**Separating the effects of composition and fictive temperature on Al and B coordination in
Ca, La, Y aluminosilicate, aluminoborosilicate and aluminoborate glasses**

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Abstract

Glass transition temperatures often change significantly (100's of degrees) as the boron oxide to silica ratio, or the field strength of the modifier oxide, is varied in aluminoborosilicate glasses. At the same time, fictive temperature itself can strongly affect the glass structure, most notably in the coordination environments of the network cations boron and aluminum. The latter are especially significant when proportions of $^{[5]}\text{Al}$ (AlO_5 groups) and $^{[6]}\text{Al}$ (AlO_6 groups) are high, as in glasses with high field-strength (small, highly charged) modifier cations. To obtain a clearer picture of how composition and temperature independently control structure, we present new data from differential scanning calorimetric (DSC) and high-field ^{11}B and ^{27}Al NMR on a series of Ca, La, and Y aluminosilicate, aluminoborosilicate and aluminoborate glasses prepared with different cooling rates, and compare results in detail with other recently published data on the same compositional joins. We find that previous, apparently disparate results on effects of temperature on Al coordination are in fact related to B/Si ratios: average Al coordination number increased with increased T in aluminosilicates and low-B aluminoborosilicates, but decreased with increased T in glasses with high B/Si ratios, indicating some interaction of the two network cations. We find that effects of T on boron coordination (always lower at higher T) are consistent with a simple thermodynamic view, but may be difficult to detect in some compositions simply because of relative proportions of species. We confirm as well that in boron-rich aluminoborosilicates, B and Al coordination number decreases with increasing temperature are quantitatively linked when calculated per formula unit, again suggesting a strong coupling, and that Al coordination systematically increases with modifier field strength and $\text{B}_2\text{O}_3/\text{SiO}_2$ ratio.

1. Introduction

Aluminoborosilicate glasses are incorporated into a variety of existing and emerging technologies, including optical and photochromic components, high temperature sealants, bioactive materials, materials for nuclear waste sequestration and flat panel display substrates. These glasses typically include the network formers Al_2O_3 , B_2O_3 , and SiO_2 , as well as modifier oxides. Structure and properties are often tuned by varying the type and proportions of modifier oxides.[1-7] These are distinguished by cation field strength, which is defined as the ratio of the formal charge divided by the square of the first shell cation-oxygen distance. For example, as modifier cation field strength increases in high cation field strength aluminosilicate glasses, there is a systematic increase in both Al coordination and microhardness.[8] The increase in Al coordination results from competition between the modifier cation and Al for short, strong bonds to oxygen; smaller, more highly charged modifiers are better able to secure short, strong bonds to oxygen, forcing Al into higher coordination.[7] Glasses containing high field strength modifier cations- such as Y, and La and other rare earths- are particularly interesting, because temperature and composition both have large effects on structure.[1] There have been many structural investigations of La and Y-containing aluminosilicate,[7-9] borosilicate,[10] aluminoborate [11, 12] and aluminoborosilicate [1, 2] glasses.

Since fictive temperature (T_f) may have a large effect on structure in some compositions, a common lack of fictive temperature characterization introduces some uncertainty into comparisons among different studies, at least when T_g varies strongly with composition; i.e. effects of temperature and composition are not always clearly separated. Understanding in which compositions fictive temperature effects are larger or smaller, and thus when they must be

included in models of glass properties or can be neglected, is especially important. For example, the shift in reaction 1 to the right at lower temperature is probably of key importance in all boron-containing glasses, but in compositions that have low contents of non-bridging oxygens (NBO), both thermodynamic modeling [13] and experiments [14] show that measurable changes in boron coordination may be very small with obtainable ranges in T_f .

In Al-containing glasses, existing literature shows that not only the magnitude, but the direction of the effect of fictive temperature on Al coordination can vary. In aluminosilicate glasses, Al coordination typically increases with increasing fictive temperature.[9, 15-17] Yet, in some aluminoborate [18] and aluminoborosilicate [1, 19] glasses, Al coordination clearly decreases with increasing fictive temperature. The origin of this apparent disparity has not been systematically investigated, however.

