Mechanisms of boron coordination change between borosilicate glasses and melts

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ABSTRACT

The structure of two borosilicate glasses and melts has been investigated by neutron diffraction coupled with Reverse Monte Carlo (RMC) simulation. For both compositions ($10B_2O_3 \cdot 30Na_2O \cdot 60SiO_2$ and $10B_2O_3 \cdot 15Na_2O \cdot 15CaO \cdot 60SiO_2$), the fraction of tetrahedral boron ($^{[4]}B$) drops from 0.7 to 0.3 from the glass to the melt. The change from a modifying to a charge compensating role of cations during quench is related to the boron coordination change. These molecular scale modifications explain the low viscosity of alkali/alkaline-earth borosilicate melts relative to alkali/alkaline-earth silicate melts, as the viscous flow is enhanced with the proportion of $^{[3]}B$. RMC simulations of soda borosilicate glass and melt show a preferential interbonding between B and Si polyhedra. Such medium range order interbonding is unfavored in the soda-lime borosilicate glass showing a nearly random network. The effect of Ca enhancing the proportion of B–B pairs is here highlighted.

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1. Introduction

Borosilicate glasses are used in a broad range of applications, including insulating glass fibers, bioactive glasses, optical components, radioactive waste and panel display substrates [1,2]. In these systems, most structure–property relationships are linked to boron coordination, either in a trigonal ($^{[3]}B$) or tetrahedral ($^{[4]}B$) site. We conveniently express the proportion of each coordination state by the N_4 ratio ($^{[4]}B/[^{[4]}B + ^{[3]}B]$), whose values can be affected by internal (e.g. chemical composition [3,4]), and external parameters such as temperature [5,6] or quenching rate [7–9]. These structural changes influence ionic transport whose non-Arrhenian behavior is still not understood at a structural level [10,11]. Viscosity is also driven by boron coordination change and is of major importance in the processing of insulating fibers formation [12,13].

N_4 value may be evaluated by ^{11}B magic-angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR), but this approach is restricted to glasses as the ^{11}B NMR signal is averaged in melts [6,10,14,15]. In alkali borate glasses and melts, in situ investigations of boron coordination by Raman spectroscopy [16–18] or neutron diffraction [11,16,19] show a decrease of N_4 from glass to melt, indicating a structural relaxation during melting.

Borosilicate melts have been less investigated than borate ones despite their structure directly govern the viscosity of the melt [20]. Understanding their structure and how the quenching rate and annealing conditions influence their N_4 ratio is important for a broad

range of applications, e.g. in the processing of insulating glass fibers. The examination of simplified equivalent sodium borosilicate system indicates that these compositions correspond to a domain in which the Dell, Yun and Bray (DY&B) model [21] predicts that the borosilicate network contains reedmergnerite units, a $^{[4]}B$ site surrounded by four SiO_4 tetrahedra, $^{[4]}B(0B,4Si)$. These superstructural rings are transformed into pyroborate units ($^{[3]}B$ site with two non bridging oxygens) as the oxide modifier content increases [22]. Contrary to DY&B model, it was proposed that a random distribution of alkali ions, i.e. a proportional sharing of alkalis between silicate and borate structural units, leads to an important Si/B mixing [23–25]. MAS NMR [4,23,25] and Raman spectroscopy [26] have supported this model suggesting danburite-like ring structures, $^{[4]}B(1B,3Si)$, based on $^{[4]}B$ pairs.

^{11}B MAS NMR studies of borosilicate glass fibers have shown that thermal history plays an important role in determining the boron speciation, with N_4 decreasing as fictive temperature increases [10,14,27,28]. A recent ^{11}B MAS-NMR qualitative investigation up to 800 K also concluded to a N_4 reduction with increasing temperature [29]. Qualitative observations by Raman spectroscopy confirm that borosilicate rings tend to disappear at high temperature [5,24,30]. Thus it is challenging to obtain quantitative in situ measurements of the boron coordination conversion from glass to melt though they are thus necessary to shed light on the structural processes governing the glass to melt transformation in borosilicate systems.

