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Letter to the Editor

Pressure-induced structural changes in a borosilicate glass-forming liquid: boron coordination, non-bridging oxygens, and network ordering

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Abstract

Two of the most important structural controls on the properties of borosilicate glasses and glass melts are the variation between three- and four-coordination of network-forming boron cations, and the extent of mixing of Si and B. The effects of composition on these key parameters are relatively well studied. However, proposed mechanisms could be better constrained by testing with another, independent parameter that can also strongly affect the network. Here we present some of the first quantitative structural data on the effects of high pressure on the network structure of a sodium borosilicate glass. Using high-resolution ^{11}B and ^{17}O NMR on a sample melted at 5 GPa, we demonstrate that the formation of tetrahedral boron from trigonal boron is indeed closely coupled to the conversion of non-bridging to bridging oxygens. The increased fraction of tetrahedral boron at high pressure also causes increased mixing of boron and silicate structural units, as oxygens bridging between two BO_4 groups are energetically relatively unfavorable.

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1. Introduction

The structures of most glass-forming oxide liquids at ambient pressure are dominated by networks of small, high-valence cations (e.g., B^{3+}, Al^{3+}, Sb^{3+}, Si^{4+}, P^{5+}) with three or four strongly bonded oxygen anions in their first coordination shells. Among these, boron is unique in readily transforming between three- to four-coordination ($^{[3]}B$ and $^{[4]}B$) with variation in composition and temperature. This allows considerable latitude in tailoring of the physical properties of boron-containing oxide glasses to match a host of technological needs. As early as 1960, the apparent ease of local, transient boron coordination change was also suggested to be critical in reducing the viscosity of pure B_2O_3 melt many orders of magnitude below that of SiO_2 liquid, which is comprised almost entirely of SiO_4 tetrahedra [1]. For B, Si, and Al in oxide liquids, computer simulations and considerable experimental data have shown as well (at least for silicates and aluminosilicates) that network cation coordination increases are induced by high pressure and can lead to anomalous drops in viscosity even while density increases [2–11], possibly again through the role of transient high coordination in facilitating diffusion.

In compositionally simple network liquids such as B_2O_3 and SiO_2, theoretical studies and molecular dynamics simulations suggest that increases in cation coordination with pressure are accompanied by increases in oxygen coordination numbers from two to three [5,6,12–14]. In more complex systems where a significant fraction of non-bridging oxygens (NBO) are bonded to single network cations and to multiple, lower-charged modifier cations, it has been suggested [5,8] that a displacement of the following equilibrium to the right may occur with increasing pressure:

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$$\mathrm{NBO} + \mathrm{TO}_n = \mathrm{TO}_{n+1}. \qquad (1)$$

Here, 'T' symbolizes a network cation initially in trigonal or tetrahedral coordination ($n = 3$ or 4) and the subscripts indicate the number of coordinating oxygens, which in general are each shared with a second network cation. Several ^{17}O NMR studies have demonstrated the reduction of NBO content in high pressure alkali silicate glasses containing $^{[5]}$Si and $^{[6]}$Si groups [11,15]. With direct measurements of concentrations of $^{[4]}$Si, $^{[5]}$Si, and $^{[6]}$Si and of NBO using high-resolution ^{29}Si and ^{17}O NMR, the mechanism has recently been more precisely confirmed [9,16].

Equilibrium (1) is essentially the same as one of the most fundamental structural reactions that controls many of the chemical and transport properties of borate glasses and their technologically ubiquitous borosilicate relatives (with $n = 3$). In these systems, the addition of a modifier oxide such as Na_2O to B_2O_3 initially converts $^{[3]}$B to $^{[4]}$B groups. At some points (perhaps because the latter become abundant enough to generate energetically relatively costly $^{[4]}$B–O–$^{[4]}$B linkages) further addition of the modifier begins to produce NBO. The latter is preferentially associated with Si if the latter is present. This model has long been validated by ^{11}B NMR [17,18], and confirmation by ^{17}O NMR measurements has recently begun [19,20]. In borate and borosilicate systems, the thermodynamic argument that reaction (1) should be shifted to the left with increasing temperature [21] has been partially confirmed by ^{11}B NMR [19,22,23].

