J. Am. Chem. Soc. **1995**, *117*, 1397–1402

On the Formation of Tetracoordinate Boron in Rubidium Borate Glasses

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Received May 9, 1994[⊗]

Abstract: We have studied the compositional dependence of the microstructure of rubidium borate glasses, $(Rb_2O)_x(B_2O_3)_{1-x}$, by means of dynamic angle spinning (DAS) NMR spectroscopy of boron-11. Our NMR spectra simultaneously resolve three distinct boron sites, which we assign to boroxol rings, BO_3 groups that are not in rings, and tetrahedral BO_4 groups. These assignments are based on isotropic and anisotropic shifts of the sites in different magnetic fields and on comparison to the boron-11 DAS NMR spectra of polycrystalline borates of known structure. We observe an essentially constant fraction of boron atoms in the boroxol rings as a function of modifier concentration. In contrast, the fraction of boron atoms in nonring BO_3 sites is reduced as the Rb_2O concentration increases, while the population of the fourfold coordinate site increases. The compositional dependence we observe, and its dependence on the thermal history of the glass, suggests that the boroxol ring is an especially stable structure.

Introduction

Binary alkali borates, $(A_2O)_x(B_2O_3)_{1-x}$, are excellent glass formers and are precursors to glassy superionic conductors. The structure of these glasses is complex and has been conjectured to consist of a variety of different ring and chain boron oxide species, coordinating the A^+ alkali ions.[1,2] Rings, in the form of boroxol, B_3O_3, are thought to exist already in pure boron oxide glass, though their concentration is still debated. In this view B_2O_3 glass consists of two different structural units: the six-membered boroxol rings and nonring BO_3 (Figure 1), which are bound together through bridging oxygen to form a complete three-dimensional network.[2-6] Magnetic resonance and Raman spectroscopies have been especially useful in probing the structure of vitreous boron oxide. The Raman spectrum shows a sharp feature at 808 cm^{-1}; which is assigned to the boroxol ring breathing mode.[2,7] Bray and co-workers utilized boron NQR to resolve two different three-coordinate boron sites,[4] assigned to ring and nonring species, and used ^{17}O NMR to show the existence of multiple oxygen sites.[3] The different boron sites cannot be resolved by standard NMR methods, such as continuous-wave or magic angle spinning, but we could resolve them using dynamic angle spinning (DAS) NMR.[6]

The addition of alkali oxide modifiers, A_2O, to B_2O_3 results in formation of four-coordinate boron (BO_4^-). The existence of tetrahedrally-coordinated boron is clear from boron NMR, where it gives rise to a relatively narrow resonance superimposed on the broader pattern due to the three-coordinate boron. This peak is sharp enough to be quantified accurately in spite of its overlap with the broad feature of the spectrum, and the ratio of four-coordinate to three-coordinate boron in modified borates has been studied extensively for a wide variety of modifiers.[8-10] The three- and four-coordinate sites are also not fully resolved by magic angle spinning NMR, but are well-separated by the newly developed satellite transition NMR spectroscopy (SATRAS) technique.[11,12] Using ^{10}B continuous-wave NMR, Jellison and Bray inferred the existence of multiple three- and four-coordinate boron sites, differing in their near-neighbor bonding configurations[13] (see also refs 14 and 15). Bray and

