

First sharp diffraction peak in silicate glasses: Structure and scattering length dependence

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The source of the experimentally observed anomalous behavior of the first sharp diffraction peak (FSDP) in lithium silicate glasses was determined using classical molecular dynamics simulations. Partial structure factors obtained from simulations were used to investigate the sensitivity of the total structure factor to the scattering length of alkali ions. The result clearly establishes that the major difference of the FSDP between lithium and sodium disilicate glasses is due to the negative scattering length of lithium ions. Additionally, it was determined that the unusual intense FSDP in lithium silicate glass has little to do with differences of the medium-range structure in these glasses.

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The first sharp diffraction peak (FSDP), or prepeak, observed in a number of network-forming glasses is considered to be an indication of the medium-range order.^{1,2} The origin of the FSDP and its relation to real space structural features in a network glass remain highly controversial.³ Two structural interpretations are frequently invoked to explain the origin of the FSDP. One interpretation considers that the origin of the FSDP is due to the ordering of interstitial voids around network-forming cations.⁴ The other relates the FSDP with crystallinelike layers⁵ or, as in a more recent version, with quasilattice planes.⁶ Atomic-level structures obtained from molecular dynamics (MD) and other simulation methods are commonly used for the verification of these interpretations. Mixed results have appeared in the literature, ranging from supporting one,^{4,6} both,⁷ or none³ of the interpretations so that the role of the medium-range structure remains undetermined.

The intensity and position of the FSDP is known to change with temperature, pressure, composition, and neutron irradiation doses.^{4,5,8–11} The composition dependence of the FSDP in silicate glasses reveals a trend in the lithium silicate glasses inconsistent with other alkali silicate glasses. The origin of this anomaly has been suggested to come from the negative scattering length of lithium.⁴

The purpose of this brief report is to determine the dependence of the FSDPs in silica, sodium, and lithium disilicate glasses on the medium-range structure and scattering lengths of the modifier (Na and Li) cations using the results obtained from classical MD computer simulations that provide detailed atomic-level structural information. Structure analyses based on the bridging oxygen coordination around the silicon cations and ring size distributions are used to determine differences in medium-range structure. The contribution of partial structure factors are constructed from the partial structure factors obtained from MD simulations and weighted using the composition and corresponding scattering lengths. It is then possible to determine the contribution of each partial structure factor and the influence of the scattering lengths to the FSDP. Although isotope substitution experiments have been used to obtain partial structure factors in some simple systems,¹² they remain difficult to apply to the systems of interest here.

Vitreous silica is a canonical network-forming glass system. It has a pronounced FSDP at around 1.52 \AA^{-1} .² Introduction of network modifiers [that rupture the covalent network connectivity and introduce nonbridging oxygen (NBO) bonds], such as sodium oxide to silica decreases the FSDP intensity and shifts the peak position to higher Q values.^{4,9} These changes have been considered to be an indication of the decrease of the medium-range order as compared to pure vitreous silica. In a simple model, the modifier ions in silicate glasses were thought to enter the interstices of the network structure.⁴ Purportedly, the positive scattering length of the sodium ion decreases the contrast between the cation center (Si^{4+}) and the voids such that the FSDP intensity decreases.⁴ A concomitant decrease of the chemical ordering in the depolymerized network structure could also contribute to the change of the FSDP.⁴ However, in lithium silicate glasses, the intensity of the FSDP is as strong as in vitreous silica. It has been suggested that the negative scattering length of lithium ions increases the contrast between the cation centers and the voids.⁴ Recent developments in glass structure models imply that the modifier ions do not randomly occupy the interstices in the network structure; instead, the modifiers and nonbridging oxygen (NBO) tend to cluster and form modifier-rich regions side-by-side with the silicon oxygen network.^{13,14} The void model fails to explain the observations of the FSDP change in silicate glasses since it is difficult to define voids about modifiers in clustered and enriched regions.

In this work, the MD simulations were carried out using a partial charge pair potential set that has been successfully used to study the structure and ion diffusion in silicate glasses.^{15,16} Each simulation cell contained 3600 atoms with cell volumes based on experimental densities. A standard

TABLE I. Faber-Ziman factors for the glasses ($M=\text{Li}$ or Na).