The formation of $^{[4]}$B groups in alkali borosilicate glasses and melts also provides the drive for substantial chemical ordering of the network, as linkages between two such groups may be unfavorable with respect to Si–O–B linkages because of the difficulty of compensating the enhanced negative charge on the $^{[4]}$B–O–$^{[4]}$B oxygen with singly-charged, relatively large, alkali cations. This 'tetrahedral boron avoidance' (by analogy to relatively well-studied 'aluminum avoidance' [24,25]) has been shown to be important in ambient pressure alkali borosilicates by recent NMR studies [26].

Both roles for $^{[4]}$B have been derived solely from studies of compositional effects on structures of glasses formed at ambient pressure. The increase in $^{[4]}$B/$^{[3]}$B expected at high pressure (simply as the result of denser oxygen packing) thus provides a unique opportunity to independently test models of chemical effects on structure that apply to ambient pressure glasses. Despite this, very few studies of pressure effects on borate or borosilicate glasses have been made. An early 'wideline' NMR study [27] reported no detectable effects on $^{[4]}$B/$^{[3]}$B in several potassium borate glasses melted at 2.5 GPa. If reaction (1) is indeed an energetically 'easy' pathway to boron coordination increases, this negative finding probably results from the well-known fact that such compositions ($K_2O/B_2O_3 < 0.3$) contain only minimal concentrations of NBO [17]. More recent studies using vibrational spectroscopy described changes in alkali borate glasses quenched from pressures as high as 4.5 GPa [28]. These data are, however, difficult to relate quantitatively to changes in coordination. The latter samples were compressed at elevated temperatures without protective metal sample containers, using a hydrous pressure medium (pyrophyllite). The result could be unknown and perhaps high water contents. Very recently, a study of Na-boroaluminosilicate glasses using ^{11}B NMR reported increased fractions of $^{[4]}$B with pressures up to 2 GPa [29].

2. Experimental methods

The glass sample was prepared by normal melting techniques, using ≈45% ^{17}O-enriched SiO_2 and including 0.2 wt% cobalt oxide to enhance spin-lattice relaxation [30]. About 35 mg was dried at 150 °C, welded into a Pt tube, and heated at 1400 °C and 5 GPa in a 1000 ton multi-anvil press at Bayerisches Geoinstitut, temperature quenched at pressure, then slowly decompressed at ambient temperature [16]. Both ambient pressure and the 5 GPa glass were homogeneous on examination at 400× with an optical microscope; neither contained any spectroscopic indications of crystallinity. The concentrations of hydroxyls were determined from the absorption band of the OH stretching vibration at around 3600 cm^{-1} in the infrared spectra of glass chips measured with a micro-FTIR spectrometer, using the evaluation method of Paterson [31].

NMR spectra were collected at 14.1 T at 81.3 and 192.4 MHz for ^{17}O and ^{11}B, respectively, at ambient pressure and temperature. ^{17}O and ^{11}B chemical shifts are expressed relative to ^{17}O-enriched H_2O at 0 ppm and 1.0 M boric acid at 19.6 ppm. An MAS probe with 3.2 mm rotors and spinning speeds of 20 kHz was used. The ^{11}B MAS spectra were obtained using single pulse acquisition with a radio frequency (rf) power of 160 kHz and a 'solid' rf tip angle of 30° as described recently [26,30,32]. N_4 values were obtained by fitting or by direct integration of the spectra, correcting intensities for quadrupolar effects [33]. Oxygen-17 3QMAS spectra [34,35] were acquired using a shifted-echo pulse sequence with an rf power of 125 kHz, with experimental conditions and data processing, including shear transformation, also as recently described [26,32,36]. Several choices of axis and scale conventions are possible, here we continue to use those of previous studies of glasses to allow direct comparison of the 2-D spectra [37]. Gaussian fits of the isotropic projections of these spectra were used to estimate the fractions of Si–NBO, Si–O–Si, Si–O–$^{[4]}$B, Si–O–$^{[3]}$B, $^{[3]}$B–O–$^{[4]}$B and $^{[3]}$B–O–$^{[3]}$B, based on the methods of our previous detailed studies of alkali borosilicate glasses [26,30,32].

