

# High-energy X-ray and Neutron Diffraction Study of Calcium Aluminate Glasses

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## Introduction

Liquids formed from binary CaO-Al<sub>2</sub>O<sub>3</sub> (CA) materials can be vitrified to form hard, transparent, colorless glasses. The glasses exhibit infrared transmission to about 5500 nm and are potentially useful as a laser host and infrared optical material. Many crystalline calcium aluminate phases are of interest from a geological standpoint and are common components of hydraulic cements.

Hannon and Parker [1] studied the structure of splat-quenched calcium aluminate glasses containing 30 and 38 mol % Al<sub>2</sub>O<sub>3</sub> by high-resolution pulsed neutron diffraction. The structure factors showed similar features in both materials. An Al-O bond length of ~1.76 Å and coordination number of 4.0 were measured, and no significant distortion of the AlO<sub>4</sub><sup>5-</sup> tetrahedra was detected. The Ca-O peak at 2.34 Å was also found to give a coordination number of 4.0, which is smaller than expected from bond valence theory calculations. These results suggested that higher coordinate species were also present, but this could not be confirmed because of the overlap between the Ca-O and O-O correlations. Morikawa et al. performed conventional x-ray diffraction measurements on a 36.8 mol % Al<sub>2</sub>O<sub>3</sub> splat-quenched glass and calculated the Al and Ca coordination numbers to be 4.2 and 5.6 at distances of 1.77 and 2.37 Å, respectively [2]. The apparent disparities between the prior measurements suggest that the Ca and possibly the Al ions can accommodate a range of structures in the glass, which are sensitive to the glass synthesis conditions.

The materials investigated in this work were 64:36 and 50:50 mol % CaO:Al<sub>2</sub>O<sub>3</sub>. The former composition corresponds to a pseudo-binary eutectic between Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (C3A) and CaAl<sub>2</sub>O<sub>4</sub> (CA). Combined neutron and high-energy x-ray diffraction experiments were performed on the same samples to obtain a detailed picture of glass structure. Since neutrons are particularly sensitive to the positions of the lighter oxygen atoms and since x-ray scattering is more sensitive to the positions of the heavier Ca and Al component interactions, these two techniques are highly complementary in the case of oxide glasses.

## Methods and Materials

The glass samples were made by the containerless melting and cooling of liquid droplets suspended in an aerodynamic levitator. 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 into spheroids that were about 3 mm in diameter by using a CO<sub>2</sub> laser beam. The densities of the glass and partially crystallized materials were measured by using a pycnometer with perfluoromethyldecalyn as the immersion fluid. The compositions of the glasses were confirmed by microprobe analysis.

High-energy x-ray measurements were performed by using  $1 \times 1\text{-mm}^2$ , ~115-keV beams at BESSRC beamline station ID-11-C at the APS. The same samples were contained in a 4-mm-wide aluminum frame with 10- $\mu\text{m}$  Mylar<sup>®</sup> 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 same part of the Mylar window with the sample removed to obtain the scattering contribution from the container. The use of high-energy x-ray instrumentation enables experiments to be made with very low x-ray attenuation and multiple scattering factors (a few percent) and accesses a higher momentum transfer range.

## Results

The neutron/x-ray Q-space difference functions were constructed to eliminate the O-O correlations to observe any higher-order Ca-O correlations. The corresponding real space curves are given in Fig. 1. At the eutectic composition, calcium is found to be coordinated, on average, by  $3.9 \pm 2$  oxygens at 2.40 Å, while at the equimolar composition, this value increases to  $5.6 \pm 2$  at 2.38 Å. The eutectic data are in good agreement with the value of  $n_{\text{CaO}} = 4.0$  found by Hannon and Parker [1], but they are considerably lower than the value of 5.6 observed by Morikawa et al. [2]. It is interesting to note that no additional higher CaO correlations are found to exist between 2.4 and 2.7 Å. This does not preclude the existence of longer Ca-O correlations of >2.7 Å at the eutectic.

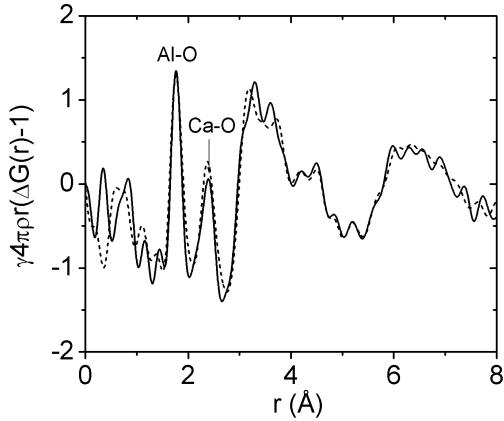


FIG. 1. Real space x-ray/neutron difference functions for the eutectic (solid line) and equimolar (dashed line) glass compositions. For the eutectic,  $\gamma = 1$ , and for the equimolar composition,  $\gamma = 0.72$ , reflecting the ratio of  $\text{Al}_2\text{O}_3$  content in the glasses.

### Discussion

The results indicate that the equimolar glass is, on average, composed mainly of  $\text{AlO}_4$  tetrahedra and that the eutectic composition glass is dominated by a mixture of both  $\text{AlO}_4$  and  $\text{AlO}_5$  polyhedra. In a dramatic change, the average calcium coordination decreases from

$5.6 \pm 2$  oxygens in the  $\text{CaAl}_2\text{O}_4$  glass to  $3.9 \pm 2$  oxygens at the eutectic composition, despite a shift of only  $0.02 \pm 1$  Å in the Ca-O bond length. Although higher Ca-O correlations beyond 2.7 Å may also exist, the Ca environment is either unusually low or highly distorted in the 36 mol% composition. While it is unexpected that the coordination of Al increases with decreasing Al content in these glasses, this increase maybe understood in terms of the Ca ion “donating” oxygen to the aluminum [3]. If so, it follows that both the Ca and Al ions may act as network formers in these glasses.

### Acknowledgments

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### References

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