Glass	O-O	O-Si	O-M	Si-Si	Si-M	M-M
SiO_2	0.543	0.388	-	0.069	-	-
Na_2Si	0.424	0.242	0.212	0.035	0.061	0.027
Li_2Si	0.750	0.429	-0.196	0.061	-0.056	0.013

MD simulation procedure was used to form the glasses.¹⁶ Final structure analyses were based on averaging 400 configurations obtained from sampling every 50 steps during the last 20,000 steps of each simulation at 300 K. The total structure factor $S_N(Q)$ is obtained from a linear combination of the contribution partial structure factor $S_{ij}^N(Q)$ defined by

$$S_{ij(i \leq j)}^N(Q) = \left(\sum_{i=1}^n c_i b_i \right)^{-2} (2 - \delta_{ij}) c_i c_j b_i b_j S_{ij}(Q). \quad (1)$$

The partial structure factor $S_{ij}(Q)$ is obtained by Fourier transforming the pair distribution functions with a Lorch window function,¹⁷ where Q is the diffraction vector. The weighting factors (known as the Faber-Zimén factors) are related to the chemical composition and the scattering lengths where c_i and c_j are the atom fractions of species i and j , b_i and b_j are the scattering lengths, and δ_{ij} is the delta function. The Faber-Zimén factors for each of the ion pairs are listed in Table I. The $S_{ij}^N(Q)$ gives clear information of the contribution from each ion pair to the features in the total neutron structure factors, including the FSDP. Neutron scattering lengths used are 5.803, 4.1491, 3.63, and -1.90 fm for O, Si, Na, and Li, respectively.¹⁸

Figure 1 shows the comparison of the total structure factors of the simulated glasses with the experimental neutron diffraction results. Good agreement is observed for all the glasses for a Q up to 20 \AA^{-1} . Most importantly, the position and intensity of the FSDP and their change with composition are correctly reproduced. In silica glass, the FSDP is located at 1.58 \AA^{-1} with an intensity of 1.4. It drops dramatically to an intensity of 0.9 and shifts to 1.80 \AA^{-1} in sodium disilicate glass. In lithium disilicate glass, the intensity and position of the FSDP are 1.4 and 1.75 \AA^{-1} , respectively. For the sodium disilicate glass, the FSDP from simulation has a slightly higher peak intensity and lower minimum than the experimental data. A good agreement with the experimental total correlation functions was also observed for silica and sodium silicate glasses simulated using the same potential set.¹⁶ The comparisons in both real and reciprocal space provide further validation of the potential models used in our MD simulations.

For silica glass, the majority of the contributions to the FSDP come from the Si-O and O-O pairs, as shown in Fig. 2(a). This is in contrast to chalcogenide glasses such as GeSe_2 , in which the major contribution to the FSDP is considered to be the cation-cation pair.⁴ In both sodium and lithium disilicate glasses shown in Figs. 2(b) and 2(c), the major contribution to the FSDP are also from the Si-O and O-O pairs. In the sodium disilicate glass, the Si-O contribution appears diminished, resulting in a decrease of the FSDP intensity, while the contribution from the Na-O and Na-Si pairs shift the peak to higher Q values. In the lithium disilicate glass, the Si-O pair appears augmented, resulting in an increase of the FSDP intensity, while the contributions from the Li-O and Si-Li pairs are negative and contribute to a reduction of the FSDP intensity. Thus, the shape and position of the FSDP are a delicate balance of contributions from all atom pairs. Moreover, it is difficult to directly compare the

