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Environment around strontium in silicate and aluminosilicate glasses

L. Cormier* and G. Calas
Laboratoire de Minéralogie-Cristallographie, Universités Paris 6 et 7 et IPGP et UMR CNRS 7590, 4 place Jussieu, 75252 Paris Cedex 05, France

S. Creux
Saint Gobain Recherche, 39 quai Lucien Lefranc, Boîte Postale 135, 93303 Aubervilliers Cedex, France

P. H. Gaskell
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, England

B. Bouchet-Fabre
LURE, Université Paris Sud, 91405, Orsay Cedex, France

A. C. Hannon
Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, England

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The environment around Sr in silicate and aluminosilicate glass has been studied by neutron and anomalous x-ray diffraction and reverse Monte Carlo modeling. The first Sr-O distances are smaller in the silicate glass than in the aluminosilicate glass, which can be related to the different structural role of the element in the glass structure. We found Sr-Sr distances at about 4 and 7 Å in both glasses, which implies a *nonhomogeneous* spatial distribution. [S0163-1829(99)08121-7]

Knowledge of the medium-range structure in oxide glasses is an important prerequisite to understand physical properties, such as ion conduction, rheology, and thermodynamic properties. Cations may be divided in two groups according to their structural role within the glass structure. Modifier cations depolymerize the network by forming nonbridging oxygens (NBO) while charge compensating cations ideally occur inside the interstices formed by a fully polymerized network, which contains only bridging oxygens (BO), and charge-compensate, typically, nontetravalent elements. The environment around a few cations in multicomponent glasses has been extensively studied using neutron diffraction with isotopic substitution.[1–3] The combined use of neutron and x-ray diffraction provides two independent kinds of information and gives access to some chemical selectivity.[4] However, the structural differences around cations in modifying or charge compensating position have not received much attention. A recent neutron-diffraction study with isotopic substitution of Li finds a similar local environment around Li acting as modifier or charge compensator in silicate glasses.[5] More important differences were evident at medium-range distances: specifically, the absence of clustering of Li in aluminosilicate glasses, whereas clustering is observed in silicate glasses by neutron diffraction and NMR.[6,7] Furthermore, the linkage with the network-forming tetrahedra differs, depending on whether the Li atoms are charge compensating or modifying the network. These structural modifications should depend on the size of the cation but recent detailed studies are lacking for heavy elements in silicate and aluminosilicate glasses.

In this paper, we report a direct study of the environment around Sr in SrO $0.19\mathrm{Na_2O}$ $1.9\mathrm{SiO_2}$ and SrO $\mathrm{Al_2O_3}$ $4\mathrm{SiO_2}$ glasses using a combination of neutron and anomalous x-ray wide-angle scattering and reverse Monte Carlo modeling. The quantitative atomic models provide evidence for a different environment around Sr in a silicate glass, where Sr acts as network modifier, and an aluminosilicate glass, where Sr charge compensates the $\mathrm{AlO_4}$ tetrahedra.

Samples of composition SrO $0.19\mathrm{Na_2O}$ $1.9\mathrm{SiO_2}$ and SrO $\mathrm{Al_2O_3}$ $4\mathrm{SiO_2}$ were prepared by melt quenching. The homogeneity and the chemical compositions of the samples were determined by electron microprobe. Densities of 3.30 and 2.80 $\mathrm{g\,cm^{-3}}$ for the silicate glass and the aluminosilicate glass, respectively, were measured by Archimedes method with toluene as reference liquid. Neutron-diffraction measurements were made at the spallation neutron source ISIS (United Kingdom) on the LAD instrument. Anomalous wide-angle x-ray scattering (AWAXS) measurements were made at the synchrotron radiation source DCI/LURE (France) on the wiggler beam line DW31,[8] using two energies (about 1000 and 5 eV below the Sr absorption *K* edge). All the data were appropriately corrected and normalized. The combined use of these two diffraction methods is important to obtain an overall picture of the glass structure since the partials are differently weighted in x-ray and neutron diffraction. The latter provides more specific information on the (alumino)silicate network, and the former on the Sr-centered correlations.