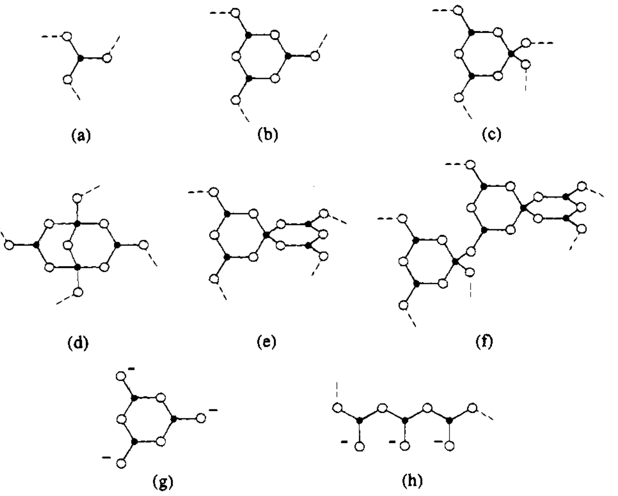

Figure 1. Examples of the structural moieties proposed to exist in vitreous B_2O_3 and modified borate glasses, based on their presence in crystalline borates: (a) nonring BO_3 unit, (b) boroxol ring, (c) triborate, (d) diborate, (e) pentaborate, (f) tetraborate, (g) ring-type metaborate, and (h) chain-type metaborate. The di-triborate structure in $K_2B_4O_7$ is similar to triborate (c), but with two fourfold-coordinate boron atoms in the ring. Filled circles and open circles represent boron and oxygen atoms, respectively. Dashed lines in the structures denote connections to the network and charges are shown for the nonbridging oxygen in the metaborates.

[⊗] Abstract published in *Advance ACS Abstracts*, January 15, 1995.

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colleagues have also used boron-11 NQR to monitor the changes in the three-coordinate boron sites in modified borate glasses.[4,16]

In contrast to magnetic resonance experiments, which are particularly sensitive to short-range interactions, Raman spectroscopy can detect larger structures involving several atoms. While this method cannot accurately quantify the extent of four-coordinate site formation, it has been applied to probe the structural changes associated with network modification.[2,17,18] As the modifier content is raised, the feature at 808 cm^{-1} assigned to boroxol rings gradually decreases in intensity and another feature between 740 and 780 cm^{-1} appears. This change has been interpreted as indicative of modification of the boroxol rings to other ring-type structures containing four-coordinate boron (Figure 1).[2,7,17,19] Such groups dominate the structure of the analogous crystalline compounds;[7] however, direct comparison of the crystalline and glassy spectra is ambiguous. For example, the Raman spectra for polycrystalline metaborates, diborates, triborates, and other alkali borates all include features in the range of 700−800 cm^{-1}.[19] Although the glassy borates show a strong feature in this range, direct comparison of the structures is difficult due to the numerous structural units that may contribute to this important feature. Furthermore, the large Raman cross section of the boroxol ring and other ring structures in these materials may overemphasize the apparent changes in the boroxol ring unit.[20]

Although the investigations described above have contributed greatly to our understanding of the alkali borate glasses, there have not been experiments that simultaneously resolve both ring and nonring BO$_3$ sites and the formation of four-coordinate boron. We present here a quantitative study, using DAS NMR, which succeeds in resolving simultaneously these three sites. We have used this method to quantify the structural changes that accompany modification of B_2O_3 with Rb_2O. The high resolution spectra that DAS NMR provides for quadrupolar nuclei,[6,21−24] in conjunction with ^{11}B depletion to quench homonuclear dipolar broadening,[6] allow us to separate three distinct boron sites. We assign these sites to boroxol rings, nonring BO$_3$ units, and tetrahedral BO_4^-. To our knowledge, this is the first experiment on these materials that provides positive, resolved spectral signatures simultaneously for these three different basic species. This advance is significant because it allows us to determine the relative fraction of each type of site within each sample, using a single experiment. We have optimized the experimental conditions so that the response of the different boron sites is essentially the same, making estimates of relative intensities reliable. We checked our assignments of shifts and intensities by comparing to the DAS NMR spectra of polycrystalline borates with known crystal structure.

Our results for the system $(Rb_2O)_x(B_2O_3)_{1-x}$ ($0 \le x \le 0.35$) show a preferential conversion of those three-coordinate boron atoms that reside in nonring BO$_3$ units. In contrast to earlier results using Raman spectroscopy, we observe the boroxol rings to be chemically durable until high modifier content is reached. We have investigated the sensitivity of this result to sample preparation protocol and found that much of the differences to the previous results are accounted for by the thermal history of the sample. In the following section we describe in detail our experimental methods and then give the results. This is followed by discussion, interpretation, and a short concluding section.

Experimental Methods

The rubidium borate glasses studied here were prepared by fusing boric acid enriched to 97% in ^{10}B (Aldrich) and rubidium carbonate (Strem, >99.8%) at 1000 °C for 1−2 h. The melts were contained in platinum boats and quenched by removing the samples from the furnace. The clear glasses were finely ground and stored in air-tight vials to prevent any absorption of water. X-ray powder diffraction of some of the higher modified samples was used to verify their amorphous character.

