analysis it is possible to verify the nominal sample compositions against the atomic form factors which are generally reliable to within  $\sim 1\%$  [27]. This was found to work reliably for the glass compositions 66.7, 63.2 and 57.1% CaO, but not for the 62.5% CaO composition, for which the x-ray analysis suggested 59% CaO. An ICP

**Table 1.** The coordination number (CN) and peak positions (R) of Al–O and Ca–O correlations in CA glasses around the eutectic composition, determined from neutron (N), x-ray (X) and first-order difference (X–N) functions.

% CaO	Al–O			Al–O		Ca–O		Al–O		Ca–O		Number density ( $\text{\AA}^{-3}$ )
	CN	RAIO		CN	RAIO	CN	RCaO	CN	RAIO	CN	RCaO	
	N	N	RCaO	X	X <sup>b</sup>	X	X <sup>b</sup>	X–N <sup>c</sup>	X–N <sup>b</sup>	X–N	X–N <sup>b</sup>	
	$\pm 0.2$	$\pm 0.005 \text{ \AA}$	N <sup>a</sup> ( $\text{\AA}$ )	$\pm 0.2$	$\pm 0.01 \text{ \AA}$	$\pm 0.3$	$\pm 0.01 \text{ \AA}$	$\pm 0.2$	$\pm 0.01 \text{ \AA}$	$\pm 0.3$	$\pm 0.01 \text{ \AA}$	
C2A 66.7%	3.84	1.764	$2.355 \pm 0.005$	4.13	1.79	5.47	2.39	4.17	1.80	5.26	2.39	0.0729
C12A7 63.2%	3.84	1.764	$2.362 \pm 0.008$	4.16	1.79	5.59	2.39	4.19	1.80	5.32	2.39	0.0741
C3A2 59.0%	3.86	1.756	$2.378 \pm 0.012$	4.17	1.78	5.68	2.40	4.20	1.79	5.48	2.40	0.0756
C4A3 57.1%	3.88	1.756	$2.393 \pm 0.015$	4.16	1.78	5.53	2.40	4.18	1.79	5.16	2.40	0.0747

<sup>a</sup> The compositional range is narrow enough that the errors on the x-ray peaks and neutron Al–O peaks (position and coordination number) are invariant with composition. This is not the case for the neutron Ca–O peak which suffers from a strong overlap with the third O–O peak in  $G(r)$  with increasing  $\text{Al}_2\text{O}_3$  content.

<sup>b</sup> The errors on the x-ray related peak positions are larger than for the neutron due to the uncertainties in the incident beam energy calibration, although the statistical errors are less for the x-ray data.

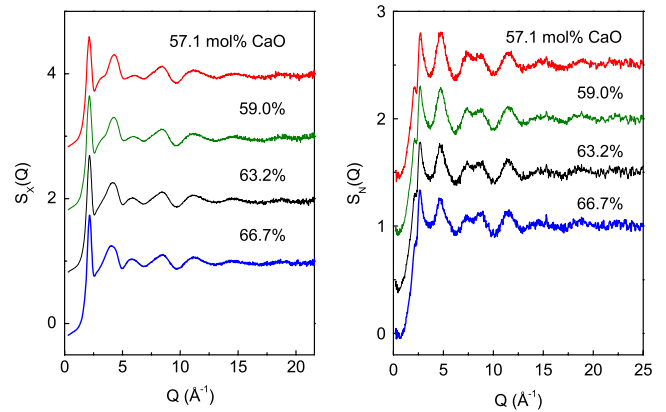
<sup>c</sup> The advantage of the difference method is that no assumptions are made in fitting peak shapes. The disadvantage is that it is prone to larger systematic errors, which are larger in the x-ray function which dominates the difference, as indicated by the larger unphysical oscillations in  $G(r)$  and  $\Delta G(r)$ .

analysis of the sample supported this conclusion indicating a composition of  $60 \pm 1\%$  CaO.

