

Tracking boron coordination change with temperature in a barium borosilicate glass melt by neutron diffraction

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Pulsed neutron diffraction measurements on a barium borosilicate glass and its supercooled liquid reveal clear, quantitative evidence for a tetrahedral to trigonal boron transition above the glass transition temperature, T_g . In particular the tetrahedral boron fraction, $N_4(T)$, is about 50(1)% in a $28\text{BaO} \cdot 48\text{B}_2\text{O}_3 \cdot 24\text{SiO}_2$ (BBS352) glass, independent of temperature, but falls continuously above $T_g = 901$ K to 36(1)% at 1200 K. The data are interpreted in terms of simplified chemical equilibria, from which it is inferred that the boron coordination change contributes between 30% to 40% of the total calorimetric configurational heat capacity at T_g , as well as to the entropy and liquid fragility. The thermal expansion coefficient of the B–O bond in BBS352 glass is measured to be $\alpha_{\text{BO}} = 6.5(1.7)$ ppm K^{-1} , slightly larger than for pure B_2O_3 glass and very similar to the known bulk expansion, implying a remarkably simple vibrational thermal expansion mechanism for the solid. Resolution of B–O and Si–O correlations in the real-space pair distribution function is demonstrated for $50\text{BaO} \cdot 25\text{B}_2\text{O}_3 \cdot 25\text{SiO}_2$ (BBS211) glass, and the factors governing if these features can be resolved are discussed.

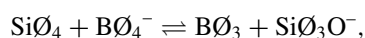
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I. INTRODUCTION

Borosilicates constitute a significant fraction of global glass production, with wide-ranging applications from displays to nuclear waste encapsulation, fibreglasses, cook and labware, glazes, and hermetic glass-to-metal seals, to name a few [1,2]. Hence, there is a broad literature dedicated to elucidation of the structure and structure-property relations in borosilicate glasses [1,2]. Arguably, the structure of the melt and its supercooled liquid are of equal importance to that of the glass, not only in high-temperature applications such as fuel cell hermetic seals, but also because they govern the melt properties during manufacture, dictating the accessible final forms, and importantly influence the relaxation behavior during annealing or exposure to elevated temperatures. The challenges of working and measuring structure in high-temperature liquids however, mean that fewer studies have been conducted, leading to a paucity of information available, despite the richness of the temperature-structure-property-composition relationships which can be gleaned from current knowledge [3–8]. Herein we will begin by briefly reviewing studies focused on assessing the temperature, or fictive temperature, dependence of structure in borosilicate melts and glasses. For our purposes, compositions containing additional network formers, such as aluminoborosilicates, will be considered out of scope, both for brevity, and because they

exhibit particular behavior relating to the variable coordination state of Al^{3+} , and the fact that it outcompetes B^{3+} for charge balancing modifiers. We will then focus on the aims of the present study—to measure the temperature dependent structure in a barium borosilicate melt and glass using neutron diffraction.

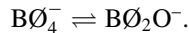
Structural studies of borate and borosilicate melts have been reviewed previously [4,9], and we discuss the most pertinent studies in the following. Michel *et al.* [5] measured the neutron structure factors of a pair of soda and soda-lime borosilicate glasses ($30(\text{Na}_2, \text{Ca})\text{O} \cdot 10\text{B}_2\text{O}_3 \cdot 60\text{SiO}_2$, mol%) and their melts at several hundred degrees above their liquidus temperatures. The most striking change between glass and melt was in the boron coordination, often parametrized as the fraction of boron in tetrahedral coordination to oxygen, N_4 . The glasses were found to have high $N_4 = 0.7(1)$, in accord with ^{11}B MAS NMR measurements on similar glasses [10], whilst the melts had much lower $N_4 = 0.3(1)$. This behavior was largely reproduced in first-principles molecular dynamics (FPMD) modeling of the $30\text{Na}_2\text{O} \cdot 10\text{B}_2\text{O}_3 \cdot 60\text{SiO}_2$ melt [11], and extrapolation of $N_4(T)$ down to the experimental glass transition temperature [12], which accounts for the exceptionally high fictive temperature of FPMD glasses. Qualitatively similar results have also been obtained on a wider range of sodium borosilicate melts modeled using classical polarizable ion model molecular dynamics [13]. This kind of dramatic change in local structure is associated with chemical equilibria between the formally negatively charged BO_4^- tetrahedra and species bearing nonbridging oxygen (NBO), either silicate Q^n , $n < 4$, or trigonal planar borate units. For example, the equilibrium



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between silicate Q^4 and tetrahedral $B\emptyset_4^-$ and silicate Q^3 and trigonal planar $B\emptyset_3$, where $\emptyset$ denotes a bridging oxygen shared between two network cations (here Si and/or B). The shifting to the right of such equilibria with increasing melt temperature has also been observed in pure borates [3,4], where nonbridging oxygen on borate species become increasingly prevalent, for example with



Such reactions contribute to the configurational heat capacity and entropy of the melt, and thereby to the fragility [14,15], influencing how rapidly the viscosity changes with temperature—a key parameter in melt processing and glass production. It has also been noted that the thermal expansion coefficients of borate melts are anomalously high compared to those of their glasses [16], as compared to several other families of glass-forming liquids, including silicates. This behavior is also presumably strongly influenced by boron coordination-changing chemical equilibria.

Angeli *et al.* [6] conducted an in-depth study of a sodium cesium borosilicate glass-forming composition ($20M_2O \cdot 17B_2O_3 \cdot 63SiO_2$, mol%), both in terms of the glass fictive temperature, T_f , and the melt temperature itself. Using ^{11}B MAS NMR, N_4 was found to increase from 71% to 78% with a decrease in T_f from 902 down to 790 K. By calibrating a deconvolution of the measured Raman spectra using the NMR results, the authors were also able to infer *in-situ* a decrease in N_4 from 78% down to 62% between $T_g \approx 800$ K and $T \approx 1040$ K. Importantly, this was directly correlated with an increase in the number of nonbridging oxygen found on silicate Q^n , $n < 4$ species. Earlier ^{11}B MAS NMR work by Stebbins and Ellsworth [7] and Sen, Xu, and Stebbins [8] had also demonstrated dependence of N_4 on T_f , for a handful of $Na_2O - B_2O_3 - SiO_2$ glass compositions.

Although nonexhaustive, the literature review above serves to illustrate the preponderance of studies aimed at sodium or alkali-bearing borosilicates, which should not be too surprising given the widespread importance of these glasses. On the other hand, several applications require or benefit from alkali-free borosilicate compositions. These include alkaline earth borosilicate bioglasses [17], as well as display and sealing glasses [18–26] which require low ionic conductivities and melt volatilities, along with thermal expansion coefficients matching those of adjoining metal or ceramic interconnects. Among alkaline earth borosilicates, barium borosilicates have the lowest working temperatures, which can be favorable depending upon application, as well as in terms of cost savings during manufacture. Barium also imbues the highest refractive indices and is used in optical glasses, as well as for photon radiation shielding. Applications such as nuclear waste encapsulation [27–29] and wastewater treatment [30] typically involve mixed alkali-alkaline earth (e.g., Na-Ba) borosilicate glasses.

Herein we focus on two exemplary $BaO - B_2O_3 - SiO_2$ compositions: $50BaO \cdot 25B_2O_3 \cdot 25SiO_2$ (BBS211) and $28BaO \cdot 48B_2O_3 \cdot 24SiO_2$ (BBS352). BBS211 lies close to the deep eutectic on the $BaSiO_3 - BaB_2O_4$ join, is an end-member of a series of candidate sealing glasses investigated by Lin *et al.* [18], and shows a high tendency toward crystallization. BBS352 is similar to the sealing glass composition

developed by Hsu *et al.* [24] and demonstrates exceptionally good glass formability. Glass compositions, transition and melting temperatures are listed in Table I. It is worth stating that herein J and L are used to denote the molar ratios of modifier oxide and silica, respectively, to B_2O_3 , in order to reserve the more conventional R and K for the molar gas and equilibrium constants, respectively.

Neutron diffraction is an ideal option for observing the structure around light elements, such as boron, in the presence of heavier ones, such as barium, which dominate the interactions with x-rays. Indeed, high-energy x-ray total scattering diffraction has been used previously to extract detailed information on the borate network structure, including $N_4(T)$, in lithium [14,31] sodium [32,33], and barium [15] borate melts and glasses, but with significantly higher uncertainties in the latter case due to the large x-ray scattering cross section of barium. Whilst synchrotron x-ray sources have the great advantage in terms of measurement times (seconds, *c.f.* minutes-hours for neutrons), neutrons have the edge in cases such as the barium borosilicate system, where the modifier (Ba) is heavy and the presence of multiple network formers (B and Si) means that the signal from either of them is diluted, as compared to a similarly modified pure borate or silicate. Moreover, the B–O and Si–O bonds are relatively similar in length, at around 1.371 Å in BO_3 , 1.477 Å in BO_4 , and 1.624 Å in SiO_4 units. This raises the distinct possibility of resolving the B–O and Si–O bond length distributions using pulsed neutrons, which can provide high real-space resolution in the measured pair distribution functions, by way of large maximum momentum transfer magnitudes, Q_{max} . Resolving these two features has rarely, if ever, been achieved in previous diffraction studies, owing either to an insufficient Q_{max} , such as those typically obtained with reactor neutron sources [5,34,35] or with x-rays [36,37] ($Q_{max} < 25 \text{ Å}^{-1}$), and/or to additional broadening applied by a modification function used to reduce the effects of termination at finite Q_{max} [36,38–40].