Figure 1 shows the total neutron and x-ray structure factors, $S(Q)$ [Figs. 1(a) and 1(b), solid curves], and the differential x-ray structure factors, $\Delta_{Sr}S(Q)$ [Fig. 1(c), solid curves] which are obtained from the difference of two measurements at 1000 and 5 eV below the Sr *K* edge. ($\mathbf{Q}$ is the scattering vector and $Q=|\mathbf{Q}|=4\pi\sin\theta/\lambda$, where 2θ is the

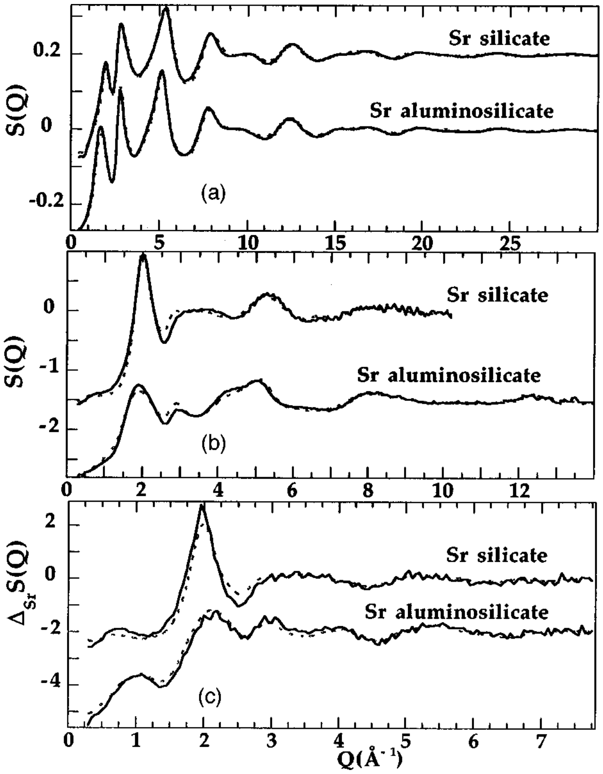

FIG. 1. Comparison between the experimental (a) neutron, (b) x-ray, and (c) differential x-ray structure factors (solid curves) and the RMC simulations (dashed curves) for the Sr silicate and aluminosilicate glasses.

scattering angle and λ the wavelength of the probing radiation.) The $\Delta_{Sr}S(Q)$ function is a weighted sum of all the partial structure factors involving Sr and gives a detailed description of the environment around this element. The neutron correlation functions, calculated by a Fourier transform of the $Q[S(Q)-1]$ data truncated at 35 Å^{-1}, are compared in Fig. 2 with Gaussian fits of the first peak. The mean Si-O distance is 1.62 and 1.61 Å for the strontium silicate and aluminosilicate glasses, respectively, with a coordination number of 4 and a standard deviation σ of 0.055 Å. Aluminum atoms are located in tetrahedral sites with a mean Al-O distance of 1.75 Å ($\sigma = 0.055$ Å). The second peak at 2.63 Å corresponds to O-O and Sr-O correlations. The shoulder at high-r values in the aluminosilicate glass is due to the longer O-O distances in the AlO_4 tetrahedra compared to those in the SiO_4 tetrahedra. Differences in the intensities and positions of the structural features at high-r values are observed between the two glasses. The neutron weighting factors indicate that the most intense partial pair distribution functions (PPDF's) are those related to the (alumino)silicate network (O-O, T-O, T-T with $T=$Si or Al) and the Sr-O pairs. The Na-centered PPDF's in the silicate glass are negligible due to the small Na concentration. Well-defined structures exist beyond 10 Å in the $G(r)$ function of the aluminosilicate glass, while almost no structure is present in $G(r)$ over the same region for the silicate. This suggests a more ordered framework in the aluminosilicate glass.

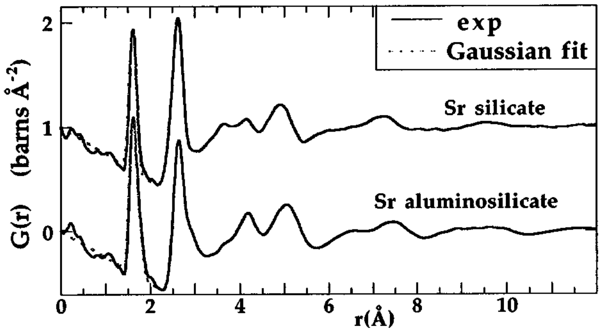

FIG. 2. Total neutron correlation function (solid curves) for the Sr silicate and aluminosilicate glasses, compared with Gaussian fits of the first peak (dashed curves).