High energy x-ray measurements were performed using 1 mm  $\times$  1 mm square beam on the ID-11-C beamline at the Advanced Photon Source (APS) using a solid-state Ge detector [28]. The incident energy in this experiment was calibrated with known gamma ray sources and found to be  $115.1 \pm 0.8$  keV. The samples were contained in a 10  $\mu\text{m}$  thin Kapton windows arranged such that only the sample and the windows were in the path of the x-ray beam. Background measurements were made on the adjacent part of the Kapton window where there is no sample to obtain the scattering contribution from the container. Pulsed neutron diffraction measurements were made on the Glass, Liquid and Amorphous Diffractometer (GLAD) at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory [29]. About 1 g of the same batch of glass beads were contained in a thin walled vanadium can with an inner radius of 3 mm. Neutron measurements were also performed on the instrumental background, empty vanadium can and a 6 mm diameter solid vanadium rod.

### 3. Data analysis

For the x-ray data analysis, corrections were made for detector deadtime, container scattering and Compton scattering. The software program *ISOMER-X* [30] was used to reduce the high energy x-ray diffraction data. At the high x-ray energies used, the x-rays act as a bulk probe, and attenuation and multiple scattering effects were assumed to be negligible. The incident x-ray beam energy was calibrated independently from our diffraction measurements using a radioactive source. In the neutron scattering data analysis, corrections were made for container scattering, attenuation, multiple scattering, inelastic scattering and normalized to the scattering from a vanadium rod. This was performed using the *ISAW* software package for time-of-flight neutron diffraction data [31]. The neutron scattering lengths were obtained from Sears [32] and the atomic form factors and Compton scattering from the tabulated

**Figure 2.** The measured total x-ray (left) and neutron (right) structure factors for the different composition CA glasses.

values of Hubbell [33]. The measured number densities for the glasses were listed in table 1.

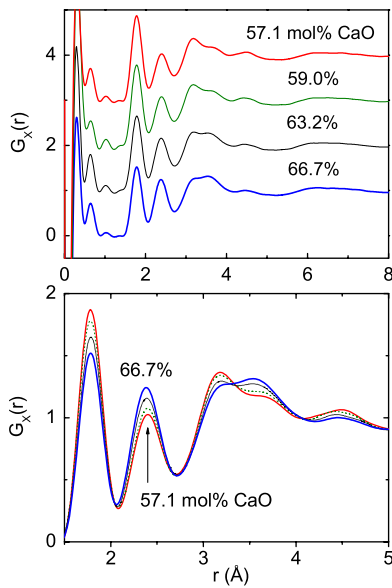
The formalism used in this study has previously been outlined by Benmore *et al* [21]. In brief, the x-ray  $S_X(Q)$  and neutron  $S_N(Q)$  structure factors have been obtained and Fourier transformed to give the corresponding x-ray and neutron radial distribution functions  $G_X(r)$  and  $G_N(r)$ , respectively.

### 4. Results

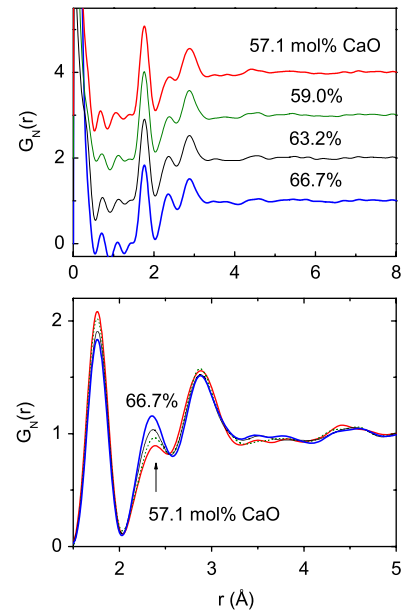
Figure 2 shows the total high energy x-ray and neutron structure factors for  $(\text{CaO})_x \cdot (\text{Al}_2\text{O}_3)_{(1-x)}$ , where  $x = 57.1, 59.0, 63.2$  and  $66.7$ . The poorer statistics on the neutron data were due to the small amount of sample available produced using the containerless technique. Figures 3 and 4 show the corresponding total high energy x-ray and neutron pair distribution functions for CaO–Al<sub>2</sub>O<sub>3</sub> glasses. The peaks at  $\sim 1.76 \text{ \AA}$  is assigned to Al–O bonds and the peak at  $\sim 2.39 \text{ \AA}$  is assigned to Ca–O bonds. The peak positions are listed in table 1, together with the calculated coordination number for Al–O and Ca–O. There exists some discrepancy in first two

**Table 2.** The coordination number (CN) of Al–O and Ca–O in CA glasses close to the eutectic composition compared to literature values. The variation in the CaO CN is primarily due to different integration ranges or methods used in the analyses (see text). Errorbars for this study are given in the top row.