Polycrystalline $K_2B_4O_7$, enriched to 90% in ^{10}B, was made by fusing together appropriate amounts of ^{10}B-enriched boric acid, natural abundance boric acid (Strem, 99.9995%), and potassium carbonate (Strem, 99.999%) at 1000 °C for 30 min. The temperature was lowered to 765 °C, at which the sample was held for an additional 48 h. Polycrystalline potassium metaborate, $K_3B_3O_6$ was made in a similar manner using appropriate amounts of ^{10}B-enriched boric acid, natural abundance boric acid, and potassium carbonate. The isotopic abundance of boron was also chosen to be 90% ^{10}B. These starting materials were thoroughly ground together and then fused at 1000 °C for 15 min. The oven temperature was lowered to 750 °C, at which the metaborate sample was held for an additional 18 h. The resulting potassium borates were verified to be crystalline $K_2B_4O_7$ and $K_3B_3O_6$ by X-ray powder diffraction analysis.

NMR spectra were obtained with a home-built spectrometer and commercial probe at field strengths of 8.4 and 4.7 T. We used a pure phase variant of the original DAS experiment[21,22] described by Grandinetti *et al.*[25] All experiments were performed using the 37.38° and 79.19° DAS angle pair.[22] Due to the different nutation behavior of the three- and four-coordinate boron sites, which arises from the large differences in e^2Qq/h, we utilized short $\pi/2$ pulses, typically 2.4 μs at 79.19° and 4 μs at 37.38°. Under these pulse conditions, we have observed that the different boron sites behave similarly. We also used sufficient spinning of the samples, typically 6 kHz, so that the loss of signal intensity to spinning sidebands is small. The spectra of the glasses were obtained with 64 to 128 acquisitions at each of 80 delay values with 15−40 s between scans to allow for full relaxation of all sites. The potassium diborate spectra were taken with 16 acquisitions at each of 128 delay values with 120 s between scans to account for the substantially longer relaxation in this crystalline borate. The potassium metaborate spectra were obtained with 32 acquisitions at each of 128 delay values with 120 s between scans. The isotropic and anisotropic sweep widths were 20 and 30 kHz, respectively. Boron-10 enrichment was necessary to quench homonuclear dipolar coupling of the boron-11.[6] The DAS NMR experiment yields a pure phase two-dimensional spectrum, with an isotropic shift axis and a total shift axis that includes scaled anisotropic interactions. The high resolution one-dimensional spectra are obtained by projecting the entire data set onto the isotropic shift axis. The anisotropic dimension reflects the spectrum of the sample spinning at the second DAS angle, 79.19°, which contains part of the anisotropy and allows us to characterize the sites by extracting their anisotropic lineshapes from the overlapping resonances. No smoothing of any kind was used in the data processing.

Results

Figure 2 shows the ^{11}B DAS NMR spectrum of the $0.15Rb_2O\cdot0.85B_2O_3$ glass, obtained at 8.4 T (115.6 MHz resonant frequency). The projection of the 2D spectrum onto the

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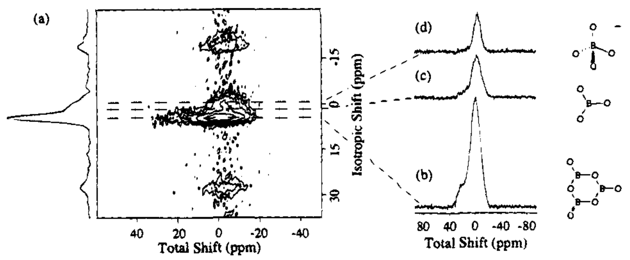

Figure 2. DAS NMR spectrum of ^{11}B in $0.15Rb_2O{\cdot}0.85B_2O_3$ glass at 8.4 T. Shifts are relative to $Et_2O{\cdot}BF_3$. (a) 2D contour plot with isotropic projection. The contours at ±30 ppm are spinning sidebands. (b) Slice at an isotropic shift of 4.5 ppm, the shift of the boroxol ring boron. (c) Slice at 0.7 ppm, the nonring BO_3 shift. (d) Slice at −0.3 ppm, the shift of the four-coordinate boron.

