Structural Transformations on Vitrification in the Fragile Glass-Forming System CaAl$_2$O$_4$

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The structure of the fragile glass-forming material CaAl$_2$O$_4$ was measured by applying the method of neutron diffraction with Ca isotope substitution to the laser-heated aerodynamically levitated liquid at 1973(30) K and to the glass at 300(1) K. The results, interpreted with the aid of molecular dynamics simulations, reveal key structural modifications on multiple length scales. Specifically, there is a reorganization on quenching that leads to an almost complete breakdown of the AlO$_3$ polyhedra and threefold coordinated oxygen atoms present in the liquid, and to their replacement by a predominantly corner-sharing network of AlO$_4$ tetrahedra in the glass. This process is accompanied by the formation of branched chains of edge and face-sharing Ca-centered polyhedra that give cationic ordering on an intermediate length scale, where the measured coordination number for O around Ca is 6.0(2) for the liquid and 6.4(2) for the glass.

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Calcium aluminates (CaO)$_x$(Al$_2$O$_3$)$_{1-x}$ ($0 \leq x \leq 1$) have been extensively studied on account of their geological, technological, and scientific importance [1–20]. For example, they are a significant component of the Earth’s mantle so that the liquid structure is of interest for understanding magma-related processes [21], they are an integral component of aluminous cement [22], the glasses have a fragility index of 0.0031-9007/12/109(23)/235501(5) 235501-1 © 2012 American Physical Society

an ideal network of fully connected corner-sharing AlO$_4$ tetrahedra where the oxygen atoms are twofold coordinated, as in the crystalline phase which has a tridymite-like structure where the tetrahedra form a fully polymerized network of six-membered rings [29]. This has motivated a range of experimental and computer simulation studies on the liquid and glass structure [2–20]. It has, however, proved difficult to measure unambiguously the Al and Ca coordination environments. For example, in the liquid state $^{27}$Al nuclear magnetic resonance (NMR) experiments observe the fast exchange limit such that individual Al coordination environments cannot be identified [2–5], and in diffraction experiments, the nearest-neighbor Ca-O and other pair correlations are strongly overlapped [16–19]. The powerful method of neutron diffraction with isotope substitution has been used to probe directly the coordination environment of Ca in (CaO)$_{48}$(SiO$_2$)$_{40}$(Al$_2$O$_3$)$_3$ glass [30,31], but the method is usually limited to large samples [32]. In this Letter we show, however, that the neutron diffraction with isotope substitution method can be used to measure the detailed atomic structure of a single aerodynamically levitated liquid drop of liquid CaAl$_2$O$_4$ at 1973(30) K. The structure of the glass at 300(1) K is also investigated. The results, interpreted with the aid of molecular dynamics (MD) simulations, characterize the nature of the structural transformations that occur on vitrification on both the local and intermediate atomic length scales. The total structure factor measured by neutron diffraction is given by $F(Q) = \sum_a \sum_b c_a c_b b_a b_b [S_{a\beta}(Q) - 1]$.
where $S_{\alpha\beta}(Q)$ is a partial structure factor for chemical species $\alpha$ and $\beta$, $Q$ is the magnitude of the scattering vector, while $c_\alpha$ and $b_\alpha$ are the atomic fraction and coherent neutron scattering length of chemical species $\alpha$, respectively [32]. If three structurally identical samples of $\text{CaAl}_2\text{O}_4$ are prepared containing nat$^{44}\text{Ca}$ [$b_{\text{nat}} = 4.70(2)$ fm [33]], predominantly $^{44}\text{Ca}$ [$b_{44} = 1.45(6)$ fm] or a 50:50 mixture of the two $^{\text{nat}}\text{Ca}$ [$b_{\text{mix}} = 3.08(3)$ fm], then the Ca correlations will receive different weighting factors and give rise to observably different $F(Q)$ functions. The $S_{\alpha\beta}(Q)$ with $(\alpha, \beta) \neq \text{Ca}$ will, however, receive identical weighting factors and can therefore be eliminated by taking a difference function such as

$$\Delta^\text{Ca}(Q) \equiv [\text{nat}\ F(Q) - 44\ F(Q)] = c^2_{\text{Ca}}(b^2_{\text{nat}} - b^2_{44}) [S_{\text{CaCa}}(Q) - 1] + 2(c_{\text{Ca}}b_{\text{nat}} - b_{44})\delta^\text{Ca}(Q),$$