In this paper, the structure of borosilicate glasses and melts is investigated using neutron diffraction and Reverse Monte Carlo (RMC) modeling. A Na borosilicate composition is compared with a borosilicate in which CaO has replaced half Na_2O. The latter composition is representative of soda-lime borosilicate glass fibers for thermal insulation.

An original processing of the pair distribution function allows the extraction of the B coordination number. We show important molecular scale modifications between glass and melt, including a decrease of the N_4 ratio. RMC modeling embeds these observations within the medium range reorganization, showing a change of the structural role of Na^+ and Ca^{2+} cations from charge compensator to network modifier, causing the N_4 ratio to decrease. The distribution of Si and B sites is described by a preferential surrounding of B atoms by Si ones in sodium borosilicate glass and melt, while the soda-lime borosilicate glass and melt show a random mixing. This observation indicates that Ca^{2+} cations favor B–B pair formation.

2. Experimental

2.1. Sample preparation

Two samples with the nominal composition $10B_2O_3 \cdot 30Na_2O \cdot 60SiO_2$ and $10B_2O_3 \cdot 15Na_2O \cdot 15CaO \cdot 60SiO_2$ (thereafter referred as BSN and BSNC, respectively) have been prepared from reagent grade powders ($^{11}B_2O_3$, SiO_2, Na_2CO_3, $CaCO_3$) melted in a platinum crucible at 1423 K for 1 h. B_2O_3 enriched with the ^{11}B isotope (99.62% enrichment) has been used in order to avoid the high neutron absorption cross section of the ^{10}B isotope. After immersing the crucible bottom into water, the resulting glass has been ground and molten twice to obtain optically homogeneous, colorless and transparent glasses. Glass compositions (Table 1) have been analyzed by electron microprobe analysis (CAMECA SX50) at the Camparis Facility (University Pierre et Marie Curie, Paris, France) (± 0.01 mol%). Glass density has been measured in toluene using the Archimede's principle (Table 1). Melt densities have been calculated using the model proposed by Fluegel [31].

2.2. Neutron diffraction

Neutron diffraction data have been obtained on the 7C2 diffractometer at the Orphée reactor of the Laboratoire Léon Brillouin (Saclay, France), with hot neutrons ($\lambda = 0.72$ Å), thermalized by graphite, giving access to a momentum transfer, Q, from 0.52 to 15.2 Å^{-1}. Glass powders were contained in a cylindrical vanadium cell at the center of a cylindrical vanadium furnace. Neutron diffraction has been measured at room temperature and 1423 K and 1273 K for BSNC and BSN melts, respectively. Each acquisition lasted ~12 hours to get a good signal to noise ratio. Data have been corrected from detector efficiency, background from the furnace and the container, multiple scattering attenuation and inelastic scattering and have been normalized against a vanadium standard to obtain the total scattering structure factor $S(Q)$ [32,33]:

$$S^N(Q) = \sum_{i,j} c_i c_j \overline{b}_i \overline{b}_j \left[F_{ij}(Q) - 1 \right] \qquad (1)$$

Table 1
Composition (in mol%, ± 0.05), density (in g cm^{-3}, ± 0.02), T_g and $T_{melting}$ values of the glasses investigated.

	BSN	BSNC
SiO_2	60.64	59.79
B_2O_3	9.28	10.28
Na_2O	29.73	14.47
CaO	0	15.12
R	3.2	2.9
K	6.5	5.8
T_g (K)	763[a]	798[b]
T_m (K)	1003[a]	1103[b]
d_{glass} (g cm^{-3})	2.55	2.62
d_{melt} (g cm^{-3})	2.20	2.31

[a] From ref. [58].
[b] From DTA measurements.

with c_i and $\overline{b}_i$ the atomic concentration and coherent scattering length for species i, respectively, and $F_{ij}(Q)$ the partial pair structure factor (PPSFs) for the correlation between species i and j. Fourier transform of the total structure factor from 0.52 to 15.2 Å^{-1} delimited with a step function provides the correlation function $G^N(r)$:

$$G^N(r) = \sum_{i,j} c_i c_j \overline{b}_i \overline{b}_j g_{ij}(r) \qquad (2)$$

with $g_{ij}(r)$ the partial pair distribution functions (PPDFs) between species i and j.