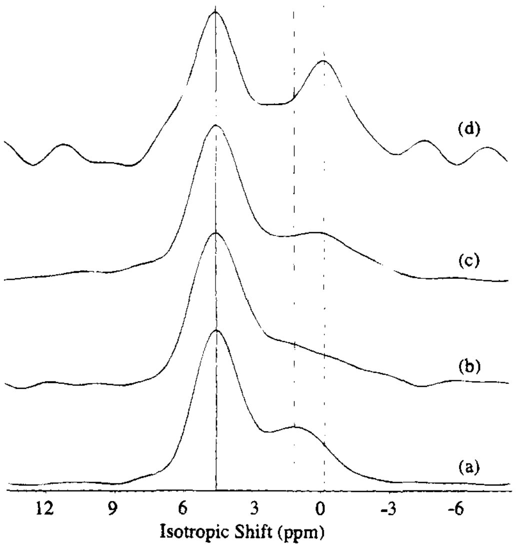

Figure 3. Isotropic shift spectra of ^{11}B in $(Rb_2O)_x(B_2O_3)_{1-x}$ glass, from DAS NMR: (a) $x = 0.0$ (glassy B_2O_3); (b) $x = 0.15$; (c) $x = 0.20$; (d) $x = 0.30$. The vertical lines are drawn at the shifts of Figure 2: solid line, 4.5 ppm, the boroxol ring; long dashed line, 0.7 ppm, nonring BO_3 units; short dashed line, −0.3 ppm, BO_4^-.

isotropic shift axis is displayed, as well as slices along the total shift axis extracted at key isotropic shifts. Isotropic projections of the DAS NMR data (8.4 T) as a function of composition are shown in Figure 3. Figure 4 gives the isotropic projection of the ^{11}B DAS NMR data of the $0.25Rb_2O{\cdot}0.75B_2O_3$ glass, obtained at 4.7 T (64.1 MHz resonant frequency). The reproducibility of these results was verified by studying multiple samples, prepared with the same protocol, at selected compositions. Figure 5 shows the isotropic projections of the ^{11}B DAS NMR spectra obtained at 8.4 T for polycrystalline potassium diborate and potassium metaborate.

Discussion

The DAS NMR experiment yields an isotropic shift spectrum for quadrupolar nuclei. For a spin-$^3/_2$ nucleus like boron-11, subject to both chemical shift and second-order quadrupole effects, the isotropic shift δ_{iso} takes the form[23,24]

$$\delta_{\text{iso}} = \delta_{\text{iso}}^{(\text{CS})} - (25 \times 10^3)\frac{P_Q^2}{\nu_0^2} \qquad (1)$$

with isotropic chemical shift $\delta_{\text{iso}}^{(\text{CS})}$ in ppm, Larmor frequency ν_0 in MHz, and quadrupole product[26]

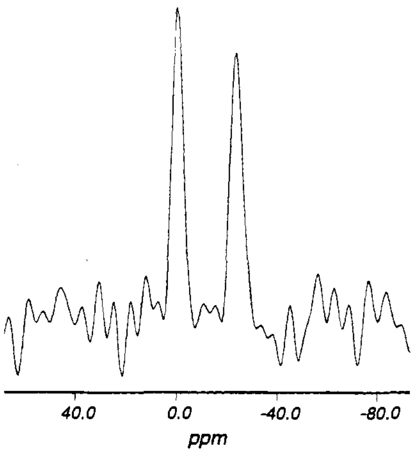

Figure 4. Isotropic projection of the DAS NMR data obtained at 4.7 T for the $0.25Rb_2O{\cdot}0.75B_2O_3$ sample. The peak at −0.2 ppm is due to fourfold-coordinate boron and the peak at −22.9 ppm from boroxol ring three-coordinate boron. The shifts are relative to $Et_2O{\cdot}BF_3$. The isotropic shift of the three-coordinate site is significantly upfield compared to the shift at 8.4 T due to the field-dependence of the second-order quadrupole effect (see eq 1).

