Polyhedral Units and Network Connectivity in Calcium Aluminosilicate Glasses from High-Energy X-ray Diffraction

V. Petkov,[1] S. J. L. Billinge,[1] S. D. Shastri,[2] B. Himmel[3]

[1]*Department of Physics & Astronomy & Center for Fundamental Materials Research, Michigan State University, East Lansing, MI, USA*

[2]*Advanced Photon Source, Argonne National Laboratory, Argonne, IL, USA*

[3]*FB Elektrotechnik and Informationtechnik, Universität Rostock, Rostock, Germany*

Silicate glasses, in general, and aluminosilicate glasses, in particular, are of great industrial and geological importance. Despite this, some very basic issues about their structure are still not well established. This prompted us to investigate the atomic ordering in a series of glasses with composition $Ca_{x/2}Al_xSi_{1-x}O_2$ (x=0,0.25,0.5,0.67). The experiments were carried out at the SRI-CAT 1-ID beamline using x-rays of energy 80.6 keV. The experimental structure factors, S(Q), are shown in Fig. 1, and the corresponding atomic pair distribution functions (PDF), g(r), in Fig. 2.

As can be seen, the experimental structure factors extend up to 40 Å^{-1}. This makes it possible to resolve the contributions of Si-O, Al-O and Ca-O coordination polyhedra to the experimental atomic PDFs, as shown in Fig. 2. The individual peaks in the experimental PDFs have been fit with Gaussians, and the corresponding coordination numbers and distances determined. It has been found that both Si and Al are four-fold coordinated and so participate in a continuous tetrahedral network at low values of x. The number of network-breaking defects in the form of non-bridging oxygens (NBO) increases slowly with x until x=0.5 (NBOs ~ 10% at x=0.5). By x=0.67, the network breaks as evidenced by the significant drop in the average coordination number of Si. By contrast, Al-O tetrahedra remain free of NBOs and are fully integrated in the Al/Si-O network for all values of x. Calcium maintains a rather uniform coordination sphere of approximately 5 oxygen atoms for all values of x. The results suggest that not only Si/Al-O tetrahedra but Ca-O polyhedra, too, play a role in determining the glassy structure. A more detailed account of the present experiment can be found in Ref. 1.

Acknowledgments

Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-ENG-38. The work was supported by NSF Grant No. CHE-9903706.

References

[1] V. Petkov, S.J.L. Billinge, S.D. Shastri and B. Himmel, Phys. Rev. Lett. **85**, 3436-3439 (2000).

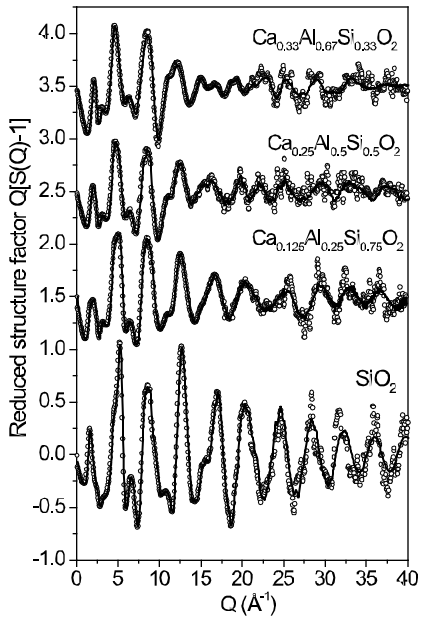

FIG. 1. Experimental structure factors together with the optimum smooth line.

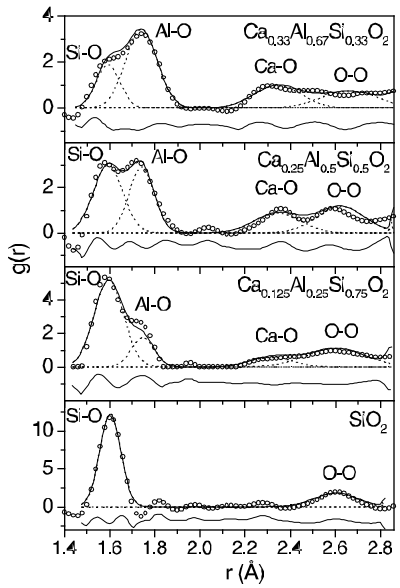

FIG. 2. Gaussian fit to the first peaks in the PDFs, g(r) = ρ(r)/ρ$_o$, for $Ca_{x/2}Al_xSi_{1-x}O_2$ (x=0,0.25,0.5,0.67) glasses. Experimental data: symbols; fitted data: full lines; individual Gaussians: broken lines; residual difference: full lines (bottom of each panel). Peaks are labeled with the corresponding atomic pairs.