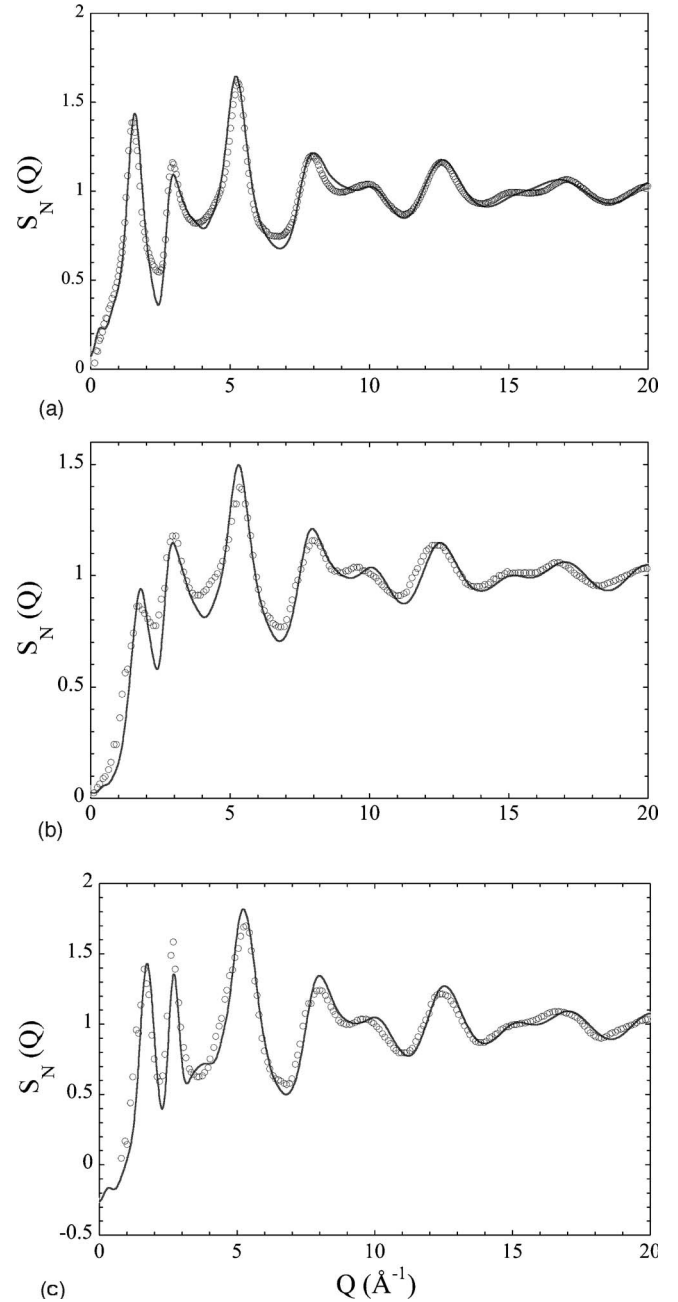


FIG. 1. The simulated (solid line) and experimental (circles) neutron scattering structure factors are compared for (a) silica, (b) sodium disilicate, and (c) lithium disilicate glasses. The experimental data are from Johnson *et al.* (Ref. 19) for silica and Mizawa *et al.* for sodium and lithium disilicate glasses (Ref. 9).

structural contribution of the silica backbone in the alkali disilicate glasses because of the net scattering contribution of the alkali ions.

A change of identity simulation experiment can be carried out to determine both the structural contribution of the network backbone and the role of the negative scattering length. In the sodium disilicate glass, the scattering length of sodium was set to 0.0 fm and to the scattering length of lithium of -1.9 fm. In the lithium disilicate glass, the scattering length of lithium was set to 0.0 fm and to the scattering length of