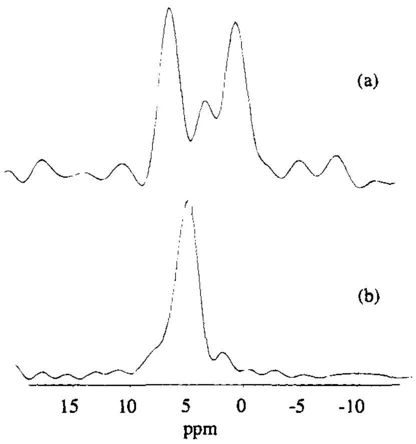

Figure 5. ^{11}B DAS NMR isotropic spectra for two different crystalline alkali borates: (a) isotropic projection of the data obtained for polycrystalline $K_2B_4O_7$ from DAS NMR at 8.4 T (115.6 MHz resonant frequency); (b) isotropic data obtained for polycrystalline $K_3B_3O_6$ at 8.4 T. Shifts are relative to $Et_2O{\cdot}BF_3$.

$$P_Q = (e^2Qq/h)\sqrt{1 + \eta^2/3} \qquad (2)$$

also in MHz. In eq 2, e^2Qq/h is the quadrupole coupling, and η the asymmetry of the quadrupole interaction. The experiment thus provides a spectrum of the isotropic shift of each site, including contributions from both the chemical shift and the quadrupole interaction. These effects can be separated by performing the experiment in different magnetic field strengths (thereby varying ν_0).

The isotropic projections in Figures 2, 3, and 4 show clearly the existence of multiple boron sites in all rubidium borate glass compositions. At zero and low modifier content, two dominant features exist at 4.5 and 1 ppm, in an intensity ratio of about 70:30. As the modifier content is raised, the peak at 1 ppm is gradually replaced by a feature at slightly negative isotropic shift (−0.3 ppm). We previously assigned the peak at 4.5 ppm to three-coordinate boron in boroxol rings,[6] and we note that

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this peak does not noticeably shift or broaden as a function of glass composition, up to about 30% modifier concentration. We assign the less intense feature near 1 ppm to threefold-coordinate boron in nonring BO_3 units, again as in pure boron oxide.[6] A third peak gradually appears in these spectra as the modifier content is increased, which is due to the formation of four-coordinate boron. Support for this assignment comes from both the isotropic chemical shift and the anisotropic lineshape, as shown in Figure 2. The symmetric lineshape is the result of the near tetrahedral symmetry of the fourfold coordination (cf. the noticeably asymmetric shape of the resonances from the threefold-coordinate sites). The chemical shift of four-coordinate boron is typically near zero and slightly negative, and the small value of e^2Qq/h for such a site will not cause a significant upfield shift, especially at high magnetic field (see eq 1).

DAS NMR in different magnetic fields enables us to obtain both the isotropic chemical shift and the quadrupolar coupling product P_Q (eq 2) for each site through the field dependence of the isotropic shift. Figure 4 shows two well-resolved features at the lower field (4.7 T). We have already observed the peak at −22.9 ppm in pure boron oxide glass, which is due to three-coordinate boron at this field strength. The feature at −0.2 ppm is assigned to BO_4^- groups due to the value of the isotropic shift of the peak as well as its symmetric anisotropic lineshape. Unfortunately, the two distinct three-coordinate sites in the low modified glasses are not well-resolved at this field. This is because the chemical shift difference is roughly offset by the quadrupole shift difference at this particular field, and the inhomogeneous broadening due to the disorder masks any small differences between the sites. Nonetheless, we could determine the isotropic chemical shift and the quadrupole coupling product P_Q for the boroxol ring boron and the four-coordinate boron, since at 25 mol % Rb_2O, these are the two dominant boron sites. The boroxol ring boron atoms have a chemical shift of 17.8 ± 0.2 ppm and $P_Q = 2.66 \pm 0.04$ MHz. We found in glassy boron oxide that the nonring three-coordinate boron atoms are characterized by a chemical shift of 13.3 ± 0.2 ppm and $P_Q = 2.61 \pm 0.04$ MHz. For both three-coordinate sites, the anisotropic lineshapes suggest that the quadrupole asymmetry η is about 0.2 ± 0.1. For the four-coordinate site $P_Q = 0.220 \pm 0.04$ MHz and the isotropic chemical shift is −0.3 ± 0.2 ppm. These values are in reasonable agreement with other measurements of the tetrahedral boron site in modified borate glasses.[9,11]