Herein we seek to achieve comparable results to those obtained at synchrotron x-ray sources (albeit on longer timescales), and hence go beyond previous state-of-the-art [5], particularly in terms of extraction of $N_4(T)$ over multiple state points, and to do so for a heavy-metal modified borosilicate system that would not be feasible using x-ray sources. Furthermore, investigation of the ability to resolve B–O and Si–O bond length distributions using pulsed neutrons is of interest, since this enables more accurate determination of N_4 as well as other structural parameters of interest.

A. Sample preparation

Batches were mixed to yield 30 g of glass product, accounting for water and carbon dioxide evolution from the $^{11}B(OH)_3$ (Eagle Picher, 99.96% ^{11}B isotopic purity) and $BaCO_3$ (SLS select $\geq 99\%$) reagents. Isotopic enrichment of ^{11}B is crucial for eliminating the majority of the strongly neutron absorbing ^{10}B isotope. Quartz (Wacomsil 99.9% SiO_2) for the batches was dried at 873 K prior to weighing. The BBS211 batch was added one spoon at a time to a hot Pt/Au crucible taken from the electric furnace held at 1348 K, in order to avoid overflow due to frothing during evolution of volatiles. Once all material had been added, the melt was left

TABLE I. Codes for the two glasses of the present study, with nominal molar compositions. Glass transition and liquidus temperatures are taken or estimated from the literature. Mass and atom number densities measured herein by helium pycnometry are also given. Herein J and L are used to denote the molar ratios of modifier oxide and silica, respectively, to B_2O_3 , in order to reserve the more conventional R and K for the molar gas and equilibrium constants, respectively.

Code	BaO mol%	$^{11}B_2O_3$ mol%	SiO_2 mol%	$J = BaO/B_2O_3$	$L = SiO_2/B_2O_3$	T_g (K) [51]	T_m (K) [18,52,68]	ρ_M g cm $^{-3}$	ρ_0 atoms nm $^{-3}$
BBS211	50	25	25	2	1	830	1252	4.217(3)	69.77(5)
BBS352	28	48	24	0.583	0.5	901	1223	3.453(3)	84.13(7)

to homogenize for 1 hour in the furnace, following which it was poured onto a brass plate and splatted with a steel plate, with the material remaining in the crucible quenched by dipping its base into deionized water. Visual inspection revealed that this initial splat quench yielded a product with glassy exterior, and a white crystalline layer sandwiched in between, belying the poor glass forming ability of this melt composition. As such, the material was returned to the crucible, the furnace temperature increased to 1373 K, and remelted for 1 hour, prior to repeating the splat quenching procedure as rapidly as possible. This second attempt yielded a product that appeared glassy throughout.

BBS352 glass was synthesized in a similar manner, starting with the furnace at 1373 K. The melt was visually checked after 1, 1.5, and 2 hours at temperature, with some bubbles and froth observed in the initial two checks. Hence, after 2 hours at temperature, the BBS352 melt was splat quenched, yielding a glass, by visual inspection.

B. Density

Glass densities were measured by helium gas pycnometry immediately following their syntheses using an Anton Paar Ultrapy 5000. Sample volumes were measured to be approximately 2.2 cm 3 (BBS211) or 2.4 cm 3 (BBS352), and using the measured sample weights, mass densities were calculated as shown in Table I, along with atom number densities based on the nominal chemical and isotopic glass compositions. The density of pure aluminium pellets of similar sample volumes were also measured as a secondary calibration, and found to be 2.700(1) and 2.6945(2) gcm $^{-3}$ prior to the BBS211 and BBS253 density measurements, respectively, in good agreement with the crystallographic expectation.

To estimate the high-temperature density of BBS352 glass, the linear thermal expansion coefficient (TEC) measured by Tupy and Skrivan [41] of $\alpha_L = 7.05$ ppm K $^{-1}$ was used. The volume TEC $\alpha_V = 3\alpha_L = 21.15$ ppm K $^{-1}$ was then assumed constant over the $294 \leq T$ (K) $\leq T_g \approx 901$ interval yielding

$$\rho_{BBS352}^{glass}(T) = \rho_{T_{ref}} \exp(-\alpha_V(T - T_{ref})),$$

with $T_{ref} = 294$ K and $\rho_{T_{ref}} = 3.446$ gcm $^{-3}$ for natural isotopic boron, based on the pycnometric glass density.

In lieu of high temperature density or TEC measurements for BBS352 melt, the melt density was estimated based on those of binary barium borates [42,43]. In particular, the measurements of Shartsis and Shermer [42] for a 32.1 mol% BaO borate melt were fitted, constrained with the BBS352 glass density at $T_g = 901$ K of 3.402 gcm $^{-3}$ using the following

equation, as in previous work [15]:

$$\rho_{BBS352}^{melt}(T) = \rho_{\infty}^{melt} + B \exp\left(-\frac{T - T_0}{b}\right),$$

with $\rho_{\infty}^{melt} = 2.646$ gcm $^{-3}$, $B = 0.706$ gcm $^{-3}$, $T_0 = 946.5$ K, and $b = 668.2$ K. Note that this result yields BBS352 melt densities slightly in excess of GlassNet [44] deep neural network predictions, but lower than measurements on a more silicate-rich barium borosilicate optical glass melt [45] (approximately 23BaO · 5CaO · 7BeO · 13B $_2$ O $_3$ · 51SiO $_2$ molar composition, ignoring minor impurities).

C. Neutron diffraction

Neutron diffraction time-of-flight (tof) spectra were collected with the Small Angle Neutron Diffractometer for Amorphous and Liquid Samples (SANDALS) instrument at the ISIS Neutron and Muon Source, UK. Calibration of the detector positions was performed as described previously [46]. A null-scattering V-Nb alloy rod of 8 mm diameter was measured for purposes of absolute normalization, as was an empty instrument background. Initial ambient temperature measurements were made on glass pieces inside drawn vanadium cylindrical cells. The empty V cell was also measured for purposes of subtraction. High-temperature measurements were performed using a combination of an all vanadium vacuum furnace and thin-walled Pt cell (described previously) [46]. The empty furnace was measured for purposes of background subtraction, and it was determined to be sufficient to make this measurement only at ambient temperatures. The furnace containing the empty Pt cell was measured at 300 K, and in 100 K increments up to 1400 K. Following these measurements, 9.2442 g of BBS352 glass pieces were added to the Pt cell and the assembly was measured at the same temperature points, for 500 μ Ahr of accumulated proton beam on target ($\lesssim 3.5$ hr) at each step up to 1200 K, and 400 μ Ahr ($\lesssim 2.7$ hr) for the final two steps.

In order to increase the sample/cell (S/C) volume ratio in the neutron beam, a BN beam mask was used, external to the furnace, defining a beam width of 8.5 mm. This beam mask width was chosen as a reasonable balance between maximizing both the S/C ratio and the sample signal, S , itself, as described in the Supplemental Material [47], for the 11 mm external diameter, 130 μ m wall Pt cell.

For measurements of glass samples inside vanadium cells, the full SANDALS neutron wavelength range of $0.05 \leq \lambda \leq 4.95$ Å was used. For measurements utilizing the Pt cell, a slightly reduced wavelength range of $0.09 \leq \lambda \leq 4.95$ Å was

used, in order to avoid effects of the 12 and 20 eV nuclear resonances of Pt.

Data reduction, normalization, corrections and merging of the 620+ tof spectra to yield the final neutron structure factor, $S^N(Q)$, was performed using the GudrunN software package. The $S^N(Q)$ has been defined previously [3,46] and $Q = (4\pi/\lambda)\sin\theta$ is the magnitude of the momentum transfer in $\hbar$ (reduced Planck constant) units, with 2θ the scattering angle. Renormalization of the $S^N(Q)$ and their Fourier transforms $D^N(r)$ were performed using the procedure described previously [48], utilizing the measured or estimated atom number densities, ρ_0 , to ensure that the low r region of $T^N(r)$, devoid of structural correlations, correctly oscillates about zero. In practice this was performed through fitting the low r slope of $D^N(r) = T^N(r) - 4\pi r \rho_0 \langle b \rangle^2$, in the $0 < r < 2.1$ Å range, including two peaks to approximately fit the B–O and Si–O correlations in that range, where $\langle b \rangle$ denotes the compositionally averaged bound coherent neutron scattering length. The renormalization factor then follows from the ratio between the expected slope, proportional to ρ_0 , and this fitted slope. Gudrun input files and numerical data for the neutron structure factors $S^N(Q)$ and total correlation functions $T^N(r)$ are available at [49].