2.3. Reverse Monte Carlo simulations

The Reverse Monte Carlo (RMC) technique permits to reproduce the experimental data with the most disordered structure. In order to generate a realistic structural model, minimum atom–atom distances were chosen to avoid an unphysical overlapping of the atoms and Si atoms were imposed to be tetrahedrally coordinated. Only $^{[3]}B$ and $^{[4]}B$ coordination were allowed during the RMC fitting, with no other constraints imposed on the B environment. The cut-off distances are: 2.7 Å for Si–Si, 2.6 Å for Si–B and Ca–Ca, 1.4 Å for Si–O, 2.5 for Si–Na, Si–Ca, B–B and Na–Na, 1.15 Å for B–O, 2.4 Å for B–Na, B–Ca, O–O, 2.1 Å for Na–O and 2.2 Å for Ca–O. RMC modeling has been performed using the RMCA code, starting with a disordered atomic configuration obtained by hard sphere simulations [34,35]. Using Molecular Dynamics simulation for borosilicate glasses is complex due to composition dependence (and in our case the temperature dependence) of the boron coordination [36]. A simulation box contains 4000 atoms, using the density values reported in Table 1. Our discussion will be focused on the partial pair functions implying oxygen which have the highest weights in neutron diffraction. The pairs Si–Si, Na–Si, B–B, Si–B, B–Na, Na–Na, Ca–Na, Ca–Ca are thus too small to be taken into account. The $G(r)$ functions have been obtained by Fourier Transform of the simulated structure factors, in the same way as for the experimental data to allow a direct comparison. The factor of agreement (square difference between the measured and calculated structure factors) is typically 6.5×10^{-6} after the RMC procedure.

3. Results

3.1. Total structure factors

The normalized total structure factors $S(Q)$ of BSN and BSNC glasses and melts (Fig. 1a) do not differ from each other beyond 2.4 Å^{-1}. This similarity indicates that the short-range order is not strongly affected by the nature of the modifier cation. The most striking differences between the two glasses are observed in the low-Q region below 2.4 Å^{-1}.

For BSN glass a broad contribution is present between 1.7 and 2.2 Å^{-1}, with a smaller intensity than that in BSNC glass. The shape of this low-Q feature suggests two overlapping contributions. For BSNC, the low Q peak is centered at 1.85 ± 0.05 Å^{-1}. It indicates a strong difference of intermediate-range order in the two glasses. The position of these peaks, Q_p, is associated with a real-space repeat distances $D_p = 2\pi/Q_p$. After melting, the low-Q features of BSN become less broad, more intense and shift to 1.60 ± 0.05 Å^{-1}, which corresponds to an increase of D_p from 3.2 ± 0.1 Å to 4 ± 0.1 Å. For BSNC, the peak intensity increases slightly and its position shifts from 1.85 ± 0.05 Å^{-1} to 1.60 ± 0.05 Å^{-1}, which corresponds to an increase of D_p from 3.4 ± 0.1 Å to 3.8 ± 0.1 Å.

The behavior for BSN is anomalous because a smaller intensity due to thermal disorder effects might be expected in the melt, as for the peaks located beyond 2.4 Å^{-1}. By comparison with the BSN melt, the low-Q feature remains less intense and broader in the BSNC melt.

Though the peak shift in BSN may arise from the thermal expansion of the sample, the increase in intensity is a clear indication of an important structural organization in the melt. A similar enhancement in