% CaO	Technique	CN (AlO)	$r$ (AlO) Å	CN (CaO)	$r$ (CaO) Å
Eutectic (CaO) <sub>64</sub> (Al <sub>2</sub> O <sub>3</sub> ) <sub>36</sub>		±0.2	±0.01 Å	±0.4	±0.01 Å
Glass (this study 63.2%)	HEXRD & Neutron	4.0	1.77	5.32	2.39
Glass (63.2%) [18]	XRD	4.2	1.77	5.6	2.37
Glass (62%) [19]	Neutron	3.97	1.75	4.00	2.34
Glass (61%) [20]	Neutron	4.1	1.76	4.7	2.36
Glass (64%) [21]	HEXRD & Neutron	4.7	1.76	3.9	2.40
		4.8	1.76	—	—
Glass (62%) [22]	MD simulation	4.14	1.76	5.57	2.32
Glass (62.5%) [23]	MD simulation	4.0	1.77	6.2	2.40



**Figure 3.** The total x-ray radial distribution functions for different composition CA glasses (top), and the changes in the local structure compared in detail (bottom). The curves were obtained by Fourier-transforming the total structure factors of figure 2 after the data sets were truncated at  $Q_{\max} = 21.6 \text{ \AA}^{-1}$ . A Lorch function was applied to reduce Fourier artifacts. In the bottom plot 57.1% CaO is represented by the solid red line, 59.0% CaO by the green dashed line, 63.2% CaO by the thin black dotted line and 66.7% CaO by the thick solid blue line.



**Figure 4.** The total neutron radial distribution functions for different composition CA glasses (top), and the changes in the local structure compared in detail (bottom). The curves were obtained by Fourier-transforming the total structure factors of figure 2 after the data sets were truncated at  $Q_{\max} = 25 \text{ \AA}^{-1}$ . A Lorch function was applied to reduce Fourier artifacts. In the bottom plot 57.1% CaO is represented by the solid red line, 59.0% CaO by the green dashed line, 63.2% CaO by the thin black dotted line and 66.7% CaO by the thick solid blue line.

peak positions for Al–O and Ca–O between neutron data and x-ray data. We note that the main contribution for the peak shift in the neutron data around 2.39 Å with composition is from the overlapping contribution of the O–O correlation. The third peak at 2.88 Å in neutron  $G_N(r)$  arises from O–O correlation and this peak is not resolved in x-ray data due to the lower (but still significant) weighting factor of the O–O correlations. This correlation distance is in good agreement with published neutron data [19, 20] and slightly different ( $\sim 0.08 \text{ \AA}$ ) from the MD simulation results published by the same group [22].

The coordination number of oxygen around aluminum was determined to be 4.0, within a 5% error margin, for all the compositions of neutron and x-ray data. This is consistent with NMR results [13], which suggest glasses with  $\text{CaO}/\text{Al}_2\text{O}_3 \geq 1$  contain only  $\text{AlO}_4$  groups. We note that the 64% CaO

eutectic glass  $S(Q)$  differs slightly from our previous  $S(Q)$  measurement on this glass composition [21]. The reason for this is unknown, although possibilities include a strong asymmetric overlap of the Ca–O peak with the Al–O peak or a small deviation from the nominal composition as we found for 62.5% CaO sample in this study. It is also noteworthy that the shift in position of the first diffraction peak suggests a small density difference between the two samples. Our new results are in better agreement with literature values (see table 2).