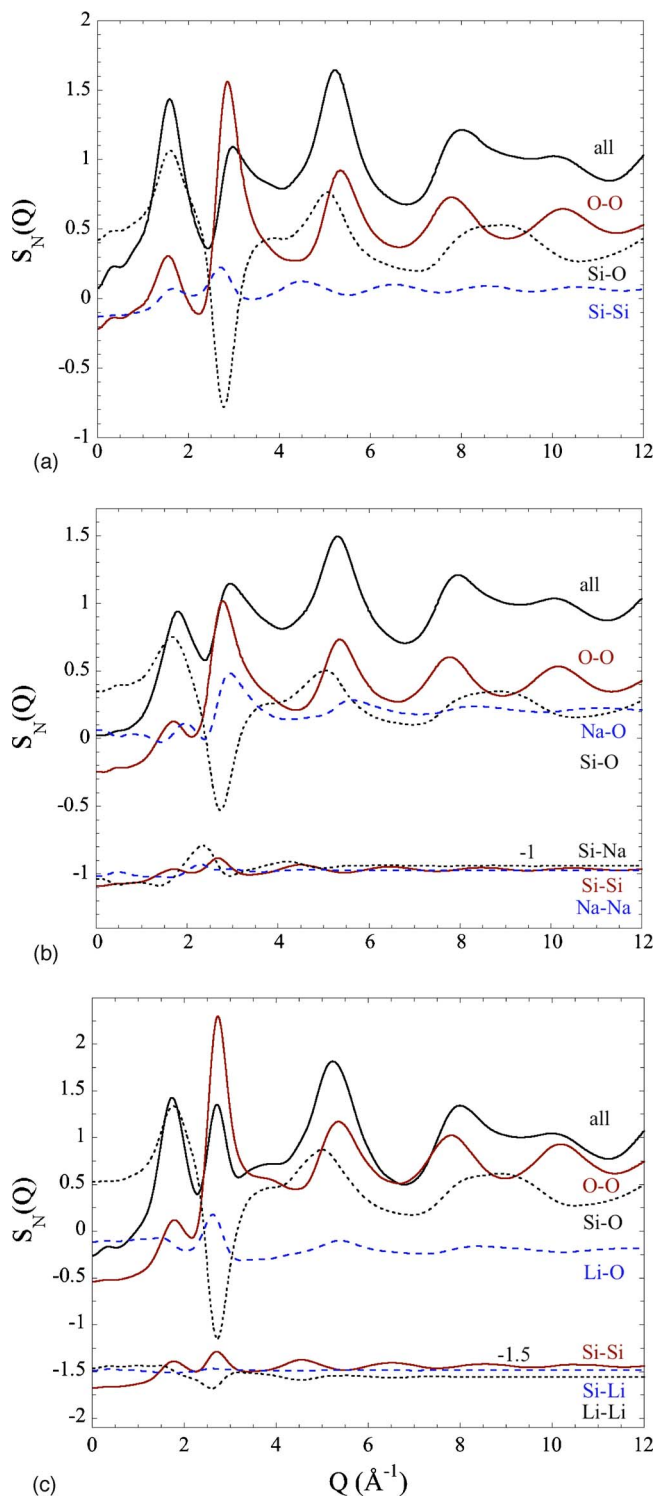


FIG. 2. (Color online) The contribution partial structure factors $S_{ij}^N(Q)$ and the total structure factors $S_N(Q) = \sum_{i \leq j} S_{ij}^N(Q)$ for (a) silica, (b) sodium disilicate, and (c) lithium disilicate glasses from MD simulation.

sodium of 3.63 fm. The final structure factors are compared in Fig. 3. It can be seen that when the scattering length of sodium and lithium are set to zero, the intensity of the FSDP of both glasses becomes similar. However, the intensity of the FSDP in the silicate glasses is still lower than that of pure

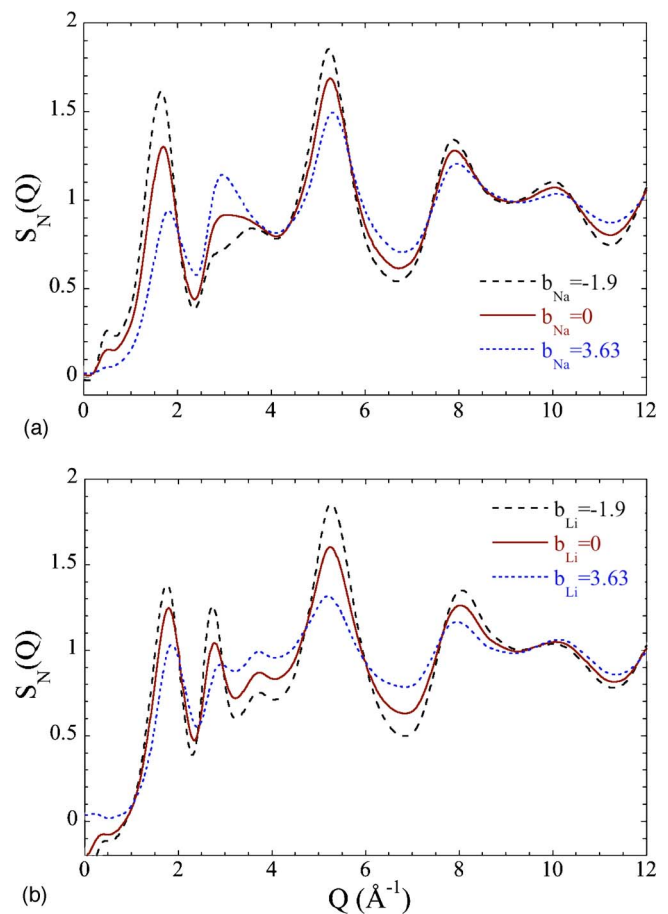


FIG. 3. (Color online) Influence of the neutron scattering length on the total structure factors in (a) sodium disilicate and (b) lithium disilicate glasses.