D. Peak fitting

The first sharp diffraction peak (FSDP) *circa* 1.5 Å^{-1} was characterized by Lorentzian peak fitting to its leading edge, including a contribution from an equivalent peak at negative Q to ensure that the overall derivative vanishes as $Q \rightarrow 0$. This function has the form

$S_1(Q)$

$$= S_0 + \frac{2A}{\pi} \left(\frac{\Delta Q_1}{4(Q - Q_1)^2 + \Delta Q_1^2} + \frac{\Delta Q_1}{4(Q + Q_1)^2 + \Delta Q_1^2} \right),$$

where S_0 is the limiting value far from the peak, A is a scaling factor, Q_1 is the peak position, and ΔQ_1 its width. Characteristic periodicities and correlation lengths associated with the FSDP are given by $\xi = 2\pi/Q_1$ and $\zeta = 2\pi/\Delta Q_1$, respectively.

The first two or three peaks in the real-space $T^N(r)$ were fitted with Gaussian bond-length distributions,

$$\tilde{t}_{ij}(r) = \frac{n_{ij}}{c_j r_{ij} \sqrt{2\pi \langle u_{ij}^2 \rangle}} \exp\left(-\frac{(r - r_{ij})^2}{2\langle u_{ij}^2 \rangle}\right) \otimes P_{ij}^N(r)$$

broadened by convolution ($\otimes$) with the appropriate peak-shape function

$$P_{ij}^N(r) = \frac{1}{\pi} \int_0^\infty W_{ij}^N M(Q) \cos Qr \, dQ.$$

In the above the r_{ij} are mean bond lengths, n_{ij} mean coordination numbers, $\langle u_{ij}^2 \rangle^{1/2}$ the root-mean-square deviations in bond-length, c_j the fraction of j atoms in the composition, and W_{ij}^N the neutron pair weighting factors [3]. $M(Q)$ is a modification function, which herein is a simple step function which abruptly truncates the $S^N(Q)$ at $Q_{\max}$ in the Fourier transform to real-space, yielding the highest possible real-space resolution for the given $Q_{\max}$ [3,14]. The program PFIT [50] was used to perform the fitting.

II. RESULTS AND DISCUSSION

A. Density measurements

The measured glass densities are recorded in Table I, alongside the atom number densities calculated using the nominal glass chemical and isotopic compositions. Results are in good agreement with the previous study of Feller *et al.* [51] who measured $4.23(4) \text{ g cm}^{-3}$ for BBS211, whilst a density of $3.47(3) \text{ g cm}^{-3}$ can be estimated for BBS352 by linear interpolation. Our measured densities are slightly lower than those reported by Hamilton, Cleek, and Grauer [52] who reported densities of 4.249 and 3.488 g cm^{-3} for glasses very close in composition to BBS211 and BBS352, respectively. This systematic offset is opposite to expectations based on the ^{11}B enrichment used herein, which slightly increases the mass densities, but is nonetheless small and may arise from any number of differences in sample preparation and density measurement methods.

B. Diffraction patterns and FSDP fitting

The neutron diffraction patterns for the two BBS glasses under ambient conditions are shown in Fig. 1(a). These display qualitatively similar features to neutron diffraction measurements on silica-free barium borate glasses [3,15,53–55] over the full Q -range. The evolution of the $S^N(Q)$ for BBS352 with temperature is shown in Fig. 1(b), displaying systematic changes that are most pronounced above T_g . There are small artefacts associated with imperfect subtraction of the Pt container scattering, but these are kept small and consistent with temperature owing to the use of the beam mask, and as such are considered negligible throughout the analysis. During the experiment, the Pt cell eventually failed upon heating from 1200 to 1300 K, and so no data are available above 1200 K. This failure was caused by creep of the sample up the inside of the cell and in-between the cell wall and the Ta lid, and was likely exacerbated by the exposure to vacuum inside the furnace.

Parameters derived through fitting of the first sharp diffraction peak (FSDP) are plotted in Fig. 2. This lowest- Q feature of the diffraction patterns can be associated with the borate network, since its amplitude diminishes with increasing BaO content of the glasses in Fig. 1(a), as well as in binary barium borate glasses by both neutron [3,15,53–55] and x-ray [15] diffraction methods. Furthermore, the FSDP amplitude compared to the subsequent features *circa* 2 and 3 Å^{-1} is much smaller in x-ray diffraction patterns for barium borate [3,15] and borosilicate [56] glasses, implying that scattering from Ba atoms is not a primary contributor. It is interesting to note that the periodicity in Fig. 2(a) actually begins to decrease above T_g , which is in opposition to the expected positive bulk thermal expansion, and opposite to the behavior observed for pure $^{11}\text{B}_2\text{O}_3$ [46]. On the other hand, the correlation length of the FSDP in BBS352, which is much longer than in pure $^{11}\text{B}_2\text{O}_3$, decays more rapidly above T_g , such that they approach a similar value at 1200 K.

The dimensionless parameter $\iota = \zeta/\xi = Q_1/\Delta Q_1$ gives a measure of intermediate range ordering in terms of the number of periods per correlation length. By this measure, BBS352 glass is more ordered than B_2O_3 glass, with $\iota = 3.1(1)$

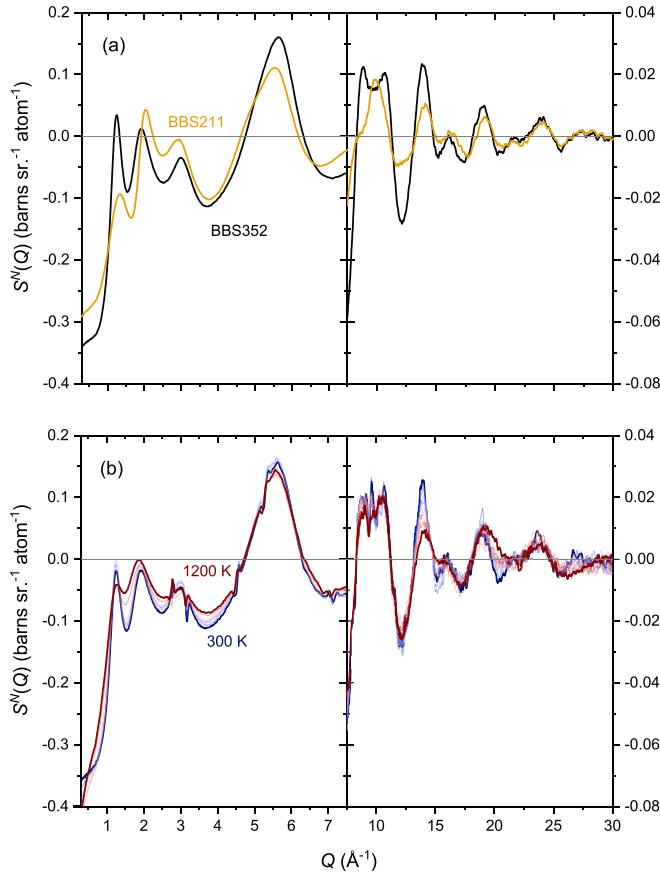


FIG. 1. Total neutron structure factors measured on the SANDALS instrument at ISIS Neutron and Muon Source for (a) BBS352 and BBS211 barium borosilicate glasses, in vanadium cells under ambient conditions, and (b) BBS352 glass and supercooled liquid, inside a platinum cell and vanadium vacuum furnace. Thick curves are used for the lowest and highest temperature data, while thin curves are used for the eight intermediate temperatures, with their colors transitioning from blue to red with increasing temperature. Small artefacts arising from the residual Pt container Bragg peaks can be discerned, particularly at 2.77 and $3.20 \text{ \AA}^{-1}$, from the 111 and 200 lattice planes. Note the change of vertical scale at $7.5 \text{ \AA}^{-1}$.

cf. $2.45(6)$, respectively. However, by 1200 K the two liquids have reached the same $\iota = 1.37(2)$.