Coordination number of oxygen around calcium for neutron and x-ray data were calculated using several methods since the Ca–O and O–O correlations have significant overlap: (i) a 2-peak Gaussian fit (using the Faber–Ziman weighting factors at  $Q = 0 \text{ \AA}^{-1}$  for x-ray data) (ii) the coordination



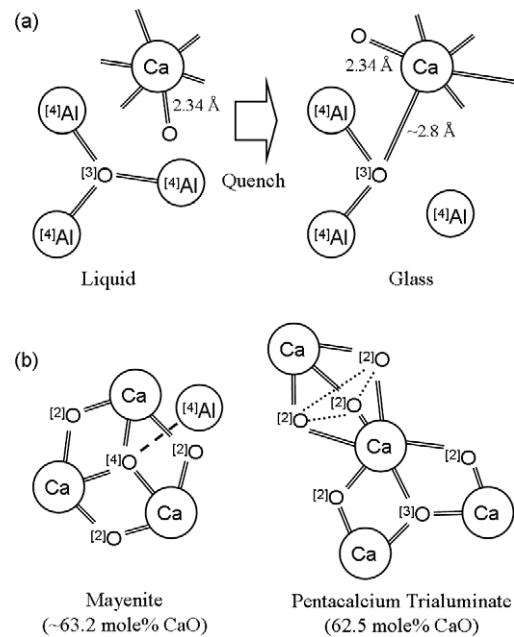
number of Ca–O for the x-ray data distribution functions were calculated using integral methods between two minimum values either side of the peak centered on 2.38 Å again using the Faber–Ziman weighting factors at  $Q = 0 \text{ \AA}^{-1}$  (iii) a 2-peak Gaussian model fit to the data in  $Q$ -space which takes into accounts in the  $Q$ -dependence of the Faber–Ziman weighting factors obtained from atomic x-ray form factors. The difference between methods (i) and (iii) were found to be less than 1% in this system. The coordination number determined from high energy x-ray data varies in the range of 5.4–5.7, and it does not show any significant trend with the compositional variation outside the errorbars of this experiment (see table 1). This is consistent with the crystalline analogues over this compositional range, which show no discernable trend of the Ca–O coordination number change with composition [19].

In our measurements the third double peak feature observed in the x-ray radial distribution functions (see figure 3) are expected to be dominated by cation–cation distances on the basis of recent molecular dynamics simulations [22], but also contain a significant contribution from the O–O peak on the low- $r$  side, which is so prevalent in the neutron functions. These features shift systematically inward with increasing CaO content, from 3.21 and 3.64 Å in 57.1% CaO glass to 3.23 and 3.55 Å in 66.7% CaO glass. The peak at 4.51 Å in the 57.1% CaO glass is expected to be dominated by second nearest neighbor Al–O correlations [22] and moves to 4.41 Å at the eutectic composition.

## 5. Discussion

We have previously reported [21] that the radial distribution function for 50 mol% CaO glass is consistent with a fully polymerized three-dimensional network of Al tetrahedra as found in the crystalline tridymite-like structure of monocalcium aluminate. The Ca coordination number is about six in both the liquid and glass and by analogy with the crystal structure the calcium ion may be expected to occupy voids within the Al network. For the  $(\text{CaO})_x \cdot (\text{Al}_2\text{O}_3)_{(1-x)}$  system (where  $x \geq 0.5$ ), the aluminate network is considered to be modified through a decreased degree of polymerization by formation of more non-bridging oxygen atoms when the CaO is increased [13]. If  $Q^n$  represents an aluminum surrounded by  $n$  bridging oxygens, the fraction of  $Q^4$  is expected to decrease with the addition of CaO. Molecular dynamics simulations for the 62.5% CaO:37.5%  $\text{Al}_2\text{O}_3$  glass for example have found  $n = 3.3$  [23]. The slight increase of the Al–O bond length with increasing CaO content is likely an indication of the increasing fractions of  $Q^3$  and  $Q^2$  tetrahedra because  $Q^3$  tetrahedra has a longer average Al–O bond length than the  $Q^4$  site [34].

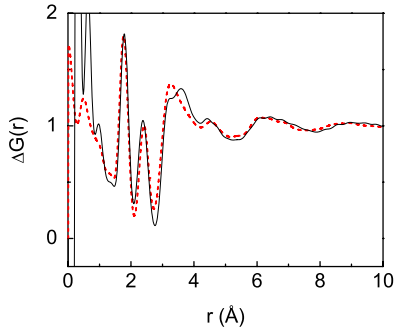
The O–Al–O average bond angles were calculated based on the first and third peak positions (assuming symmetric bond angle distributions) in the neutron radial distribution functions. It is found that O–Al–O bond angles are 110.4° and 109.2° for 57.1% CaO and 66.7% CaO glasses, respectively. This strongly supports that the glass network is dominated by  $\text{AlO}_4$  tetrahedra. MD simulations suggests that there is more than 30% of edge-sharing Al tetrahedra in CA glass and the fraction