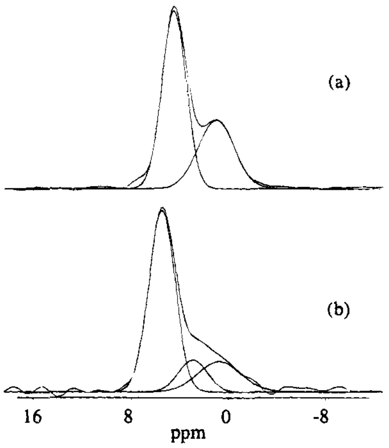

Figure 6. Results showing the Gaussian fits to the isotropic shift data: (a) two-peak fit to the DAS NMR data obtained for vitreous B_2O_3 at 8.4 T; (b) three-peak fit to the DAS NMR data for $0.15Rb_2O{\cdot}0.85B_2O_3$ at 8.4 T. Shifts are referenced to $Et_2O{\cdot}BF_3$.

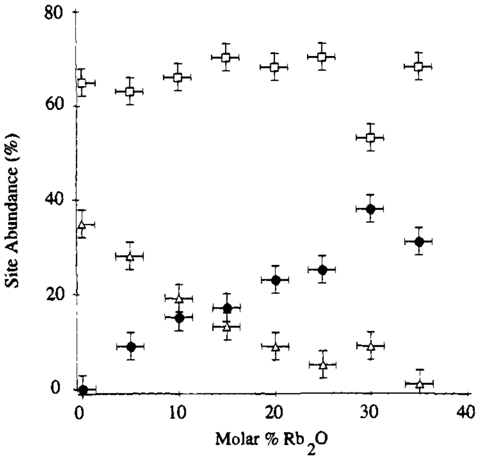

Figure 7. Plot of site abundance as a function of Rb_2O modifier content, resulting from Gaussian fits of the isotropic projections of the DAS NMR data: □, boroxol ring site; △, nonring BO_3 site; ●, BO_4^- site. The boroxol ring site concentration may contain contributions from rings terminated by nonbridging oxygen, in addition to normal boroxol rings, at modifier concentrations higher than 25 mol %.

Table 1. Line Widths and Relative Site Intensities Resulting from Gaussian Fits to the Isotropic DAS NMR Data[a]

	boroxol ring BO_3		nonring BO_3		BO_4^-	
mol % Rb_2O	width (ppm)	rel pop. (%)	width (ppm)	rel pop. (%)	width (ppm)	rel pop. (%)
0	2.30	65	3.50	35		
5	2.28	63	3.14	28	3.80	9
10	2.32	66	3.30	19	4.12	15
15	2.52	70	2.79	13	4.17	17
20	2.52	68	1.88	9	3.52	23
25	3.03	70		5	3.16	25
30	2.65	53	1.15	9	2.77	38
35	2.94	68		1	3.06	31

[a] Missing line widths for the nonring three-coordinate sites are due to the difficulty in fitting those data points.

From the isotropic shift spectra of Figure 3, we can extract the relative peak intensities and estimate the population of boron sites at each composition in the rubidium borate glass series. The lower modified samples, 5 and 10 mol % Rb_2O, give definitive isotropic shifts of both three-coordinate boron sites. The high modified glasses, 25 mol % Rb_2O and higher, give the isotropic shift of the four-coordinate peak. We fit three overlapping Gaussian functions to each of the isotropic spectra by fixing the centers at the measured isotropic shifts of each of the three sites and varying the widths and amplitudes to obtain the best fit. A typical result of this fitting route is given in Figure 6, where we have fit the three peaks in the isotropic spectrum of the $0.15Rb_2O{\cdot}0.85B_2O_3$ glass and also the two three-coordinate sites in pure B_2O_3 glass. Quantitative estimates for the three boron sites over the range of Rb_2O modifier content are shown in Figure 7, with the fit parameters listed in Table 1. As indicated by the tabulated line widths, the three boron peaks do not change greatly upon modification, with some slight broadening due to an increase in disorder. The fourfold-coordinate boron peak shows a surprising amount of disorder, but in fact, in crystalline borates such sites show a range of e^2Qq/h spanning 600 kHz. This range is sufficient to explain the peak widths observed here.[27]

We confirmed the precision of this method by checking that our estimated intensities in the ^{11}B DAS NMR spectrum of polycrystalline $K_2B_4O_7$ agreed with the population of boron sites