C. Correlation functions and real-space peak fitting

The neutron diffraction total correlation functions for the two BBS glasses at ambient temperature are shown in Fig. 3. Remarkably the peak arising due to Si–O bonds *circa* $1.6 \text{ \AA}$ is resolved from that arising from B–O bonds *circa* $1.4 \text{ \AA}$ in BBS211 glass. This is something rarely, if ever, observed in past total scattering diffraction measurements of borosilicates, and attests to the power of pulsed neutron diffraction to yield larger Q_{max} and better resolution than either typical x-ray sources or reactor neutrons. The fact that resolution is not observed for BBS352 is largely due to the dominance of the B–O peak over the Si–O peak. Indeed, for the best chance of resolving the two peaks, they should have similar areas, which

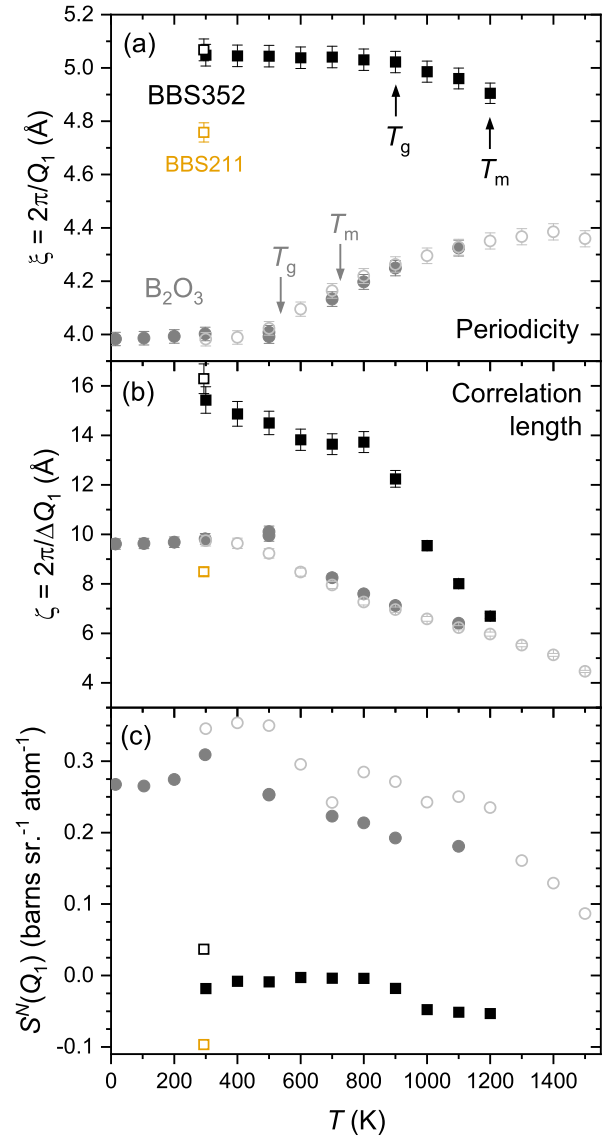


FIG. 2. Parameters characterizing the first sharp diffraction peak (FSDP) for BBS352 glass, supercooled liquid and melt, and ambient BBS211 glass. (a) Periodicities $\xi = 2\pi/Q_1$ from the FSDP position Q_1 , (b) Correlation lengths $\zeta = 2\pi/\Delta Q_1$ from the FSDP width ΔQ_1 , (c) value of the structure factor at Q_1 . Equivalent parameters for $^{11}\text{B}_2\text{O}_3$ are shown for comparison [46].

implies

$$\frac{c_{\text{Si}}}{c_{\text{B}}} = \frac{n_{\text{BO}} r_{\text{SiO}} \bar{b}_{\text{B}}}{n_{\text{SiO}} r_{\text{BO}} \bar{b}_{\text{Si}}} \approx \frac{3.5 \times 1.6 \times 6.65}{4 \times 1.4 \times 4.15} \approx 1.6,$$

which is equivalent to $L = [\text{SiO}_2]/[\text{B}_2\text{O}_3] \approx 3.2 \pm 0.6$, where the uncertainty range accounts for the expected range in n_{BO} and bond lengths. Of course, the chances of resolution are also enhanced when the difference $r_{\text{SiO}} - r_{\text{BO}}$ is maximized, i.e., for $n_{\text{BO}} = 3$, $N_4 = 0$, such that $r_{\text{SiO}} - r_{\text{BO}} \approx 0.25 \text{ \AA}$, and also when the peak widths are small, e.g., at low temperatures. Both BBS compositions considered herein are far from the ideal $L \approx 3.2$, but BBS211 ($L = 1$) is slightly closer and resolution is just about achieved with the Q_{max} of $35 \text{ \AA}^{-1}$ and step modification function. This is despite the fact that the N_4 , and

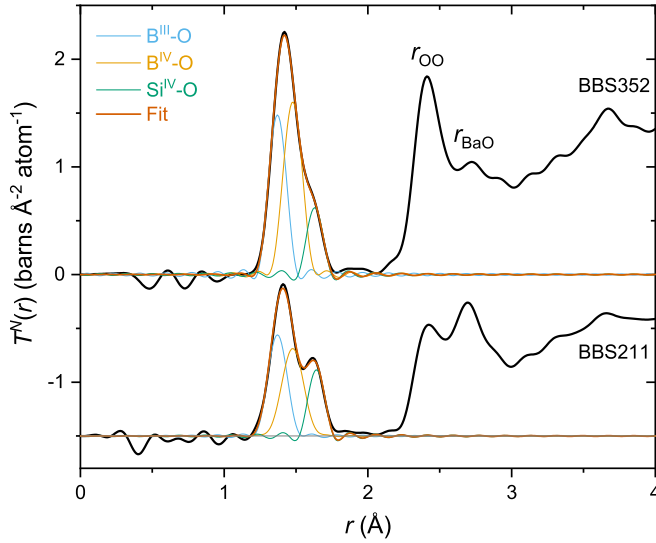


FIG. 3. Total neutron correlation functions for BBS352 and BBS211 barium borosilicate glasses measured on the SANDALS instrument at ISIS Neutron and Muon Source, in vanadium cells at ambient temperature. A step modification and $Q_{\max} = 35 \text{ \AA}^{-1}$ were used in the Fourier transforms of the $Q S^N(Q)$, yielding resolution of the nearest-neighbor Si–O and B–O peaks for BBS211, but not for BBS352. Results from peak fitting are also displayed.

hence the $r_{\text{SiO}} - r_{\text{BO}}$, are also far from ideal resolution-wise, as can be seen in the following.

In order to characterize the B–O and Si–O bond length distributions, peak fits to the $T^N(r)$ were performed in the $1.1 \leq r \leq 1.8 \text{ \AA}$ interval. Fitting of just two distributions (one B–O and one Si–O) indicated that fitting constraints were needed in order to prevent unexpected results such as $n_{\text{SiO}} > 4$, and this was achieved by fixing the $n_{\text{SiO}} = 4$. Nonetheless, as has been observed previously with high real-space resolution neutron diffraction data on borates [3,15,57,58] and borosilicates [38], improved fits were obtained by including an additional bond length distribution, owing to the presence of distinct $\text{B}^{\text{III}}\text{--O}$ and $\text{B}^{\text{IV}}\text{--O}$ bond lengths, where the roman superscripts denote coordination numbers. In order to obtain sensible results, with bond lengths within the range expected from crystallographic and bond-valence considerations, and similar peak widths for all three peaks, additional constraints were required. This was achieved, somewhat arbitrarily, through fixing the $\text{B}^{\text{III}}\text{--O}$ and $\text{B}^{\text{IV}}\text{--O}$ peak positions at those estimated from standard bond-valence parameters [59], and for fully symmetric trigonal planar and tetrahedral units, i.e., at 1.371 and 1.477 Å, respectively. The resulting fits for the two glasses are shown in Fig. 3, and the fit parameters are given in Table II. The

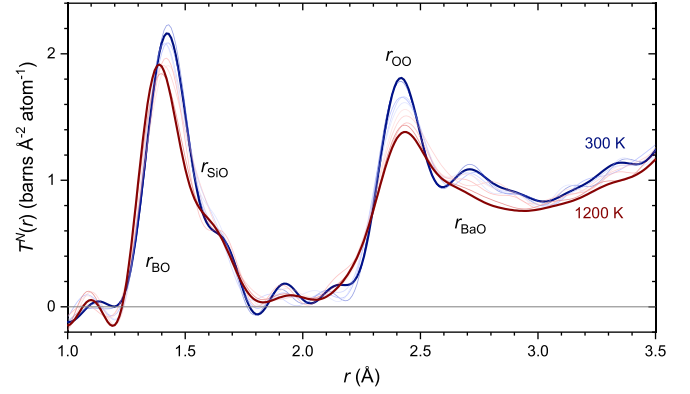


FIG. 4. Total neutron correlation functions for BBS352 glass, supercooled liquid and melt, measured on the SANDALS instrument at ISIS Neutron and Muon Source, in a platinum cell inside a vanadium vacuum furnace. A step modification and $Q_{\max} = 30 \text{ \AA}^{-1}$ were used in the Fourier transforms of the $Q S^N(Q)$. Thick curves are used for the lowest and highest temperature data, while thin curves are used for the eight intermediate temperatures, with their colors transitioning from blue to red with increasing temperature.

key results are the N_4 fractions, which, from the total B–O peak areas, are 0.33 for both glasses. However, as we have shown previously [3,14,15,31,33], more accurate and precise N_4 fractions can often be derived from the mean B–O bond lengths using a bond-valence based mapping

$$N_4(T) = n_{\text{BO}}(T) - 3 = 3 \left(\exp \left(\frac{r_{\text{BO}}(T) - R_{\text{BO}}(T)}{b} \right) - 1 \right),$$

with $b = 0.37 \text{ \AA}$ and $R_{\text{BO}}(294 \text{ K}) = 1.3741(2) \text{ \AA}$ taken in this case from an analogous measurement of $^{11}\text{B}_2\text{O}_3$ glass in a vanadium cell on SANDALS [46]. This yields for BBS352 an $N_4 = 0.49(2)$, where the uncertainty quoted here accounts for the range of r_{BO} in $^{11}\text{B}_2\text{O}_3$ observed in different studies [3,46] [and hence the possible range in $R_{\text{BO}}(294 \text{ K})$]. This result agrees very well with that from ^{11}B MAS NMR of $N_4 = 0.52(1)$ from Zhao, Kroeker, and Stebbins [60]. N_4 fractions in barium borosilicate glasses are also reported by Feller *et al.* [51] who reproduce the data from the PhD thesis of Stallworth [61]. However, for binary barium borate glasses, the Stallworth data are clear outliers to lower N_4 compared to a host of other studies [3,15]. Therefore, it is not too surprising that for BBS352, a lower $N_4 = 0.37$ is reported [51,61]. Interestingly however, Feller *et al.* [51] and Stallworth [61] give for BBS211 an $N_4 = 0.33$, which is consistent with the difference between the two glasses found herein, that is $N_4 = 0.49(2)$ for BBS352 and $N_4 = 0.45(2)$ for BBS211.