**Figure 5.** (a) Schematic of the  $\text{OAl}_3$  tricluster model originally proposed by McMillan and co-workers (slightly modified figure 4 from [16]) that is consistent with the asymmetric distribution of Ca–O correlations to higher distances observed in the quenched glasses. (b) Schematic diagrams of edge shared Ca polyhedra in crystalline Mayenite (C12A7) [35] compared to both edge and face shared Ca polyhedra in crystalline pentacalcium trialuminate (C5A3) [36].

of edge-sharing tetrahedra decreases with further addition of CaO [22]. However, a signature of edge-sharing tetrahedra is a relatively short Al–Al distance of  $\sim 2.7 \text{ \AA}$  which cannot be confirmed directly by our experimental data, due to the low Faber–Ziman weighting factors of Al–Al in neutron and x-ray diffraction (2.3% for neutron and 8.8% for x-ray data at  $Q = 0 \text{ \AA}^{-1}$ ). According to MD simulations [22, 23], the existence of edge-sharing  $\text{AlO}_4$  tetrahedra and oxygen triclusters that connect three tetrahedra is more preferable compared to the  $\text{AlO}_5$  and  $\text{AlO}_6$  polyhedra in CaO-rich CA glasses.  $\text{OAl}_3$  triclusters are known to occur in aluminate crystals [15] and it has been suggested that as the liquid is quenched to the glass the triclusters break up and the Al network removes an oxygen only bound to a Ca ion (see figure 5).

In the 62.0% CaO glass the average number of oxygens surrounding a Ca atom has been reported to be 4 [19], this relatively low value has been called into question, since values of 6 or 7 occur in other crystal structures surrounding this composition [22]. There exists however, very different connectivity of the  $\text{CaO}_6$  polyhedra in the crystal structures of Mayenite ( $\sim 63.2 \text{ mol\% CaO}$ ) and pentacalcium trialuminate (62.5 mol% CaO), better known as ‘unstable C5A3’ to cement chemists. In Mayenite, three irregular Ca octahedra share edges, stabilized by a four-coordinated oxygen linking to an Al tetrahedra (see figure 5) to form two-dimensional sheet structures [35]. Whereas in crystalline Pentacalcium trialuminate,  $\text{AlO}_4$  tetrahedra form a network of five membered rings with a layered arrangement of Ca atoms. Some Ca–Ca distances are very short ( $\sim 3.2 \text{ \AA}$ ) resulting in some face-



**Figure 6.** The first-order difference function with the O–O correlations eliminated for the measured 63.2% CaO glass (thin black line) compared to the same function calculated for 62.5% CaO glass from molecular dynamic simulations [23] (dashed red line). Identical  $Q$ -ranges of 2.0–21.6  $\text{\AA}^{-1}$  were used for both data sets.

sharing (as well as edge-sharing)  $\text{CaO}_6$  polyhedra [36]. A major distinguishing factor is the Ca–Ca coordination number, which is 6 in crystalline pentacalcium trialuminate (62.5% CaO) and 4 in crystalline mayenite (63.2% CaO).

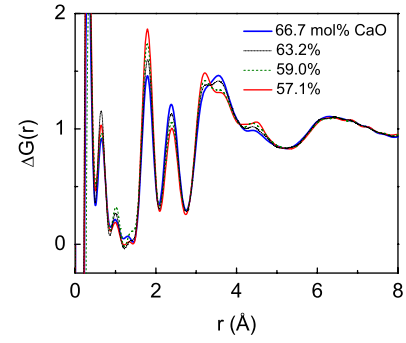
In order to isolate the CaO correlation from our data, we combine our neutron and x-ray structure factors to eliminate the O–O contribution from the structure factor using a first-order difference method. We note that the structure factor  $S(Q)$  is related to the Faber–Ziman partial structure factors [18] by,

$$S(Q) = \frac{I(Q)}{(\sum_{\alpha} c_{\alpha} W_{\alpha}(Q))^2} = \frac{1}{(\sum_{\alpha} c_{\alpha} W_{\alpha}(Q))^2} \times \sum_{\alpha, \beta} c_{\alpha} W_{\alpha}(Q) c_{\beta} W_{\beta}(Q) (S_{\alpha\beta}(Q) - 1) \quad (1)$$