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known from its crystal structure.[28] This material contains four four-coordinate sites and four three-coordinate sites. The isotropic shift spectrum of potassium diborate at 8.4 T is shown in Figure 5a. Three resolved peaks are evident in these data. The peak at −0.4 ppm is due to fourfold-coordinate boron, and the two peaks at 1.5 and 6 ppm are due to threefold-coordinate boron. The threefold-coordinate borons are easily separated into two distinct groups based on the bonding configuration in this crystalline borate. The three-coordinate borons in both the diborate and di-triborate units (Figure 1) have two longer B−O bonds and a relatively shorter third B−O bond. In contrast, the nonring BO_3 contains relatively equivalent B−O bond lengths. This difference, although small, should noticeably affect the isotropic shifts of each boron type, giving rise to two separate peaks. From the relative populations of ring three-coordinate and symmetrical BO_3 groups, the strong peak at 6 ppm must be those three-coordinate boron atoms in diborate and di-triborate units, and the peak at 1.5 ppm must be those in nonring BO_3 groups. The measured peak intensity ratio of 3:1 confirms this assignment. The remaining peak at −0.4 ppm, due to four-coordinate boron, is slightly less intense than the 1:1 three-coordinate to four-coordinate ratio predicted by the crystal structure. This gives us a good measure of the error in the quantitative interpretation of our DAS NMR data, which is accounted for by the vertical error bars in Figure 7. This source of error, however, does not affect the relative population estimates of the two three-coordinate sites in the rubidium borate glass series. The shifts of the peaks in polycrystalline potassium diborate confirm our assignment of the resonances in the glasses. The shifts of both the nonring BO_3 (1.5 ppm) and four-coordinate boron (−0.4 ppm) correlate well with those observed in the rubidium borate glasses, 1 and −0.3 ppm, respectively. However, we do not observe any feature in the glass data at the shift of the diborate and di-triborate threefold-coordinate boron, in contrast to predictions based on the Raman studies.[2,17]

The quantitative interpretation of the DAS NMR data is based on the above-fitting routine of the isotropic spectra for the rubidium borate glasses. Our data show that as Rb_2O modifier is added to this boron−oxygen network, formation of four-coordinate boron occurs at the expense of only those borons in the nonring sites. The fraction of boron in boroxol rings, however, is essentially constant over the entire range of compositions, emphasizing the relative resistance of this structure to modification by rubidium oxide. Our estimates for the fourfold-coordinate boron are smaller than that determined by the composition stoichiometry, as has previously been observed in other studies of the heavier alkaline oxide borate glasses.[9,29] Figure 8 compares our results for the fraction of four-coordinate boron (N_4) with other published measurements of the same quantity in rubidium borate glasses. Our results are consistent with both the wideline boron NMR studies of Bray and co-workers,[9] as well as with the IR results.[30] At higher modification levels, the maximum fraction of fourfold-coordinate boron sites is not followed. This suggests that some of the modifier may cause formation of nonbridging oxygen. The isotropic shift of boron in rings bound to nonbridging oxygen is virtually the same as that of boron in rings bound to bridging oxygen, as seen from the ^{11}B DAS NMR results for crystalline $K_3B_3O_6$ (Figure 5b). These spectra show that the isotropic shift of boron in $(B_3O_6)^{3-}$ is 4.9 ppm, versus 4.5 ppm for the ring boron in B_2O_3. Therefore, our inability to resolve fully ring boron attached to nonbridging oxygen from boroxol ring sites prevents a more thorough examination of the formation of nonbridging oxygen in these glasses, although the shoulder on the boroxol ring peak at 30% Rb_2O may be due to the formation of metaborate-type sites. Therefore, also the concentration of boroxol ring boron we report in Figure 7 may include contributions from nonbridging oxygen-terminated rings, especially at high modifier concentration. We are currently investigating these sites with ^{17}O NMR. The data in Figure 7 and 8 show that the fraction of four-coordinate boron reaches a maximum at approximately 30% Rb_2O, in agreement with Bray and co-workers.[9] This maximum N_4 necessitates some modification of boroxol ring boron, since nearly all of the nonring boron atoms have already been exhausted at this composition. The slight rise in nonring BO_3 site abundance at this composition is within our error estimates and is presumably due to the increase in spectral noise at the higher Rb_2O compositions, as observed in Figure 3.