TABLE II. Parameters for individual bond length distributions derived from peak fitting to the $T^N(r)$ for BBS glasses shown in Fig. 3. Parameters held fixed during fitting were $n_{\text{BO1}} = 1.371 \text{ \AA}$, $n_{\text{BO2}} = 1.477 \text{ \AA}$ and $n_{\text{SiO}} = 4$. N_4 fractions were calculated by bond-valence mapping from the mean bond lengths. Uncertainties in parentheses.

Code	$u_{\text{BO1}} (\text{\AA})$	n_{BO1}	$u_{\text{BO2}} (\text{\AA})$	n_{BO2}	$r_{\text{SiO}} (\text{\AA})$	$u_{\text{SiO}} (\text{\AA})$	Σn_{BO}	$\bar{r}_{\text{BO}} (\text{\AA})$	N_4	χ^2
BBS211	0.062(1)	1.60(3)	0.073(2)	1.73(4)	1.642(1)	0.045(1)	3.33(6)	1.4259(9)	0.451(8)	1.709
BBS352	0.0546(7)	1.47(2)	0.0610(9)	1.86(2)	1.631(1)	0.043(1)	3.33(3)	1.4302(5)	0.491(4)	0.931

TABLE III. Parameters for individual bond length distributions derived from peak fitting to the $T^N(r)$ for BBS352 glass and supercooled liquid shown in Fig. 4. The three peak widths were all held fixed during fitting and their values are marked by asterisk. $n_{\text{SiO}} = 4$ was also held fixed. N_4 fractions were calculated by bond-valence mapping from the mean bond lengths. Uncertainties in parentheses.

T (K)	r_{BO1} (Å)	n_{BO1}	r_{BO2} (Å)	n_{BO2}	r_{SiO} (Å)	u_{ij} (Å)	Σn_{BO}	$\bar{r}_{\text{BO}}$ (Å)	N_4	χ^2
300	1.3754(14)	1.58	1.4863(19)	1.58	1.6475(25)	0.04972*	3.16(4)	1.4308(14)	0.481(13)	0.829
400	1.3786(18)	1.60	1.4865(25)	1.61	1.6423(33)	0.05106*	3.21(6)	1.4326(18)	0.492(17)	1.364
500	1.3793(9)	1.68	1.4961(14)	1.53	1.6535(19)	0.05240*	3.21(3)	1.4351(10)	0.511(9)	0.447
600	1.3839(5)	1.89	1.5058(9)	1.34	1.6421(14)	0.05374*	3.23(2)	1.4346(6)	0.501(6)	0.241
700	1.3880(2)	2.02	1.5149(5)	1.20	1.6494(7)	0.05508*	3.22(2)	1.4352(4)	0.501(3)	0.058
800	1.3755(13)	1.63	1.5004(20)	1.52	1.6665(29)	0.05642*	3.16(4)	1.4358(14)	0.501(13)	0.908
900	1.3822(11)	1.91	1.5182(22)	1.37	1.6739(34)	0.05776*	3.28(3)	1.4390(13)	0.526(12)	1.117
1000	1.3828(18)	1.78	1.4979(35)	1.22	1.6632(37)	0.05910*	3.00(6)	1.4294(21)	0.431(19)	1.085
1100	1.3775(11)	1.93	1.5137(26)	1.12	1.6716(33)	0.06044*	3.05(3)	1.4275(14)	0.408(13)	1.401
1200	1.3783(10)	2.07	1.5178(27)	0.97	1.6566(34)	0.06178*	3.04(3)	1.4227(14)	0.358(13)	1.970

Moving on to the temperature series represented in Fig. 4, peak fitting was performed in a slightly different manner, which was found to yield improved fits (smaller χ^2 , Table III). Unlike with the ambient data collected in vanadium cells, the high-temperature platinum cell data were not best fitted by fixing the positions of the $\text{B}^{\text{III}}\text{-O}$ and $\text{B}^{\text{IV}}\text{-O}$ peaks, even when accounting for thermal expansion of these bonds using the expansion coefficient measured for $^{11}\text{B}_2\text{O}_3$ [46]. Instead, the peak widths of the three peaks (including the Si-O peak) were set to be equal to one another, and furthermore, this width was modeled based on that measured for the $\text{B}^{\text{III}}\text{-O}$ peak in B_2O_3 using [46,62]

$$u_{ij} \equiv \langle u_{ij}^2 \rangle^{1/2} = 0.0457 + (1.34 \times 10^{-5})T$$

in units of Å and kelvin. The results using this procedure are recorded in Table III, and the mean B–O bond length, coordination number and N_4 fractions plotted in Fig. 5. Remarkably, the mean r_{BO} appears to display thermal expansion up to T_g , before declining rapidly in the supercooled liquid state. For BBS352 glass, a linear fit yields the mean $r_{\text{BO}} = 1.429(2) + [9.3(2.4) \times 10^{-6}]T$ (in Å and K) and an expansion coefficient of $\alpha_{\text{BO}} = 6.5(1.7)$ ppm K^{-1} , slightly larger than that observed for pure $^{11}\text{B}_2\text{O}_3$ glass and melt. It is interesting to note that the α_{BO} for BBS352 glass is very similar to the bulk linear thermal expansion coefficient (Table IV), implying the possibility that the glass has a very simple vibrational thermal expansion mechanism. This is in contrast to B_2O_3 glass, for which the bulk expands at a much greater rate than the B–O bond (Table IV), likely due to the two-dimensional

nature of the B_2O_3 glass network, compared to the largely three-dimensional borosilicate network in BBS352 glass.

The decline in bond length above T_g is interpreted as arising from boron coordination reduction with increasing supercooled liquid temperature, coupled with depolymerization as nonbridging oxygen replace BO_4^- as the charge balancing species against the barium cations. This interpretation is supported by the directly determined mean n_{BO} (Table III), which are also smaller in the liquid than in the glass. The fact that the directly determined mean n_{BO} imply smaller N_4 fractions than those obtained through the bond-valence mapping is attributed to uncertainties in the normalization, as well as to an increased sensitivity to the fitting procedure. For example, fitting the ambient glass data of Fig. 3 using the same procedure as applied to the temperature series further depresses the n_{BO} from 3.33 for both glasses to 3.23 and 3.10 for BBS352 and BBS211 respectively, although the fits are also much poorer, with χ^2 of 4.585 and 8.039, respectively. Despite this, the mean bond lengths and associated N_4 fractions remain relatively unchanged, with the latter at 0.50(1) and 0.44(2) respectively, in excellent agreement with the values in Table II. This, along with the higher precision, and better agreement with ^{11}B MAS NMR derived N_4 (higher accuracy), further supports the use of the bond-valence derived N_4 fractions. Therefore in Fig. 5(b), the directly determined mean n_{BO} are shown with an *ad hoc* offset of +0.31 for better comparison to the bond-valence derived N_4 . Both sets of data in Fig. 5(b) demonstrate the expected, approximately constant coordination number behavior for the glass, followed by a decline in the supercooled liquid state.

D. Chemical equilibria involving boron coordination change

In the following section we consider some simplified chemical equilibria involving boron changing coordination number from 3 to 4 and *vice versa*. The equilibria are all intentionally kept simple enough to allow calculation of the species concentrations, and thereby equilibrium constants, from the measured $N_4(T)$ and charge balance constraints derived from knowledge of the chemical composition.

In previous studies on molten borates [14,15,31], the temperature dependence of N_4 was interpreted in terms of simple

TABLE IV. Linear thermal expansion coefficients for two glasses, compared to those measured for their mean B–O bond lengths.