3. Results and discussion

Fig. 1 shows the high-field ^{11}B MAS NMR spectra of a glass with a nominal composition of 26.1 mol% Na_2O, 24.6% B_2O_3, 49.3% SiO_2 ($R = Na_2O/B_2O_3 = 1.06$; $K = SiO_2/B_2O_3 = 2.00$). For the ambient pressure sample, integration of the well-separated peaks for $^{[3]}$B and $^{[4]}$B sites yields the fraction of total boron as $^{[4]}B(= N_4)$ of 0.62 ± 0.02, which is very close to the value predicted for this composition (0.61) by the well-known model of Dell and Bray [17]: The small difference could result from minor uncertainties in the glass composition. The glass quenched from the melt at 5 GPa has a greatly increased N_4 value of 0.85. This indicates that at least a significant part of the effects of high pressure on the structure of the liquid at its glass transition has been captured in the decompressed, but presumably densified, sample. This value of N_4 is approached in ambient pressure glasses only when Si/B is much higher [17], where Si effectively dilutes $^{[4]}$B–$^{[4]}$B interactions.

The mechanism of this structural change can be investigated by high-resolution, triple-quantum magic-angle spinning (3QMAS) ^{17}O NMR. The Dell and Bray model [17] predicts for this composition that 10.3% of the oxygens should be NBO associated with Si, with a minor fraction (1.0%) as NBO associated with B. The fraction of NBO can also be directly calculated from the composition and the observed N_4 [19] by subtracting the fraction of $^{[4]}$B from the added modifier oxide and dividing by the total number of oxygens, to yield $100 \times 2(R - N_4)/(R + 2K + 3) = 10.9 \pm 0.5\%$ NBO. Analysis of the ^{17}O 3QMAS spectrum (Figs. 2 and 3) yields a value for Si–NBO of $10.1 \pm 0.5\%$; the fraction of B-NBO, if present, is probably too small to detect. This good agreement suggests, as previously noted for spectra acquired at this field and under these experimental conditions, that the effect of the difference in the quadrupolar coupling constant (C_Q) between the NBO and bridging oxygens is surprisingly small [19,20,32], despite expected differences in 3Q excitation and reconversion efficiencies. The latter can be observed under other conditions [38]. Uncorrected relative peak areas are therefore used in the discussion of pressure effects below. In any case, the *relative* changes in NBO content from ambient to high pressure are the most relevant to understanding the mechanism of structural response to densification.

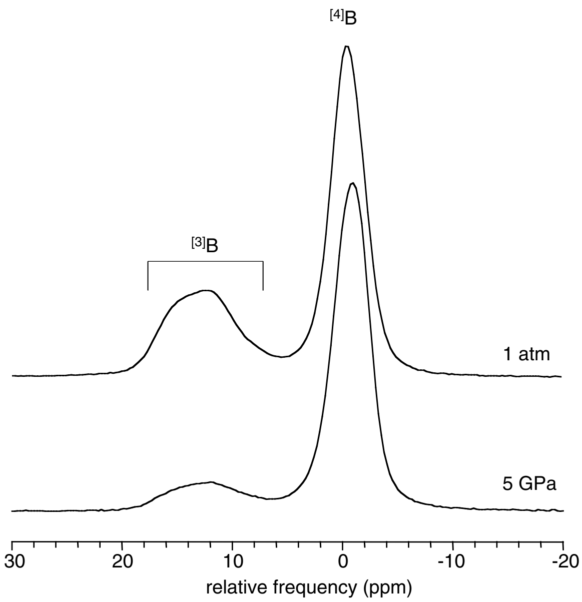

Fig. 1. ^{11}B MAS NMR spectra of ambient pressure and 5 GPa sodium borosilicate glasses. Intensities are normalized to that of the highest peak in each spectrum, but are on an arbitrary vertical scale. Note the large increase with pressure in the proportion of $^{[4]}$B.