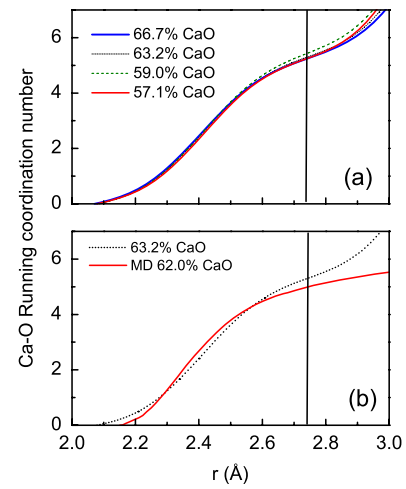
where  $c_{\alpha}$  is the atomic concentration of species  $\alpha$  and  $W_{\alpha}$  is the coherent scattering length,  $b_{\alpha}$ , for the neutrons [32] and the atomic form factor  $f_{\alpha}(Q)$  for x-rays [33].  $S_{\alpha\beta}(Q)$  are the Faber–Ziman partial structure factors [37]. The O–O correlation eliminated first-order difference structure factor can be obtained using a weighted combination of the neutron and x-ray structure factors:

$$\Delta S(Q) = \frac{1}{\left(1 - \frac{f_0^2(Q)(\sum_{\alpha} c_{\alpha} b_{\alpha})^2}{b_0^2(\sum_{\alpha} c_{\alpha} f_{\alpha}(Q))^2}\right)} \times \left(S_X(Q) - S_N(Q) \frac{f_0^2(Q)(\sum_{\alpha} c_{\alpha} b_{\alpha})^2}{b_0^2(\sum_{\alpha} c_{\alpha} f_{\alpha}(Q))^2}\right). \quad (2)$$

The scaling factor for the neutron data is, for example, 0.36 at  $Q = 0.3 \text{\AA}^{-1}$  for the 63.2% CaO glass, such that the better x-ray statistics still dominate the first-order difference function. The Fourier transform of  $\Delta S(Q)$  is the function  $\Delta G(r)$ , which is compared to that obtained from molecular dynamics (MD) simulations for 62.5% CaO [23] in figure 6. The overall agreement between the experiment and MD model is good except for some small deviations in the relative intensities of the 3.22 and 3.55  $\text{\AA}$  peaks, which mainly comprise of Al–cation and Ca–cation interactions respectively. These assignments are consistent with the intensity of the 3.22  $\text{\AA}$  peak decreasing with increasing CaO content and the 3.55  $\text{\AA}$



**Figure 7.** The first-order difference function with the O–O correlations eliminated for 66.7 mol% CaO glass (thick blue line); 63.2% CaO glass (thin dotted black line); 59.0% CaO glass (dashed green line) and 57.1% CaO glass (red line).



**Figure 8.** (a) The running coordination number of oxygen around calcium based on the integration of  $4\pi\rho \frac{(F)^2}{2c_{\text{Ca}}Z_{\text{Ca}}Z_{\text{O}}} \int_{r_0}^3 G(r)r^2 dr$  in which  $r_0$  is the minimum on the low- $r$  side of Ca–O peak. (b) The coordination number for 62.0% CaO from MD simulations is shown in comparison to the curve for 63.2% CaO [22]. The vertical line represents the estimated minimum distance at which Al–O correlations are expected to start contributing to the experimental function.

peak increasing (see figure 7). In this MD model [23] Ca is on average coordinated by three bridging oxygens and three non-bridging oxygens, and the Ca and O coordination environments were found to have a noticeable similarity with the C5A3 crystal, rather than crystalline C12A7, as previously noted by Morikawa *et al* [18].