Since all PPDF's are superimposed beyond 2 Å, thereby reducing the information that can be obtained directly, we applied the reverse Monte Carlo (RMC) method to extract more structural information from the available experimental data. Previous RMC simulations of silicate glasses have proved useful to generate three- dimensional atomic models which reproduce quantitatively the experimental data.[9,10] The RMC method has been described in detail elsewhere.[11] Each starting configuration contains 3688 atoms in a cubic box with an edge length of 18.6 Å. In a first step, a hard-sphere Monte Carlo simulation constrained the Si and Al atoms, introduced in the configuration box at random, to be fourfold coordinated. Then Sr atoms were randomly added. Periodic boundary conditions were used and constraints applied during the fitting procedure to maintain the tetrahedral units and to respect the closest atom-atom distances which avoid physically unrealistic structures (T-$T \geqslant 2.6$ Å, T-O $\geqslant 1.5$ Å, T-Sr$\geqslant 2.9$ Å, O-O and Sr-O$\geqslant 2.4$ Å, Sr-Sr $\geqslant 3.5$ Å). A simplified Sr silicate glass was used in the RMC simulation, in which Na is replaced by Sr leading to the composition 38SrO $62SiO_2$. This yields to a slight overestimate of the Sr-centered PPDF's. In the Sr aluminosilicate glass, we did not distinguish between Si and Al atoms in the simulation since neutron or x-ray experiments cannot separate their relative contributions. The RMC simulation was carried out using three sets of experimental data: the total neutron and x-ray structure factors and the differential x-ray structure factor obtained by AWAXS. We used the reciprocal space data rather than the correlation functions since they are more sensitive to medium-range ordering, especially at low-Q values. This allows fitting of both the (alumino)silicate network, mainly with the neutron-diffraction data, and the environment around Sr, with the x-ray diffraction data. It is important to note that the structure determined by RMC is not unique and, as we started with a random model, the final configuration is the most disordered structure consistent with the available data.

In Fig. 1, we compare the experimental data with the RMC simulations. Good agreement is obtained for the neutron data of the two glasses except the double peak at 8–10 Å^{-1} which is somewhat smoothed by the RMC simulation due to limitation of the computation time. The criterion for an acceptable fit was chosen larger when modeling the x-ray-diffraction data, in order to take into account the lower quality of the data compared to the neutron-diffraction data. This explains some discrepancies between the x-ray experimental data and the RMC fits. However, the RMC

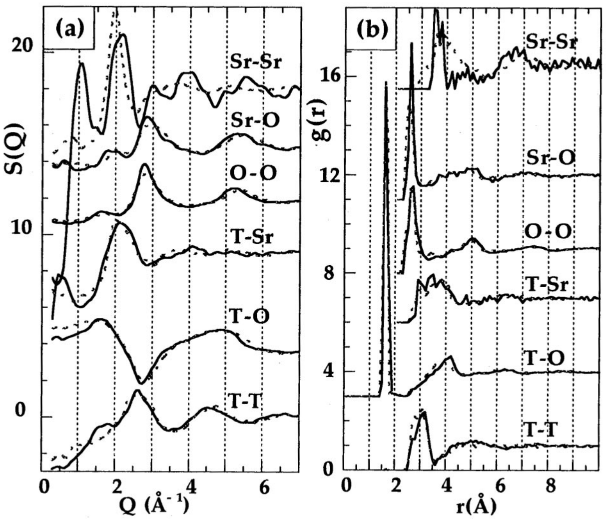

FIG. 3. (a) Partial structure factors $S_{ij}(Q)$, and (b) partial pair distribution functions $G_{ij}(r)$, calculated from the atomic position of the RMC model of the silicate (dashed curve) and aluminosilicate (solid curves) glasses.

TABLE I. Comparison of the experimental values determined for the silicate and the aluminosilicate glasses of the first O shell of neighbors around Sr and the values calculated from the RMC models.

	Neutron	AWAXS (Ref. 8)	EXAFS (Ref. 8)	RMC
Sr silicate				
R (Å)	2.62	2.68	2.5	2.55
N	6.0	4.0		5.8
σ (Å)	0.135	0.13	0.11	
Sr aluminosilicate				
R (Å)	2.63	2.56	2.54	2.7
N	7.0	6.0		5.9
σ (Å)	0.125	0.18	0.13	

simulation reproduced the x-ray data over all the Q range and especially the features at small values of Q. For the Sr aluminosilicate glass, some of the deviations may be due to the use of an average site T for Si and Al atoms.