For the 5 GPa glass, the fraction of oxygens as NBO (assumed to be almost entirely Si–NBO as at ambient P) can be calculated as above from the composition and the observed N_4, to equal $5.2 \pm 0.5\%$. The directly observed value of $7 \pm 1\%$ is close to this result, demonstrating that the link between boron coordination and NBO content as described by reaction (1) is fundamentally important. The slight discrepancy between observed and predicted values may result in part from the dissolution in the melt

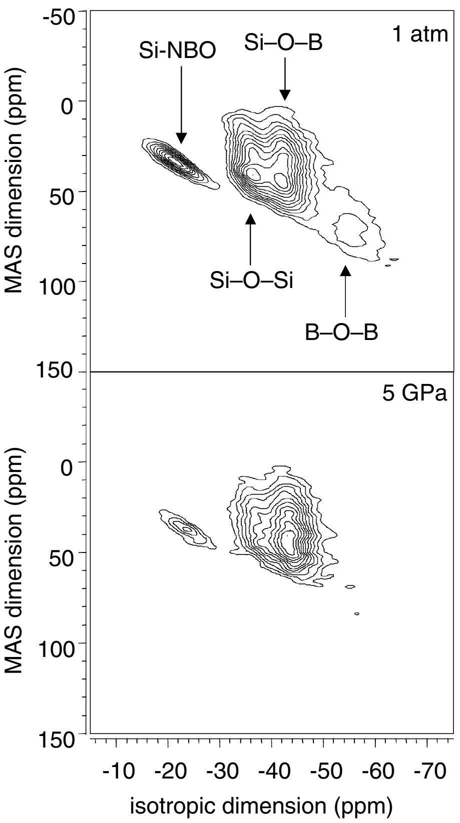

Fig. 2. ^{17}O 3QMAS NMR spectra of ambient pressure and 5 GPa sodium borosilicate glasses. Note the dramatic reduction with increased pressure in the fraction of NBO, and of Si–O–Si and B–O–B oxygens relative to Si–O–B linkages. Intensity contours are drawn at equal intervals from 12% to 100%.

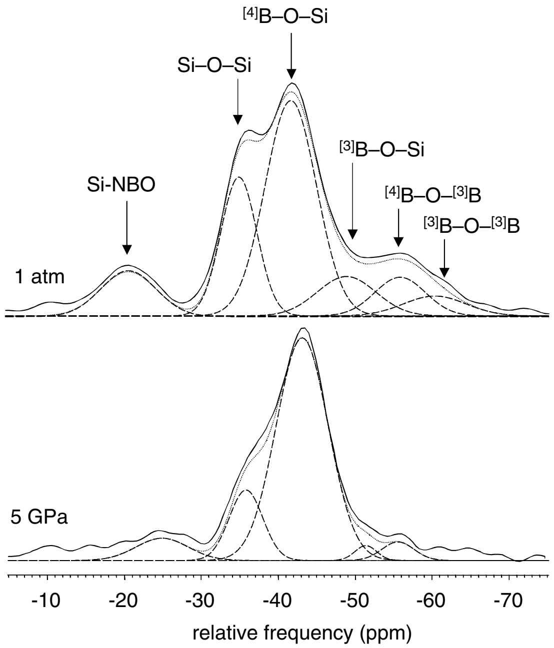

Fig. 3. Isotropic dimension projections of the ^{17}O 3QMAS NMR spectra, showing fitted Gaussians for each oxygen species, used here primarily to estimate the fractions of NBO and of Si–O–B among the bridging oxygens. Intensities are normalized to that of the highest peak in each spectrum. Frequencies and widths of fitted components are constrained within narrow ranges based on extensive previous analyses of spectra of alkali borosilicate glasses [26,30,32], which also are the source of peak assignments.