silica when the alkali scattering lengths are set to zero. This is an indication that the reduced medium-range order in these alkali silicate glasses is similar. The reversed scattering length simulations show that a negative scattering length of the alkali ion leads to an unusually intense FSDP in both sodium and lithium silicate glasses. When the scattering length of lithium is set to the value of sodium, the intensity of the FSDP of lithium disilicate glass becomes much lower than that of silica glass, as expected in most of the modified network glasses.⁴ If the scattering length of sodium is set to that of lithium the FSDP of sodium disilicate glass becomes as intense as in silica. Although the FSDP has similar contributions from the medium-range order of the Si-O backbone structure in both alkali disilicate glasses, the scattering contribution from sodium and lithium strongly affects the height and position of the FSDP where the negative scattering length enhances the FSDP.

The medium-range order was further characterized by carrying out molecular-level structural analysis of the alkali disilicate glasses. The distribution of the type of oxygen ion (bridging or nonbridging) around each silicon cation is provided by the Q_n analysis where n is the number of bridging oxygen atoms per $[\text{SiO}_4]$ tetrahedron. The nearest neighbors are determined using a Si-O bond distance cutoff of 2.25 \AA obtained from the first minimum of the Si-O pair distribution

function. In defect-free silica glass there are 100% Q_4 because all the oxygen ions around each silicon cation are bridging oxygen. In alkali silicate glasses there exist other Q_n ($n=0-3$) species because the alkali ions introduce non-bridging oxygen. In the sodium and lithium disilicate glasses the Q_n percentage distributions are 0.1, 3.8, 21.4, 45.2, 29.5 and 0.3, 4.3, 21.4, 42.3, 31.9 for $n=0-4$, respectively. The former has a slightly higher percentage of Q_3 where the difference is consistent with the NMR results that shows that Li moves the reaction $2Q_3 \rightleftharpoons Q_2 + Q_4$ to the right.²⁰ In general, the Q_n distributions are very similar in the two modified glasses, although the difference in the distributions suggests that the lithium glass is slightly more polymerized (more Q_4 and less Q_3).

Ring size distribution is a major structure characteristic of the medium-range order of network-forming structures.^{21,22} The primitive ring size is determined by the number of silicon cations that are connected by bridging oxygen to form a ring via the shortest path. Primitive ring size distributions were determined using the algorithm described in Ref. 22. The results are shown in Fig. 4. The ring size distribution of silica glass has a fairly symmetric peak shape and is dominated by six- and seven-member rings. The modified disilicate glasses have fewer small (<10) rings and more larger-sized rings. The ring size distribution of sodium disilicate glass has contributions up to 30-membered rings, whereas the lithium disilicate glass has fewer large-sized rings. The latter difference indicates a more depolymerized network in the sodium disilicate glass.

In summary, the lithium and sodium disilicate glasses are found to have similar medium-range order with respect to the

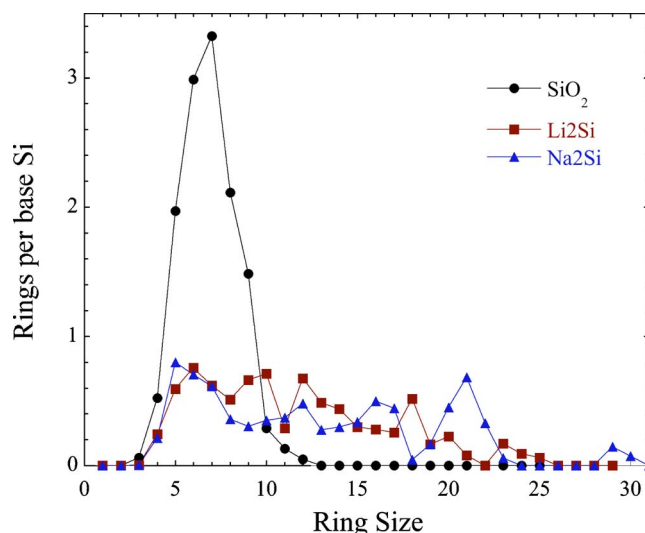


FIG. 4. (Color online) The primitive ring size distributions of silica, sodium, and lithium disilicate glasses.

Si-O backbone network structure as indicated by the total structure factors (with $b=0$) as well as by both the Q_n and primitive ring distributions. Thus, the anomalous behavior of the FSDP in lithium disilicate glass is not due to the medium-range structure but instead due to the negative scattering length of lithium ions that augment the contribution of the Si-O pair to the FSDP.

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