The partial pair structure factors [Fig. 3(a)] calculated from the RMC models may be used to analyze the low-Q region which is related to medium-range ordering of the glasses. For the Sr silicate glass, the first peak in the experimental neutron-diffraction data is clearly due to the $S_{SrSr}(Q)$ and the low-Q tail of this peak comes from the silicate network (O-O and Si-O pairs). The AWAXS data are strongly dominated by the $S_{SrSr}(Q)$ function and the peak at 2 Å^{-1} and at 0.76 Å^{-1}, in the total and differential structure factors, respectively, are due to the Sr-Sr pairs and therefore to the distribution of Sr atoms in the glass structure. On the contrary, the Sr-Sr pairs in the Sr aluminosilicate glass have a weak weighting factor and thus a negligible intensity. The peak at 1.73 Å^{-1} in the neutron-diffraction data arises thus mainly from the (Si,Al)-O and O-O partial functions. In the total x-ray structure factor, the Sr-centered partial functions are more heavily weighted than in neutron data and contribute significantly to the x-ray data. A peak in the Sr-Sr, Sr-O, and T-Sr partial functions near 2 Å^{-1} explains that the first diffraction peak observed at 1.73 Å^{-1} in the neutron-diffraction data shifts towards a higher Q value, 1.92 Å^{-1}, in the x-ray data. The small peak at 1.06 Å^{-1} in $\Delta_{Sr}S(Q)$ is due to a strong contribution of the Sr-Sr pairs. The intensity of this feature is limited in $\Delta_{Sr}S(Q)$ due to out-of-phase contributions of the Sr-O and T-Sr pairs. The presence of a positive peak in $S_{SrSr}(Q)$ at ~ 1 Å^{-1} and a negative peak in $S_{SrO}(Q)$ and $S_{TSr}(Q)$, at the same position, represents a difference with the silicate glass, where all contributions are positive. This result indicates antiphase correlations between the Sr atoms and the aluminosilicate network which are due to the position of Sr in interstitial sites.

The PPDF's are shown in Fig. 3(b) for the two glasses. The $G_{SrO}(r)$ functions indicate that the Sr-O distance is longer in the aluminosilicate glass (2.7 Å) than in the silicate glass (2.55 Å). This is in agreement with analogous crystal structures where the mean d_{SrO} is equal to 2.8 Å in c-$SrAl_2Si_2O_8$ and 2.64 Å in c-$SrSiO_3$.[12,13] The Sr-O distances determined by RMC do not agree well with those obtained by Gaussian fits of the neutron- or x-ray diffraction data or by extended x-ray absorption spectroscopy (EXAFS) Ref. 8 and reported in Table I. EXAFS data may suffer important anharmonic effects due to radial disorder.[14] The precision of the d_{SrO} distances extracted from AWAXS using the differential correlation functions $G_{Sr-\alpha}(r)$ is low, due to the low signal-to-noise ratio. The Sr-O distance of 2.56 Å found by AWAXS in the aluminosilicate glass is also small compared to reference compounds. In neutron data, the Sr-O correlation is buried by the strong O-O correlation and exact determination of the Sr-O pair is difficult.

The Sr-O coordination number (CN) obtained with the RMC models is about 5.8 O in each glass, using a cutoff distance of 3.2 Å. In crystalline compounds, a coordination number of 8–9 is usually obtained, including, in some compounds, 2 O at a longer distance (3.1–3.2 Å).[12,13] The small CN suggests that Sr atoms are located in sites of smaller size than in crystalline silicates.

The difference in Sr-O distances between the two glasses investigated may be interpreted as an indication of a different structural role of Sr in silicate and aluminosilicate glasses. In the former, Sr is a typical modifier cation, like in other alkaline-earth glasses,[1] in the latter, it plays the charge-compensating role required by the Al to Si substitution. As a consequence, Sr may be bonded mainly to NBO's in silicate glasses while it is bonded to BO's in the aluminosilicate glass. BO's will be nearly compensated by the presence of two (Si,Al) atoms in a fourfold coordination. A short Sr-BO distance would result in a strong overbonding of BO atoms. Molecular-dynamics calculations have shown in glasses that the Si-NBO distances are shorter than the Si-BO distances, by about 0.05 Å in Na-silicate glasses.[15] This observation is consistent with the distances observed in crystalline silicates. In consequence, NBO's will need further compensation by non-network-forming cations and can accomodate shorter Sr-NBO bonds than Sr-BO bonds. The Sr-O interatomic distances will then depend on this need for charge balance in the immediate oxygen surrounding. This demonstrates the ability of the RMC simulations to identify a different surrounding of the Sr atoms in these two glasses.