(1)

where $\delta^\text{Ca}(Q)$ involves only those $S_{\text{CaCa}}(Q)$ with $\beta \neq \text{Ca}$:

$$\delta^\text{Ca}(Q) = c_{\text{Al}}b_{\text{Al}}[S_{\text{CaAl}}(Q) - 1] + c_0b_0[S_{\text{CaO}}(Q) - 1],$$

(2)

$$b_{\text{Al}} = 3.449(5)\text{ fm and } b_0 = 5.803(4)\text{ fm [33]. Alternatively, the } S_{\text{CaCa}}(Q) \text{ with } \beta \neq \text{Ca} \text{ can be eliminated by taking a weighted difference function such as}

$$\Delta^\beta(Q) \equiv [b^\beta_{\text{nat}} 44\ F(Q) - b^\beta_{44}\text{nat} F(Q)]/(b_{\text{nat}} - b_{44}) = \delta^\beta(Q) - c^2_{\text{Ca}}b_{\text{nat}}b_{44}[S_{\text{CaCa}}(Q) - 1].$$

(3)

where $\delta^\beta(Q)$ involves only correlations with $(\alpha, \beta) \neq \text{Ca}$:

$$\delta^\beta(Q) = c^2_{\text{Al}}b^2_{\text{Al}}[S_{\text{AlAl}}(Q) - 1] + c^2_0b^2_0[S_{\text{O0}}(Q) - 1] + 2c_{\text{Al}}c_0b_{\text{Al}}[S_{\text{AlO}}(Q) - 1].$$

(4)

Moreover, $\delta^\gamma(Q)$, $\delta^\alpha(Q)$ and $S_{\text{CaCa}}(Q)$ can be extracted individually by solving the matrix equation

$$\begin{bmatrix}
\text{nat} F(Q) \\
\text{mix} F(Q) \\
44 F(Q)
\end{bmatrix} = \begin{bmatrix}
c^2_{\text{Ca}}b^2_{\text{nat}} & 2c_{\text{Ca}}b_{\text{nat}} & 1 \\
c^2_{\text{Ca}}b^2_{\text{mix}} & 2c_{\text{Ca}}b_{\text{mix}} & 1 \\
c^2_{\text{Ca}}b^2_{44} & 2c_{\text{Ca}}b_{44} & 1
\end{bmatrix} \begin{bmatrix}
S_{\text{CaCa}}(Q) - 1 \\
\delta^\gamma(Q) \\
\delta^\beta(Q)
\end{bmatrix}.$$ 

(5)

The real-space difference functions, denoted by $\Delta G^\text{Ca}(r)$, $\delta G^\text{Ca}(r)$, $\Delta G^\alpha(r)$, and $\delta G^\beta(r)$, are obtained by replacing each $S_{\alpha\beta}(Q)$ by its corresponding partial pair-distribution function $g_{\alpha\beta}(r)$ in Eqs. (1)–(4), respectively.

The samples were synthesized by melting mixed powders of $\text{Al}_2\text{O}_3$ (≥ 99.9%) and nat$^{56}\text{CaCO}_3$ (≥ 99%) or $^{44}\text{CaCO}_3$ (99.2% enrichment) in a platinum crucible using the method described in Ref. [12]. The resulting ceramics were levitated with argon gas (96.5% Ar, 3.5% O$_2$), melted using a CO$_2$ laser, and rapidly cooled by cutting the laser power [quench rate of ~420 K s$^{-1}$] at the melting point $T_{\text{mp}} = 1878$ K [16] slowing to ~300 K s$^{-1}$ at 1.25$T_g$ where $T_g = 1180(4)$ K [5,16] to form optically transparent and colorless spherical glass samples of diameter 2.54(1) or 3.18(1) mm for the liquid and glass diffraction experiments, respectively. The samples gave Raman spectra with bands at 558 and 785 cm$^{-1}$ that are characteristic of $\text{CaAl}_2\text{O}_4$ glass [7].