Material		α_L (10^{-6} K^{-1})
B_2O_3 glass	Bulk [69]	19.3
	B–O [46]	4.1(3)
BBS352 glass	Bulk [41]	7.05
	B–O	6.5(1.7)

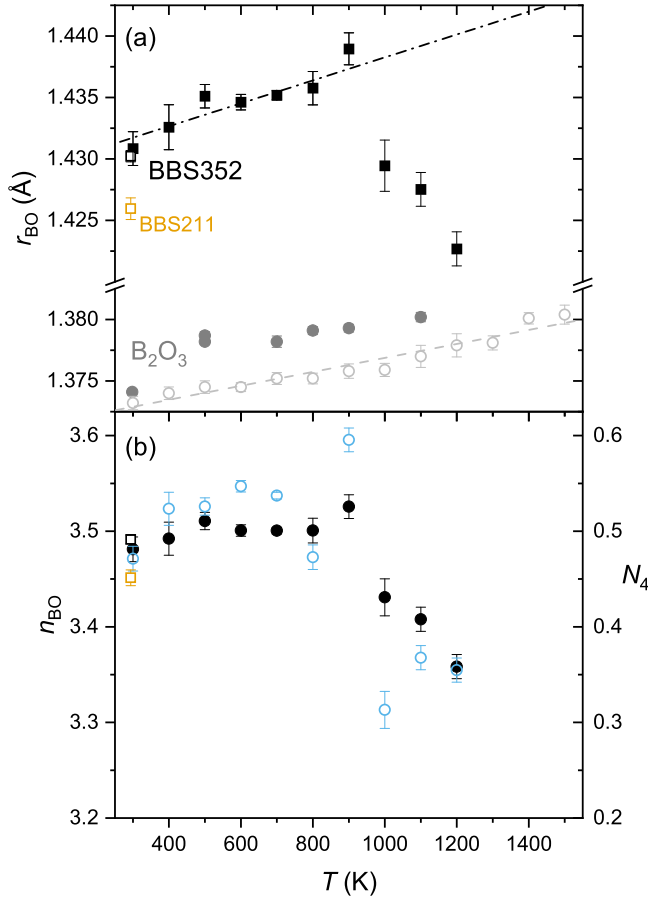
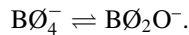


FIG. 5. (a) Mean B–O bond length, derived from peak fitting, for BBS352 glass, supercooled liquid and melt, and ambient BBS211 glass, with that for $^{11}B_2O_3$ shown for comparison [46]. Note the break in vertical scale. The chained curve is a linear fit to the data for BBS352 glass up to T_g , yielding $r_{BO} = 1.429(2) + 9.3(2.4) \times 10^{-6} T$ (K) and an expansion coefficient of $\alpha_{BO} = 6.5(1.7)$ ppm K^{-1} , slightly larger than that observed for pure $^{11}B_2O_3$ glass and melt. (b) Corresponding mean B–O coordination number and tetrahedral fraction N_4 . The filled circles are derived using a bond-valence based mapping from the mean B–O bond lengths, as are the open squares (ambient measurements in vanadium cells). Open blue circles are derived directly from peak areas, with an *ad hoc* addition of 0.31, chosen to minimize the differences between direct and bond-valence derived results.

isomerisation reactions, such as that between the metaborate anions,



This is a simplification because it neglects possible (likely) disproportionations of the species, as well as the concomitant changes in modifier cation bonding and coordination. However, the simplification is helpful for providing phenomenological understanding, as well as the simplest possible analytical form for $N_4(J, T)$, and its contributions to the configurational heat capacity and entropy. Within this simplified model, the equilibrium constant can be written as [14,31]

$$K = \frac{N_4^{\max} - N_4}{N_4} = \exp\left(-\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right), \quad 0 \leq J \leq 3,$$

where ΔH and ΔS are the enthalpy and entropy of isomerization respectively, R is the molar gas constant, and

$$N_4^{\max} = \lim_{T \rightarrow 0} N_4(J, T) = \begin{cases} J, & 0 \leq J \leq 1 \\ 1, & 1 < J \leq 3 \end{cases},$$

is chosen as the low temperature limit. In this case $N_4(J, T)$ takes its simplest analytical form,

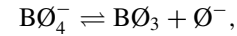
$$N_4(J, T) = \frac{N_4^{\max}(J)}{1 + \exp\left(-\frac{\Delta H(J)}{RT} + \frac{\Delta S(J)}{R}\right)}, \quad 0 \leq J \leq 3.$$

If we initially neglect the fact that the nonbridging oxygen species can reside not only on metaborate units, but also on other borate and silicate polyanions in BBS352, then we can obtain an initial estimate for ΔH and ΔS by constructing the van t'Hoff diagram for $\ln K$ as a function of inverse temperature shown in Fig. 6(a). The four data points shown are only those for $T \gtrsim T_g$ where metastable equilibrium is assumed. The corresponding $N_4(J, T)$ is shown in Fig. 7 by the thick black curve which provides one possible interpolation of the data points, as well as possible extrapolations to higher temperature, and to lower temperature if equilibrium could be attained. The uncertainties are quite large due to the small number of data points, as indicated by the shaded 95% (2σ) confidence bounds in Fig. 6(a), and the shaded 1σ uncertainty region in Fig. 7.

Since the nonbridging oxygen species in a borosilicate composition can reside on either borate or silicate units, and we do not currently know how they are distributed among these, we can choose to consider a chemical equilibrium which does not specify



or equivalently,



if now the $\emptyset$ denotes half an oxygen, rather than explicitly a bridging oxygen species. This approach and the one above have both been used in interpreting ^{11}B NMR studies of borate, borosilicate [6,8,63], and aluminoborosilicate [64,65] glasses, typically as a function of their *fictive* temperatures. Sen, Xu, and Stebbins [8] reported, for an NBS414 (44.5 Na₂O · 11B₂O₃ · 44.5SiO₂, mol%) composition, an increase in NBOs on asymmetric trigonal borate species concomitant with a decrease in N_4 at higher T_f , as observed by fitting ^{11}B MAS NMR spectra. Meanwhile, no change in silicate Q speciation was observed by ^{29}Si NMR, both observations indicating that the additional NBOs generated upon heating resided on borate species. On the other hand, Angeli *et al.* [6] were able to correlate the decrease in N_4 at higher T or T_f for a 17Na₂O · 3Cs₂O · 17B₂O₃ · 63SiO₂ (mol%) composition with an increase in NBOs on silicate species, by Raman spectroscopy. Furthermore, these authors discussed the competing effects which lead to relatively temperature invariant ^{29}Si NMR spectra, despite the structural changes. Analogous fictive temperature studies have not been performed on barium borosilicate glasses, but the NMR data which do exist for BBS352 [60] indicate an NBO content in excess of Dell-Bray model predictions (on both borate and silicate species), from which Zhao, Kroeker, and Stebbins inferred a nonzero population of oxygen triclusters (oxygen bonded to three boron). Taken together, these studies [6,8,60]