In the RMC model of the silicate glass, the Sr-Si distribution has a first peak centered at 3.7 Å with 6.5 Si neighbors around Sr (cutoff at 4.5 Å), which is somewhat lower than the value of 9 Si at 3.6 Å estimated in the $G_{Sr-\alpha}(r)$ function and 8 Si at 3.52 Å in c-$SrSiO_3$. The RMC configuration of the aluminosilicate glass has also a first broad distribution of T-Sr pairs centered at 3.4 Å, compared to 3.65 Å in $G_{Sr-\alpha}(r)$ and 3.64 Å in c-$SrAlSi_2O_8$. The Sr-T coordination number of 9.1 is close to the value of 10 estimated in the $G_{Sr-\alpha}(r)$ function and in anorthite crystal.

The Sr-Sr distribution in the silicate glass, $G_{SrSr}(r)$ [Fig. 3(b), upper curves], shows important similarities with the $G_{Sr-\alpha}(r)$ functions.[8] The $G_{SrSr}(r)$ PPDF confirms that the peaks observed near 4 and 7 Å are mainly due to Sr-Sr pairs. Shorter distances at 3.6 and 6.7 Å are obtained in the RMC model of the aluminosilicate glass, despite the small concentration of Sr atoms and thus the poorer statistics than in the silicate glass. As Sr atoms are supposed to charge compensate the $(AlO_4)^-$ tetrahedra localized nearby, this inhomogeneous distribution of Sr atoms suggests also an inhomogeneous distribution of Al atoms into the glass structure. The difference in the first cation-cation distance d_{SrSr} between the two glasses is similar to the slight decrease of the Sr-Sr distances which occurs from c-$SrSiO_3$ to c-$SrAl_2Si_2O_8$, 4.12 and 4.08 Å, respectively. Furthermore, this distance corresponds to edgesharing of Sr polyhedra. A first short Sr-Sr distance implies an inhomogeneous distribution of Sr atoms in both glasses. Indeed, Sr-Sr distances at 5.2 and 6.8 Å would be expected for a three-dimensional homogeneous distribution in the silicate and aluminosilicate, respectively. A coordination number of 6.5 Sr neighbors is obtained [using a cutoff at 5 Å in Fig. 3(b)], which is close to the 6 Sr neighbors in c-$SrSiO_3$.[12] A value of 3.8 was determined by a Gaussian fit of the $G_{Sr-\alpha}(r)$,[8] a difference likely due to a simulation box containing more Sr atoms than the real glass. In the aluminosilicate glas, a coordination number of about 1 in the RMC model is in agreement with the small value ($\leqslant 1.5$) evaluated in the $G_{Sr-\alpha}(r)$ function and with the coordination number of 1 in c-$SrAl_2Si_2O_8$.[8,13]

Similar cation-cation distances to those found in this study were determined in silicate glasses for Ca (3.8 and 6.4 Å) (Ref. 1) and Ba (4.15 and 7.3 Å).[16] Moreover, the characteristic distance at $\sqrt{2}d_{SrSr}\approx 5.7$ Å, which is due to out-of-plane polyhedra linkage, is never observed. As previously proposed for Ca and Ni silicate glasses,[1,2] the presence and the absence of these specific distances suggest a bidimensional ordering of the Sr atoms. This result indicates important similarities in the distribution of alkaline earths (Ca, Sr, and Ba) in silicate glasses.

Neutron- and anomalous x-ray diffraction experiments have been used to investigate the structure of a strontium silicate glass ($SrNa_{0.4}Si_{1.9}O_5$) and a strontium aluminosilicate glass ($SrAl_2Si_4O_{12}$). Two three-dimensional atomic models were generated by the reverse Monte Carlo method using the experimental diffraction data. The RMC models confirm that the first peak in the structure factors comes mainly from density fluctuations of the Sr-Sr pairs in the silicate glass. Due to the lower Sr concentration in the aluminosilicate glass, the (Si,Al,O) network plays a more important role in the neutron low-Q features but Sr-Sr correlations contribute significantly to the x-ray data. The Sr-O distances are longer in the aluminosilicate glass than in the silicate glass, in agreement with a different structural role. The first Sr-Sr distance is slightly shorter in the aluminosilicate glass than in the silicate glass. We found Sr-Sr distances at about 4 and 7 Å in both models indicating an inhomogeneous distribution of this element in the glass structure.

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*Author to whom correspondence should be addressed. Electronic address: cormier@lmcp.jussieu.fr

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