The first-order difference functions with the O–O correlation eliminated were used to determine the Ca–O coordination number up to a distance of 2.75  $\text{\AA}$  after which second nearest neighbor Al–O correlations start to contribute to  $\Delta G(r)$ , as shown in figure 7 and table 1. Although MD simulations on CA glasses suggest that the Ca–O correlations have a non-Gaussian distribution with a long tail persisting to  $\sim 3 \text{\AA}$  [22], our CaO coordination number using this method would be overestimated at this distance. Figure 8(a) shows the coordination number of oxygen around calcium based on

the integration of  $4\pi\rho\frac{(F)^2}{2c_{\text{Ca}}Z_{\text{Ca}}Z_{\text{O}}}\int_{r_0}^3 G(r)r^2 dr$  in which  $r_0$  is the minimum on the low  $r$  side of Ca–O peak. A comparison of the running Ca–O coordination number with the data of Kang *et al* [22] is shown in figure 8(b). The good agreement between experiment and simulation up to 2.75 Å suggests that Ca ions are weakly bounded to oxygens and form highly distorted CaO polyhedra within the Al network.

Finally, we briefly consider possible underlying mechanism(s) for the broad asymmetric distribution of Ca–O correlations extending out to 2.7 Å and beyond: (i) OAl<sub>3</sub> tricluster break up (previously suggested by McMillan and co-workers) and (ii) the Ca–Ca polyhedra edge:face-sharing ratio.

Comparison of O<sup>17</sup> NMR spectra for crystalline Grossite (33.3% CaO) which contains OAl<sub>3</sub> triclusters has been used to provide evidence for their existence in calcium aluminosilicate glasses [38, 39]. The existence of significant numbers of tetrahedral triclusters in CA glasses is supported by recent molecular dynamics simulations near the eutectic glass composition which report 5% of the oxygens are in a tetrahedral tricluster arrangement [23]. Similar studies on the liquid structure are needed to observe if there is an appreciable increase in the Al–O distance which may be associated with tetrahedral tricluster formation.

Raman spectroscopy measurements carried out on several CA glasses and crystals by McMillan and Piriou [15] have indicated that between 60 and 70 mol% CaO there is a ‘transition region’ between *sheet* and *ring* structures of Al tetrahedral units signified by a loss of Raman band structure. The range brackets the eutectic composition and may explain the relatively easy glass forming behavior of the near-eutectic calcium–aluminum oxide binary compositions. Since calcium is a large divalent ion, its field strength is relatively small, such that rather weakly bound Ca–O polyhedra can be easily distorted as they pack between the more robust AlO<sub>4</sub> tetrahedra. If structural changes in the AlO<sub>4</sub> framework occur (due to OAl<sub>3</sub> tricluster break up upon quenching for example) it may be expected that the Ca–O environment would also change significantly e.g. elongated CaO bonds as proposed in figure 5(a). In order to explore the Ca–O correlations in the liquid-state x-ray experiments on different CA compositions are to be reported in a following paper.

## 6. Conclusions

High energy x-ray and neutron diffraction measurements have been performed on a series of (CaO)<sub>x</sub>·(Al<sub>2</sub>O<sub>3</sub>)<sub>(1-x)</sub> glasses produced by containerless techniques. The results show AlO<sub>4</sub> tetrahedra dominate the glassy network. A first-order difference function obtained by combining neutron and x-ray data to eliminate the O–O contribution is in good agreement with the same function obtained from a recent molecular dynamics simulation near the eutectic composition [23], suggesting some similarity with the local coordination environment of crystalline C5A3 across the compositional range studied  $x = 57.1\text{--}66.7\%$  CaO. The Ca–O running coordination number was also extracted from the first-order difference function and yields  $\sim 5.3$  oxygens around each Ca atom up to a distance of 2.75 Å. This is in good

agreement with that obtained from a compositional molecular dynamics study [22] and provides experimental evidence of an asymmetric distribution of CaO correlations at all the compositions studied.