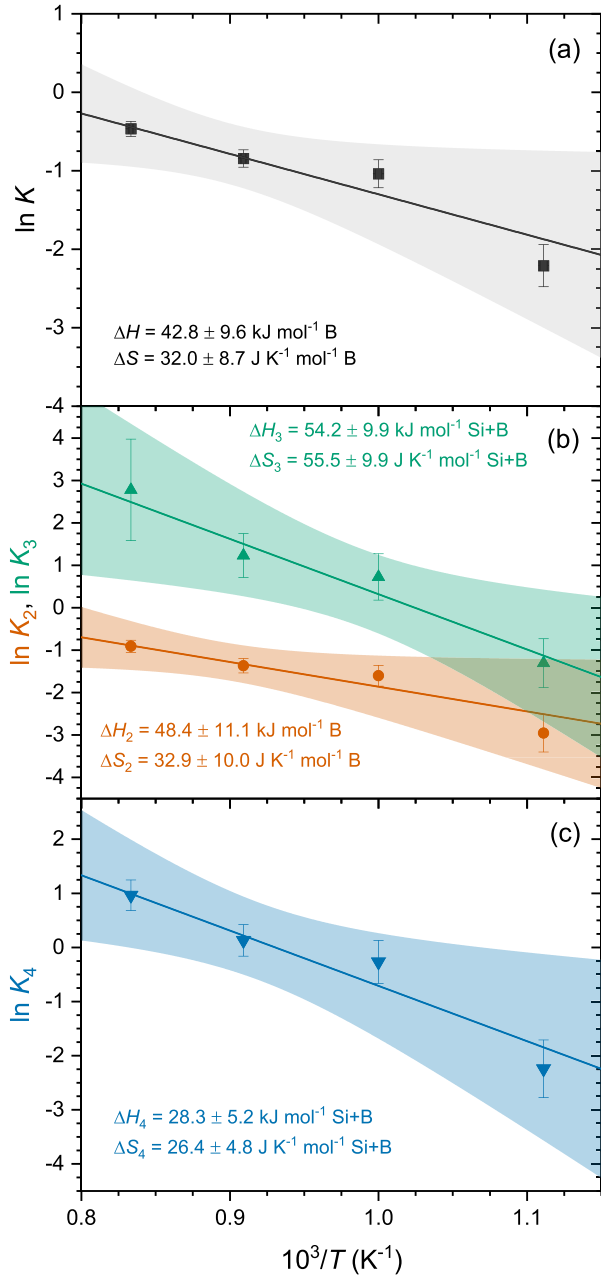


FIG. 6. Van't Hoff plots calculated for four different equilibria, with linear fits and 95% confidence bounds. (a) The simplest case of an isomerisation reaction between tetrahedral $\text{B}\text{O}_4^- \rightleftharpoons \text{B}\text{O}_2\text{O}^-$ trigonal planar units bearing nonbridging oxygen. (b) The cases with unspecified association of the nonbridging oxygen $\text{B}\text{O}_4^- \rightleftharpoons \text{B}\text{O}_3 + \text{O}^-$ (orange circles), and with nonbridging oxygen on silicate Q_3 species only, $\text{Si}\text{O}_4 + \text{B}\text{O}_4^- \rightleftharpoons \text{B}\text{O}_3 + \text{Si}\text{O}_3\text{O}^-$ (green triangles). (c) The case with nonbridging oxygen on silicate Q_2 species only, $\text{Si}\text{O}_4 + 2\text{B}\text{O}_4^- \rightleftharpoons 2\text{B}\text{O}_3 + \text{Si}\text{O}_2\text{O}_2^{2-}$. The enthalpy and entropy changes associated with each reaction are stated on the plots, per mole boron for the former two cases, and per mole network cation (Si or B) for the latter.

indicate a complex, composition dependent distribution of NBOs across silicate and borate species. Thus, in the face of such complexity, one way to proceed is to not specify which species bear the NBOs, and to write the equilibrium constant

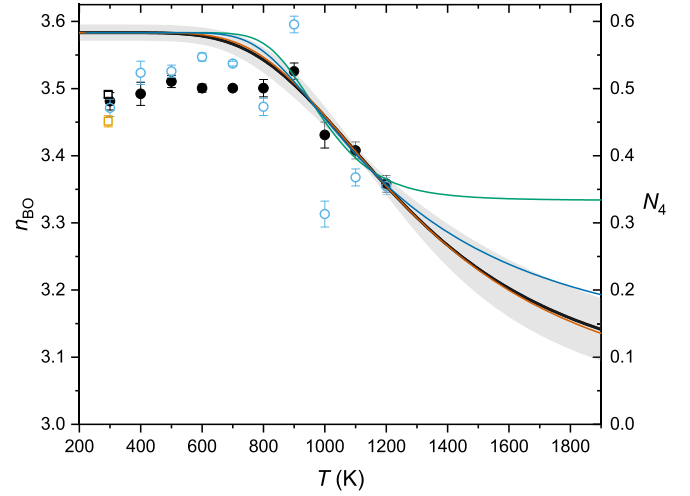


FIG. 7. Results of van't Hoff fitting plotted over an extended temperature range, as compared to the B-O coordination number data. The four curves correspond to the four equilibria covered in the main text, colors as in Fig. 6. The shaded region represents the uncertainty for the simple borate isomerization reaction, with equilibrium constant K , accounting for the positive linear correlation between fitting parameters ΔH and ΔS .

for the above reaction, as

$$K_2 = \frac{(J - N_4)(1 - N_4)}{N_4} = \exp\left(-\frac{\Delta H_2}{RT} + \frac{\Delta S_2}{R}\right),$$

since the ratio of uncharged BO_3 to BO_4^- is simply $(1 - N_4)/N_4$, the total modifier charge per boron is J , and so the nonbridging oxygen per boron is $(J - N_4)$. The above expression inverts to yield a quadratic with solution

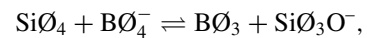
$$N_4(J, T) = \psi - \sqrt{\psi^2 - J},$$

with

$$\psi = \frac{1}{2}\left(1 + J + e^{-\frac{\Delta G_2}{RT}}\right).$$

Where $\Delta G_2 = \Delta H_2 - T\Delta S_2$. Using this model yields a slightly higher enthalpy change, Fig. 6(b), but very similar entropy change for the reaction, as compared to the simple isomerization model, and overall a very similar $N_4(J, T)$ curve, as shown in Fig. 7 by the orange line.

If we instead assume that the nonbridging oxygen tend to reside on silicate, rather than borate, species, we still need an additional simplifying assumption if we wish to quantify their abundances knowing only the composition and $N_4(T)$. This can be achieved by assuming that the silicate species have at most a single nonbridging oxygen, such that the equilibrium takes the following form:



with equilibrium constant given by

$$K_3 = \frac{2(J - N_4)(1 - N_4)}{N_4[L - 2(J - N_4)]} = \exp\left(-\frac{\Delta H_3}{RT} + \frac{\Delta S_3}{R}\right).$$

This expression now explicitly depends on $L = [\text{SiO}_2]/[\text{B}_2\text{O}_3]$ as well as $J = [\text{BaO}]/[\text{B}_2\text{O}_3]$. The K_3 follows from the assumption that only Q_4 and Q_3 silicate species

are present, such that they sum to L per formula unit, and the assumption that all nonbridging oxygen are associated with Q_3 silicate species, such that the Q_3 concentration is $2(J - N_4)$ per formula unit. The Q_3/Q_4 ratio is then simply $2(J - N_4)/[L - 2(J - N_4)]$. Inverting the expression for K_3 again leads to a quadratic in N_4 , this time with solution

$$N_4(J, L, T) = \frac{\sqrt{\phi^2 + 16J\Gamma} - \phi}{4\Gamma},$$

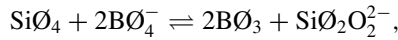
with

$$\phi = (L[\Gamma + 1] - 2J\Gamma + 2),$$

$$\Gamma = e^{-\frac{\Delta G_3}{RT}} - 1.$$

The van t'Hoff diagram for $\ln K_3$ is shown in Fig. 6(b), and yields apparently higher enthalpy and entropy changes per network cation than the previous models. For the BBS352 composition, there are too few silicon atoms available to charge balance even half of the Ba^{2+} cations as singly charged Q_3 silicate species. For this reason, the $N_4(T)$ curve in Fig. 7 has a much higher value in the high temperature limit, due to the saturation of Q_3 units. It seems rather unlikely that this would happen in reality, rather than simply the formation of more highly charged Q_2 units. Measurements to higher temperatures would easily resolve this question, most likely ruling out the K_3 model.

To avoid the unlikely saturation of Q_3 units, but retain a sufficient degree of simplification to allow quantification of the species concentrations, we could equally well assume that Q_2 units are the only charged silicate species, and so define



where again the nonbridging oxygen tend to reside on silicate, rather than borate, species, but now these are Q_2 species with two nonbridging oxygen. This leads to the equilibrium constant

$$K_4 = \frac{(J - N_4)(1 - N_4)^2}{N_4^2(L - J + N_4)} = \exp\left(-\frac{\Delta H_4}{RT} + \frac{\Delta S_4}{R}\right),$$

which now results in a cubic equation in N_4 , with solution

$$N_4(J, L, T) = (\chi + \sqrt{\chi^2 + (\omega - \Lambda^2)^3})^{1/3} + (\chi - \sqrt{\chi^2 + (\omega - \Lambda^2)^3})^{1/3} + \Lambda,$$

with

$$\begin{aligned} \chi &= \Lambda^3 + \frac{3([L - J]e^{-\frac{\Delta G_4}{RT}} - J - 2)(2J + 1)}{2\Theta^2} + \frac{J}{\Theta}, \\ \Lambda &= \frac{([J - L]e^{-\frac{\Delta G_4}{RT}} + J + 2)}{\Theta}, \\ \omega &= \frac{2J + 1}{\Theta}, \\ \Theta &= 3(e^{-\frac{\Delta G_4}{RT}} + 1). \end{aligned}$$

The van t'Hoff diagram for $\ln K_4$ is shown in Fig. 6(c), and this yields apparently lower enthalpy and entropy changes per network cation than the previous models. For the BBS352 composition, there are still slightly too few silicon atoms

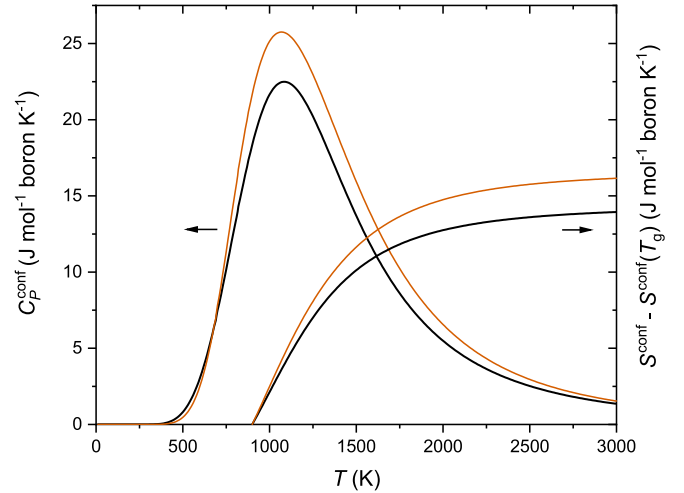


FIG. 8. Boron coordination change contribution to the configurational heat capacity and entropy above T_g (901 K), from the equilibria without explicit silicate units, colors as in Figs. 6 and 7.

available to completely charge balance all of the Ba^{2+} cations, even as doubly charged Q_2 silicate species. Therefore, the $N_4(T)$ curve in Fig. 7 still has a slightly higher value in the high temperature limit than for the K or K_2 models, due to the saturation of Q_2 units. To rule out this model would require measurements to much higher temperatures, which starts to become more and more challenging experimentally. Therefore, although we cannot currently rule out experimentally the K_3 or K_4 equilibria, we reiterate that they are likely to be highly oversimplified [for the purposes of quantification from the measured $N_4(T)$], and we would not in reality expect saturation of Q_3 (or Q_2) silicate species, without formation of Q_2 (or Q_1).