The neutron diffractometer D4c [34] was employed with an incident wavelength of 0.4978(1) A˚ to give a wide Q range extending to 23.45 Å$^{-1}$. The liquid experiments used the aerodynamic-levitation and laser-heating setup described in Ref. [35]. Diffraction patterns were measured for the samples at 1973(30) K levitated with argal gas, the empty levitator with a flow of gas, and a solid vanadium sphere of 3 mm diameter for calibration purposes. The glass experiments were made under vacuum. Diffraction patterns were measured for the samples resting on top of the levitator nozzle, for the empty levitator, and for a solid vanadium sphere of 4 mm diameter. Counting times were ~24 h for each sample. The atomic number density $\rho$ is 0.0734(5) Å$^{-3}$ for the liquid [36] and, as measured using Archimedes’ method, 0.0773(3) Å$^{-3}$ for the glass. The data were corrected and checked for self-consistency according to the methods described in Ref. [32], with sample attenuation factors calculated for the correct geometry [37]. The results are discussed by comparison with MD simulations of the liquid at 2500 K, previously reported in Ref. [19], and with new MD simulations of the glass at 300 K as prepared from the liquid in the NPT ensemble by using a quench rate of 10$^{12}$ K s$^{-1}$ to give a material with $\rho = 0.0760(3)$ Å$^{-3}$. The interaction potentials for both models take into account anion polarizability and shape-deformation effects as well as the polarizability of the calcium cations [19,38].

The measured reciprocal-space and real-space difference functions are shown in Figs. 1 and 2. The first and second peaks in $\Delta G(r)$ and $\delta G(r)$ arise from nearest-neighbor Al-O and O-O correlations, respectively. For the liquid, they give distances of $r_{\text{AlO}} = 1.77(1)$ and $r_{\text{OO}} = 2.89(2)$ Å such that the mean $\angle O - \text{Al} - O$ bond angle is 108.9(5)$^\circ$ as compared to 109.47$^\circ$ for a regular tetrahedron. The Al-O distance is consistent with a structure made predominantly from AlO$_4$ and AlO$_5$ polyhedra [39] such that the measured coordination number for O around Al, $\bar{n}_{\text{AlO}} = 4.20(4)$, points to 80(4)% AlO$_4$ and 20(4)% AlO$_5$ units. A small tail on the Al-O peak at ~2 Å may, however, indicate a small fraction of AlO$_6$ units. For the glass, $r_{\text{AlO}} = 1.75(1)$ and $r_{\text{OO}} = 2.88(1)$ Å, giving a mean $\angle O - \text{Al} - O$ bond angle of 110.7(5)$^\circ$, and the measured coordination number $\bar{n}^\text{O}_{\text{Al}} = 4.04(3)$ points to 96(3)% AlO$_4$ and 4(3)% AlO$_5$ units. This is consistent with $^{27}$Al multiple quantum magic angle spinning NMR results, which show a glass structure built from 96.5% AlO$_4$ tetrahedra and 3.5% AlO$_5$ polyhedra [10]. X-ray absorption near-edge structure spectroscopy experiments suggest that most of these tetrahedra are fully corner sharing [8].

The difference functions from MD are in good overall agreement with the diffraction results (Figs. 1 and 2).
multiple quantum correlation NMR found that \( \sim5\% \) of the oxygen atoms form triclusters [9]. In comparison, the MD simulations find that \( 12(1)\% \) of all O atoms exhibit a coordination number greater than two with \( 5(1)\% \) forming oxygen triclusters. The latter play a more prominent role in the fragile glass former \( \text{Ba}_2\text{Al}_6\text{O}_{11} \) where the O:Al ratio is less than two, such that there are insufficient oxygen atoms to form an ideal corner-sharing network of \( \text{AlO}_4 \) tetrahedra with twofold coordinated oxygen atoms. Instead, up to 21% of the oxygen atoms are involved in triclusters [41].

The first peak in \( \Delta G^{\text{Ca}}(r) \) or \( \delta G^{\text{Ca}}(r) \) is attributed to nearest-neighbor Ca-O correlations and, for the liquid, it gives a distance \( r_{\text{CaO}} = 2.35(1) \text{ Å} \) and coordination number \( \bar{n}_{\text{Ca}}^{\text{O}} = 6.0(2) \) as found by using an integration cutoff of 3 Å. For the glass, the corresponding values are \( r_{\text{CaO}} = 2.29(1) \text{ Å} \) and \( \bar{n}_{\text{Ca}}^{\text{O}} = 6.2(1) \) for the liquid [19] with \( r_{\text{CaO}} = 2.34(1) \text{ Å} \) and \( \bar{n}_{\text{Ca}}^{\text{O}} = 6.4(1) \) for the glass. By comparison, the Ca atoms in crystalline \( \text{CaAl}_2\text{O}_4 \) stuff channels made from rings of corner-sharing \( \text{AlO}_4 \) tetrahedra to occupy two distorted octahedral sites and one ninefold-coordinated site such that