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## References

- [1] Shepherd E S, Rankin G A and Wright F E 1909 *Am. J. Sci.* **28** 293
- [2] Nurse R W, Welch J H and Majumdar A J 1965 *Trans. Br. Ceram. Soc.* **64** 416
- [3] Ampian S G 1964 *US Bureau of Mines Reports* Report No 6428
- [4] Douy A and Gervais M 2000 *J. Am. Ceram. Soc.* **83** 70–6
- [5] Matsuishi S, Toda Y, Miyakawa M, Hayashi K, Kamiya T, Hirano M, Tanaka I and Hosono H 2003 *Science* **301** 626–9
- [6] Kim S W, Toda Y, Hayashi K, Hirano M and Hosono H 2006 *Chem. Mater.* **18** 1938–44
- [7] Chung W J and Heo J 2001 *J. Am. Ceram. Soc.* **84** 348–52
- [8] Hafner H C, Kreidl N J and Weidel R A 1958 *J. Am. Ceram. Soc.* **41** 315
- [9] Onoda G Y and Brown S D 1970 *J. Am. Ceram. Soc.* **53** 311
- [10] Davy J R 1978 *Glass Technol.* **19** 32
- [11] Dumbaugh W H 1985 *Opt. Eng.* **24** 257
- [12] Lines M E, MacChesney J B, Lyons K B, Bruce A J, Miller A E and Nassau K 1988 *J. Non-Cryst. Solids* **103** 279
- [13] McMillan P F, Petuskey W T, Cote B, Massiot D, Landron C and Coutures J P 1996 *J. Non-Cryst. Solids* **195** 261–71
- [14] Wallenberger F T, Weston N E and Brown S D 1991 *Mater. Lett.* **11** 229–35
- [15] McMillan P and Piriou B 1983 *J. Non-Cryst. Solids* **55** 221–42
- [16] Daniel I, McMillan P F, Gillet P and Poe B T 1996 *Chem. Geol.* **128** 5–15
- [17] Luga D, Morais C, Gan Z, Neuville D R, Cormier L and Massiot D 2005 *J. Am. Chem. Soc.* **127** 11540–1
- [18] Morikawa H, Marumo F, Koyama T, Yamane M and Oyobe A 1983 *J. Non-Cryst. Solids* **56** 355
- [19] Hannon A C and Parker J M 2000 *J. Non-Cryst. Solids* **274** 102
- [20] Cormier L, Neuville D R and Calas G 2000 *J. Non-Cryst. Solids* **274** 110
- [21] Benmore C J, Weber J K R, Sampath S, Siewenie J, Urquidi J and Tangeman J A 2003 *J. Phys.: Condens. Matter* **15** S2413
- [22] Kang E T, Lee S J and Hannon A C 2006 *J. Non-Cryst. Solids* **352** 725–36
- [23] Thomas B W M, Mead R N and Mountjoy G 2006 *J. Phys.: Condens. Matter* **18** 4697–708
- [24] Urbain G 1983 *Rev. Int. Hautes Temp. Refract.* **20** 135
- [25] Poe B T, McMillan P F, Cote B, Massiot D and Coutures J-P 1994 *J. Am. Ceram. Soc.* **77** 1823
- [26] Poe B T, McMillan P F, Cote B, Massiot D and Coutures J-P 1993 *Science* **259** 786–8
- [27] Ali M *et al* 2006 *Phys. Chem. Glasses: Eur. J. Glass Sci. Tech.* **B 47** 146
- [28] Rütt U, Beno M A, Stempfer J, Jennings G, Kurtz G and Montano P A 2001 *Nucl. Instrum. Methods A* **467** 1026–9
- [29] Ellison A J G, Crawford R K, Montague D G, Volin K J and Price D L 1993 *J. Neutron Res.* **4** 61



- [30] Urquidi J, Benmore C J, Neufeld J and Tomberli B 2003 *J. Appl. Crystallogr.* **36** 368
- [31] Tao J, Benmore C J and Worlton T G *et al* 2006 *Nucl. Instrum. Methods Phys. Res. A* **562** 422–32
- [32] Sears V F 1992 *Neutron News* **3** 26–37
- [33] Hubbell J H, Veigele W J, Briggs E A and Howerton R J 1973 *J. Phys. Chem. Ref. Data* **4** 471
- [34] Bartl H and Scheller T 1970 *Neues Jahrb. Mineral. Monatsh.* **1970** 547–52
- [35] Christensen A N 1987 *Acta Chem. Scand. A* **41** 110
- [36] Vincent M G and Jeffery J W 1978 *Acta Crystallogr. B* **34** 1422–8
- [37] Faber T E and Ziman J M 1964 *Phil. Mag.* **11** 153
- [38] Stebbins J F, Oglesby J V and Kroeker S 2001 *Am. Mineral.* **86** 1307–11
- [39] Allwardt J R, Lee S K and Stebbins J F 2003 *Am. Mineral.* **88** 949–54
- [40] Paradis P F, Yu J D, Ishikawa T and Yoda S 2003 *J. Am. Ceram. Soc.* **86** 2234–6