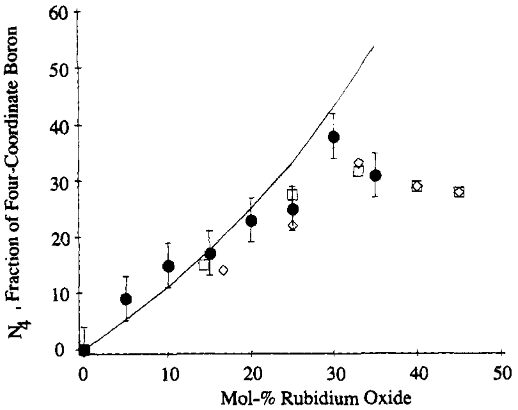

Figure 8. Measurements of the fraction of four-coordinate boron in the rubidium borates as a function of Rb_2O: ●, our DAS NMR results; □, NMR data extracted from Zhong and Bray;[9] ◇, IR data from Kerner.[30] The solid line is that predicted from the theoretical curve, $N_4 = x/(1 - x)$.

These results differ substantially from those obtained by Raman and infrared spectroscopies, which are interpreted as showing preferential modification of the boroxol rings at all modifier concentrations.[2,17,31] We have found that this discrepancy is at least in part due to differing sample preparation methods. DAS NMR showed, for samples prepared by fusing Rb_2CO_3 with B_2O_3 for 15 min (the procedure used in the Raman experiments[17]), a reduced fraction of boroxol rings as compared to the samples melted for 1 h or more. The reduction is too small to be consistent with modification of only ring boron, however. For example, we measured a ring boron fraction of 54% in $0.25Rb_2O{\cdot}0.75B_2O_3$ prepared in this way, as compared to 70% in glasses heated for 1 h or more. However, if each equivalent of Rb_2O modified two ring boron sites, one would expect the ring boron fraction to drop from 70% to 37%. We also found that in the synthesis of pure boron oxide glass, holding the melt for at least 30 min is necessary to obtain the final quasi-equilibrium fraction of boroxol rings in the glass. The extended heating time required to make quasi-equilibrium boron oxide and alkali borate glasses may reflect the necessary time for complete removal of all water and carbon dioxide byproducts. The large Raman cross section of the boroxol ring, compared to other units in the glass, may also overemphasize changes in the boroxol ring structure.[20] This is in contrast to DAS NMR, which yields a positive signal for all three boron environments, with equivalent response from each type of boron site. Also, given the propensity toward nonbridging oxygen

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formation in the heavier alkali borate glasses, the main feature in the Raman spectra may be due to six-membered rings containing one or more boron atoms bound to a nonbridging oxygen, as suggested in the original analysis of Bril.[7] As we observe in potassium metaborate, Figure 5b, these types of boron sites cannot be resolved from the boroxol ring boron by DAS NMR, although the downfield shoulder on the boroxol ring isotropic lineshapes in Figure 3, especially prevalent at higher modifier, may be due to the formation of such units.

Conclusions

In summary, DAS NMR of boron-11-depleted samples has resulted in the simultaneous resolution of three different boron environments, two threefold-coordinate and one fourfold-coordinate, in rubidium oxide modified borate glasses. The equivalent responses of the three different sites permit us to make reliable determinations of the relative population of each site in each sample. With this high-resolution NMR data, we have shown that the fraction of boron atoms in boroxol rings remains essentially constant as a function of Rb_2O content. In contrast to earlier work, we observe the formation of BO_4^- units at the expense of nonring threefold-coordinate boron sites. We cannot determine at this point the second-neighbor environments of these threefold-coordinate boron atoms, but it is clear from our data that they do not reside in boroxol rings or modified boroxol rings. Furthermore, we observe no NMR signal that we can assign to ring structures containing four-coordinate boron. Results obtained from differently prepared samples suggest the initial modification of all threefold-coordinate boron, but the boroxol ring fraction is re-established when given sufficient time in the melt. This is evidence for the stability of the boroxol ring unit in alkali borate glasses, even at high modifier content.

Acknowledgment. This research was supported by the National Science Foundation under Grant No. DMR-9115787.

JA941401F