The $N_4(T)$ curves in Fig. 7 all imply contributions to the configurational heat capacity, entropy, and fragility of the supercooled liquid. For the K and K_2 borate equilibria, the heat capacity contribution takes the form

$$C_p^{\text{conf}}(J, T) = -\Delta H(J) \frac{\partial N_4(J, T)}{\partial T},$$

from which we can calculate its value at T_g , Table V, and temperature dependence, Fig. 8. We cannot perform a similar calculation for the mixed borate-silicate equilibria, K_3 and K_4 , due to the unknown partitioning of the reaction enthalpies and entropies between the borate and silicate units. Lenoir *et al.* [66] measured the heat capacities of a range of Na and Ba borosilicate glasses and supercooled liquids, including borate and silicate endmembers. The two Ba borosilicate molar compositions studied were $33BaO \cdot 45B_2O_3 \cdot 22SiO_2$ and $33BaO \cdot 36B_2O_3 \cdot 33SiO_2$, where especially the former composition is rather similar to the BBS352 composition studied herein. The authors calculated the difference in heat capacities between the glass and supercooled melt at T_g , $\Delta C_p(T_g)$, which yields a calorimetric estimate for the total $C_p^{\text{conf}}(T_g)$. After converting to the same units ($J \text{ mol}^{-1} \text{ atom K}^{-1}$, rather than $J \text{ mol}^{-1} \text{ boron K}^{-1}$, which differ by a factor c_B) we can see that the boron coordination change reaction contributes between 30% and 40% (Table V) of the total

TABLE V. Reaction enthalpies and entropies estimated for the equilibria described in the text using the van t'Hoff plots of Fig. 6. Also shown for the borate equilibria (without explicit silicate units) are the configurational heat capacity at the glass transition, $C_p^{\text{conf}}(T = T_g)$, often denoted in the literature as ΔC_p , and the same expressed as a percentage of the total ΔC_p measured by calorimetry for similar compositions [66].

Anion with $\text{B}\emptyset_4^-$	Equilibrium constant	ΔH_i (kJ mol $^{-1}$) ^a	ΔS_i (J mol $^{-1}$ K $^{-1}$) ^a	$C_p^{\text{conf}}(T = T_g)$ (J mol $^{-1}$ K $^{-1}$) ^a	$C_p^{\text{conf}} / C_p^{\text{conf}}(\text{calor.})$ [66] (%)
$\text{B}\emptyset_2\text{O}^-$	K	43(10)	32(9)	18	32
$\emptyset^-$	K_2	48(11)	33(10)	22	38
$\text{Si}\emptyset_3\text{O}^-$	K_3	54(10)	55(10)	—	—
$\text{Si}\emptyset_2\text{O}_2^{2-}$	K_4	28(5)	26(5)	—	—

^aValues are per mole boron for K and K_2 or per mole network cation for K_3 and K_4 .

configurational heat capacity, at T_g . This is in line with similarly derived contributions of 20% to 40% for pure borates [15], which is reasonable given the relatively high borate content of BBS352. This helps to explain why the liquid fragilities of borosilicate melts increase with the borate content [66]—the melt viscosities become increasingly super-Arrhenian due to the temperature dependence of the boron coordination changing equilibrium. Indeed, the Adam-Gibbs approach relates directly the melt viscosity with the temperature dependence of the configurational entropy, $S^{\text{conf}}(T)$, and we can calculate the boron coordination change contribution to S^{conf} above T_g using

$$S^{\text{conf}}(T, J) = S^{\text{conf}}(T_g, J) + \int_{T_g}^T \frac{C_p^{\text{conf}}(T', J)}{T'} dT',$$

for the K and K_2 borate equilibria, and the results are shown in Fig. 8.

Regarding the true speciations in molten BBS, as opposed to the simplified ones discussed above, we can refer to previous work using solid state ^{11}B and ^{17}O NMR [60] where about 5% of oxygen in nonbridging environments were detected in BBS352 glass, approximately evenly distributed between borate and silicate species. This is strikingly different to the behavior in alkali borosilicates, where NBOs on silicate species tend to be favored. Furthermore, a slight excess of NBOs in the BBS352 glass led the authors [60] to hypothesize about 4% of oxygen present as triclusters (e.g., bonded to three boron), although a corresponding resonance in ^{17}O NMR spectra could not be discerned. These facts all point toward a much more complex set of interdependent chemical equilibria governing the array of short range structural species in BBS melts. Nonetheless, the simplified approach used herein provides a useful tool for semiquantitative, phenomenological understanding.

III. CONCLUSIONS

We have demonstrated the ability to extract high quality and detailed structural information as a function of temperature using neutron diffraction on a heavy-metal (Ba) borosilicate glass and its supercooled melt. This is despite the use of a chemically inert, but strongly Bragg scattering, Pt container, enabled by judicious masking of the incident neutron beam. Especially the details of the borate network structure thus derived are expected to be infeasible to obtain with equivalent x-ray diffraction methods, given that the heavy metal Ba modifier would dominate the x-ray scattering.

Furthermore we demonstrate, for the first time to our knowledge, resolution in real-space of the B–O and Si–O bond length correlations. This is attributed to the high real-space resolution accessible using high-energy pulsed neutron sources, as well as to the choice to avoid damping modification functions which typically introduce enough additional broadening to lose the resolution of the B–O and Si–O peaks in the pair correlation functions. We point out that the ability to resolve the two features depends directly on the $\text{SiO}_2/\text{B}_2\text{O}_3$ molar ratio which partly governs the relative intensities of the two peak intensities. The fraction of tetrahedral boron, N_4 , also strongly influences the ability to resolve the B–O and Si–O peaks, primarily due to the increasing B–O bond length with increasing N_4 , and hence the decreasing intrinsic separation between the B–O and Si–O peaks. This information is important for designing, analyzing, and interpreting the results of future total scattering diffraction experiments on borosilicate based materials.

Temperature dependent measurements of the mean B–O bond length in $28\text{BaO} \cdot 48\text{B}_2\text{O}_3 \cdot 24\text{SiO}_2$ (BBS352) glass up to the glass transition temperature reveal a gradual thermal expansion of the bond, with expansion coefficient $\alpha_{\text{BO}} = 6.5(1.7)$ ppm K $^{-1}$. This is slightly larger than for pure $^{11}\text{B}_2\text{O}_3$ glass and melt and very similar to the bulk linear thermal expansion coefficient for the glass. These two observations imply (i) a larger α_{BO} for tetrahedral borate species, as compared to trigonal ones; and (ii) a remarkably simple vibrational thermal expansion mechanism in the three-dimensional BBS352 glass network, as compared to the two-dimensional network in B_2O_3 glass.

Above T_g , up to the liquidus temperature, the mean B–O bond length in BBS352 supercooled liquid begins to decrease dramatically, similar to observations for some pure borate melts. This is interpreted as a configurational effect due to decreasing boron-oxygen coordination number, and mapped directly to quantitative $N_4(T)$ using established bond-valence methodology. The resulting N_4 for the BBS352 glass is in excellent agreement with ^{11}B NMR spectroscopic determinations in the literature [60], remaining relatively constant up to T_g , before declining above T_g . As such, the behavior is similar to that observed in sodium borosilicate, as well as pure borate melts.

Collection of measurements at multiple liquid state points enables a van 't Hoff analysis of simplified chemical equilibria between tetrahedral sp^3 and trigonal sp^2 boron species. The results allow for interpolation and extrapolation to higher and

lower temperatures of the metastable equilibrium $N_4(T)$. Furthermore, the contribution of the boron coordination change reaction to the configurational heat capacity and entropy can be calculated, compared to calorimetric totals, and used to infer a contribution to the liquid fragility. For BBS352, the temperature dependence of $N_4(T)$ appears to contribute 30% to 40% of the total configurational heat capacity at T_g , similar to levels in pure borates.

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DATA AVAILABILITY

The raw data that support the findings of this article are openly available [67], embargo periods may apply. Gudrun input files and numerical data for the neutron structure factors $S^N(Q)$ and total correlation functions $T^N(r)$ are available at [49]. All other data associated with this article are available from the author upon reasonable request.

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