of a small amount of water originally present on the surface of the glass fragments or in the high-pressure assembly. Analysis by FTIR gives a dissolved hydroxyl content in the 5 GPa sample of 2400 ± 500 ppm by weight, vs. 150 ± 30 ppm for the ambient P glass. If H_2O behaves analogously to Na_2O in this low concentration range, this contaminant will effectively increase R from 1.06 to 1.10, changing the predicted NBO fraction to $6.2 \pm 0.5\%$, which is within experimental uncertainty of the ^{17}O NMR value. We note that these data do not discriminate between several possible modes of reaction between H_2O and the framework, e.g. formation of Si–NBO (e.g. Si–OH) or of protonation of bridging oxygens linked to $^{[4]}$B groups.

A second, large effect of the pressure-induced boron coordination is an increase in network ordering that is obvious from the differences between the ^{17}O 3QMAS spectra of the 1 atm and 5 GPa glasses (Figs. 2 and 3). The latter show a marked concentration of intensity in the peak known from our previous studies [26,30,32] to be due to Si–O–B bridging oxygens (primarily Si–O–$^{[4]}$B), relative to those for B–O–B (primarily $^{[3]}$B–O–$^{[4]}$B and $^{[3]}$B–O–$^{[3]}$B) and Si–O–Si linkages. Because $^{[4]}$B–O–$^{[4]}$B linkages are relatively unfavorable energetically (as are $^{[4]}$Al–O–$^{[4]}$Al linkages in aluminosilicates [25,39]), the overall network mixing reaction is shifted to the right by the conversion of $^{[3]}$B to $^{[4]}$B:

$$\text{B–O–B} + \text{Si–O–Si} = \text{Si–O–B}. \tag{2}$$

The isotropic projections of the spectra can be fitted to estimate the fractions of the various bridging oxygens, as was done for a variety of alkali borosilicates in our previous studies, with constraints on widths and positions of fitted peaks applied as necessary from those found in other compositions [26,30,32]. The results give $57 \pm 2\%$ of Si–O–B in the ambient pressure sample and $74 \pm 2\%$ in the high-pressure glass. A simple combinatorial model of the linkages between the observed concentrations of Si and B species, with random mixing [32], yields 45% and 47% of Si–O–B at the two pressures, an approximation. with minimal $^{[4]}$B–O–$^{[4]}$B yields 57% and 76% of Si-O-B, respectively, in excellent agreement with the ^{17}O NMR. We thus conclude that at the relatively low temperatures of the glass transition, 'tetrahedral boron avoidance' (when allowed by composition) is indeed a good approximation. Future studies on rapidly quenched samples, which can record the structure of the liquid at a higher temperature, will help constrain the energetics of reaction (2) and predict its shift with temperature. The related issue of the effects of pressure-induced Al and Si coordination increases on order/disorder in aluminosilicate glass-forming liquids provides possibilities for extensions to network oxides systems in general [11].

Finally we note that a $^{[29]}$Si MAS NMR spectrum of the high pressure sample did not detect $^{[5]}$Si (detection limit of ≈2%), which has been observed in alkali silicate glasses from this pressure range [8,16]. B^{3+} thus appears to be analogous to Al^{3+}, in its greater ease of conversion to high coordination with pressure than the higher-valent Si^{4+} cation [7]. Nonetheless, the close relation between NBO loss and coordination change for B and Si suggests a fundamentally similar mechanism. In both cases, the consequences for the chemical order/disorder, configurational entropy, volumetric, and transport properties are large; a wealth of future high pressure experiments on these and other analogous complex network oxide liquid systems lies ahead.

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