![Diagram](image1.png)

**FIG. 1** (color online). The difference functions \( \delta^i(Q), \Delta^i(Q), \Delta^{\text{Ca}}(Q), \) and \( \delta^{\text{Ca}}(Q) \) for glassy (Gls) and liquid (Liq) \( \text{CaAl}_2\text{O}_4 \). The vertical bars show the statistical errors on the measured data points, and the solid (red) curves show the back Fourier transforms of the corresponding real-space functions shown by the solid (black) curves in Fig. 2. The chained (blue) curves show the MD results. Several of the functions are displaced vertically for clarity of presentation.

the liquid, a largely tetrahedral structure is predicted with a significant fraction of \( \text{AlO}_4 \) units \([14.7(5)\%]\), many of which are edge sharing, and with small fractions of \( \text{AlO}_6 \) units \((\leq 2\%)\) and \( \text{AlO}_8 \) units \((\leq 0.4\%)\). For the glass, a predominantly tetrahedral structure is predicted with a negligible fraction of \( \text{AlO}_4 \) units, \( 8.5(5)\% \) \( \text{AlO}_4 \) units, and a few \( \text{AlO}_6 \) motifs \((\leq 0.4\%)\). The concentration of \( \text{AlO}_4 \) units was found to be sensitive to the glass preparation method where a faster simulated quench rate of \( 10^{14} \text{ K s}^{-1} \) gave a larger fraction of \( 14.0(5)\% \). The coordination number for Al around O is given by \( \bar{n}_{\text{O}}^{\text{Al}} = (c_{\text{Al}}/c_{\text{O}}) \bar{n}_{\text{A}}^{\text{O}} \) [32]. For a system with the \( \text{CaAl}_2\text{O}_4 \) stoichiometry, the formation of units (e.g., \( \text{AlO}_4 \) and \( \text{AlO}_3 \)) such that \( \bar{n}_{\text{O}}^{\text{Al}} > 4 \) will therefore lead to \( \bar{n}_{\text{O}}^{\text{Al}} > 2 \), i.e., a fraction of the oxygen atoms will take a coordination number in excess of two. If only twofold and threefold coordinated oxygen atoms can form, then the measured value \( \bar{n}_{\text{O}}^{\text{Al}} = 2.10(2) \) for the liquid gives their fractions as 90(2)\% and 10(2)\%, respectively. In comparison, the MD simulations predict that 18(1)\% of all O atoms exhibit a coordination number greater than two with 7(1)\% forming oxygen triclusters, i.e., one oxygen atom shared by three \( \text{AlO}_4 \) tetrahedra [19,40]. Similarly, for the glass the measured value \( \bar{n}_{\text{O}}^{\text{Al}} = 2.02(2) \) gives 98(2)\% twofold and 2(2)\% threefold coordinated oxygen atoms, while a study using \( ^{17}\text{O} - ^{27}\text{Al} \) heteronuclear

![Diagram](image2.png)

**FIG. 2** (color online). The difference functions \( \delta G^r(r), \Delta G^r(r), \Delta G^{\text{Ca}}(r), \) and \( \delta G^{\text{Ca}}(r) \) for glassy (Gls) and liquid (Liq) \( \text{CaAl}_2\text{O}_4 \) as obtained by Fourier transforming the spline-fitted measured [solid (black) curves] or the simulated [chained (blue) curves] \( Q \)-space functions shown in Fig. 1. For clarity of presentation, the unphysical small-\( r \) oscillations below the distances of closest interatomic approach are omitted, and several of the functions are displaced vertically.
$n_{Ca} = 7$ for $r \leq 3.18 \, \text{Å}$ [29]. In contrast, previous diffraction experiments on calcium aluminate liquids and glasses have consistently found much smaller $n_{Ca}$ values, which have been explained by the obscuration of Ca-O correlations by other pair correlations at, e.g., large $r$ in the glass [15–20,39,42]. Some success has been had in eliminating the O-O correlations by taking the difference between x-ray and neutron total structure factors, but coordination numbers of $n_{Ca} = 3.8(3)$ [19] and $n_{Ca} = 5.6(2)$ [15] are still obtained for liquid and glassy CaAl$_2$O$_4$, respectively.

The measured $S_{CaCa}(Q)$ function for the glass is shown in Fig. 3 along with the partial pair-correlation function $d_{CaCa}(r) = 4\pi r\rho g_{CaCa}(r) - 1$. The latter exhibits two peaks at $r_{CaCa} = 3.59(2)$ and 4.41(5) Å and gives a coordination number $n_{Ca} = 5.4(1)$ by integrating up to the minimum at 5.22 Å. The simulated function has a single peak at $r_{CaCa} = 3.81(5)$ Å and yields a comparable coordination number of $n_{Ca} = 4.9(1)$ by integrating up to the minimum at 5.09 Å. The mean Ca-Ca distances for corner-, edge-, and face-sharing polyhedra are 4.40, 3.74, and 3.41 Å, respectively. By comparison, crystalline CaAl$_2$O$_4$ has one Ca site with four Ca neighbors and two Ca sites with five Ca neighbors such that $n_{Ca} = 4.7$ for distances in the range 3.55–4.99 Å [29]. For the liquid, the smaller sample size precluded a reliable extraction of $S_{CaCa}(Q)$, but the MD results give $r_{CaCa} = 3.86(2)$ Å with $n_{Ca} = 5.1(1)$ [19]. Overall, the MD simulations of the liquid and glass show that all Ca-centered polyhedra share at least one corner, but that there are larger numbers of edge-sharing and, to a lesser extent, face-sharing connections in the glass. This is illustrated in Fig. 4 for the case of edge-sharing polyhedra which form large branched chains in the glass as compared to the liquid. Indeed, on cooling the liquid the maximum cluster size increases significantly between 1500 and 1300 K; in a regime where time-resolved studies indicate a change in the temperature dependence of the structure and thermal properties of liquid CaAl$_2$O$_4$, perhaps marking a dynamical cross over at about $1.25T_g \approx 1475$ K [16].

We note that the Ca-Ca pair-correlation functions measured for CaAl$_2$O$_4$ glass (Fig. 3) are similar to those measured for (CaO)$_{48}(SiO_2)_{90}(Al_2O_3)_3$ glass [31]. The latter were originally interpreted in terms of a structure comprising sheets of edge-sharing CaO$_6$ octahedra, a model that has subsequently been revised in favor of more chainlike linkages of Ca-centered polyhedra [43,44].

The following picture thus emerges for the significant structural changes that occur on both the local and intermediate length scales upon glass formation in the fragile CaAl$_2$O$_4$ system. On quenching, the AlO$_4$ polyhedra and threefold coordinated oxygen atoms found in the liquid reorganize to form a glass network made predominantly from corner-sharing AlO$_4$ tetrahedra. In this process there is a removal of Al-centered edge-sharing motifs, where the latter promote fragile behavior in glass forming systems [45]. The Ca-O coordination number shows a small increase from 6.0(2) to 6.4(2), and there is a large change in the connectivity of the Ca-centered polyhedra with the formation in the glass of branched chains involving edge- and face-sharing linkages.

Glasses can explore localities on an energy landscape that are inaccessible to the crystalline state and they are widely used as analogs for the liquid in materials of geophysical interest on account of the extreme conditions involved [21,46–50]. Although this is known to be an approximation [49,50], the nature of the problem makes it difficult to assess the extent of associated structural differences. The present work describes the reorganization on vitrification for a representative fragile glass former, a taxonomy that encompasses a range of magma-related liquids [51–53], and shows that significant changes occur not only in the character of the network-forming motifs but also in the nature of the intermediate ranged cationic ordering.

**FIG. 3** (color online). (a) The measured (points with vertical error bars) and simulated [chained (blue) curve] partial structure factors $S_{CaCa}(Q)$ for CaAl$_2$O$_4$ glass. The solid (red) curve shows the back Fourier transform of $d_{CaCa}(r)$ given in (b) by the solid (black) curve. (b) The partial pair-correlation function $d_{CaCa}(r)$ as obtained by Fourier transformation of the spline-fitted measured [solid (black) curve] or the simulated [broken (red) curve] $S_{CaCa}(Q)$ function shown in (a) after applying a Lorch modification function with $Q_{\text{max}} = 8.5$ Å$^{-1}$. The chained (blue) curve shows the results obtained directly from the MD model.

**FIG. 4** (color online). Snapshots illustrating the largest clusters of edge-sharing Ca-centered polyhedra in the MD simulations of CaAl$_2$O$_4$ for (a) the liquid at 2500 K and (b) the glass at 350 K. The clusters are represented by the light (yellow), dark (blue), and medium (green) shaded units which involve 16, 9, and 8 Ca atoms in the liquid or 44, 24, and 19 Ca atoms in the glass, respectively.
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