Here, we present results for a series of carefully selected glass compositions in order to better understand how variations in modifier cation field strength influence structure and how temperature induced changes in coordination vary with composition. We expand upon our recent studies of five component aluminoborosilicates of intermediate boron contents,[1] which, for simplicity, compared alkaline earth and lanthanides in compositions containing only single modifier oxides. As in previous studies, we vary the type of modifier cation on an “equal oxygen” basis (e.g. CaO vs. $\text{La}_{2/3}\text{O}$), since the proportions of structural species, including NBO, formed depend first of all on the amount of modifier oxide. We contrast the effects of the relatively high field strength cations Ca^{2+} (0.26), La^{3+} (0.50) and Y^{3+} (0.57), and qualitatively examine effects of cooling rate and thus T_f . Here, we focus on the effects of B vs. Si in the

network by varying the ratio $r_{BS} = [B_2O_3] / ([B_2O_3] + [SiO_2])$ from 0 (aluminosilicate) to 1 (aluminoborate). In our recent publication, we reasoned that interactions between B and Al might be responsible for the observed change in Al coordination with fictive temperature. Studying glasses with a range of r_{BS} allows us to investigate that idea. Furthermore, fictive temperature studies can be used to facilitate an isothermal comparison across compositions, which is useful when making substitutions that have large effects on T_g (including B for Si [1]).

2. Experimental

2.1 Sample preparation

Glasses were prepared from reagent grade $CaCO_3$, La_2O_3 , Y_2O_3 , Al_2O_3 , B_2O_3 and SiO_2 . Mixtures were melted in 1 to 2 g batches in platinum crucibles for one-half hour at 1,400 to 1,600 °C, and then quenched by dipping the crucible in water to yield “fast cooled” samples (100±50 K/s). To obtain samples with “medium” cooling rates, portions of the water-quenched samples were reheated to 50 °C above T_g and then cooled at 10 K/min to room temperature in a Netzsch 404F3 differential scanning calorimeter (DSC). The fast cooling rate samples did not contain crystals visible through cross polarized optical microscopy at 400X. No crystallization was detected in the DSC signals in experiments producing glasses with medium cooling rates. Additionally, no evidence of crystallization was seen in ^{27}Al NMR, which is very sensitive to some crystalline phases. Compositions in the system $M^x_{2/x}O-Al_2O_3-B_2O_3-SiO_2$, where $M^x=Y^{3+}$, La^{3+} , Ca^{2+} , were designed on an “equal oxygen” basis, i.e. swapping 1 mole of $Y_{2/3}O$ or $La_{2/3}O$ for one mole of CaO , to make comparisons of the role of oxygen in the network more straightforward (Table 1). For example, a glass with molar proportions of 43:14:43 on a $Y_{2/3}O-Al_2O_3-B_2O_3$ basis would be equivalent to 20:20:60 mol % on a more conventional basis of $Y_2O_3-Al_2O_3-B_2O_3$.

Al₂O₃-B₂O₃ components. Modifier and alumina contents were selected to be comparable with those in our recent previous study [1] when possible. However, the 43% La_{2/3}O, silica-free composition was somewhat more difficult to control and attempts to make this glass resulted in two samples with the intended La/Al and varying B, which bracketed the composition of interest. The lanthanum aluminoborate sample compositions were determined by ICP-AES after dissolving the samples in nitric acid. Reported compositions of the silica-containing glasses are nominal, and there was less than 2% weight loss during melting. This introduces some uncertainty in r_{BS} ($0.07 < r_{BS} < 0.11$) and compositions (± 2 mol% for boron oxide and ± 1 mol% for all other oxides), which does not affect the general conclusions of this paper. The glass YAS-43_0F was originally synthesized by Schaller and Stebbins, but new spectra were collected; additionally, YAS-43_0M was synthesized in this publication by heating and then cooling the original glass at 10K/min.[7] Glass compositions are specified using the first letter of the modifier's atomic symbol, with abbreviations for the other elements included in the composition (A for Al, B for B and S for Si) followed by the mole percent of the modifier oxide and then the ratio $r_{BS} = [B_2O_3] / ([B_2O_3] + [SiO_2])$. When applicable, the cooling rate is appended to the label: fast or "F" (ca. 100 K/s); medium or "M" (10 K/min). For instance, a fast cooled calcium aluminoborosilicate glass with 43 mol% CaO and $r_{BS}=0.1$ would be labeled CABS-43_0.1F.

2.2 Fictive temperatures and heat capacities

The fictive temperatures (T_f) of the fast quenched (100 ± 50 K/s) samples were determined by DSC using the "energy matching" method.[20] The onset of the glass transition temperature (T_g) was determined as in [19] by reheating at 10 K/min after cooling at 10 K/min from well above T_g . To determine the activation energy for relaxation near the glass transition temperature,

ΔH_A , glasses were heated and cooled at rates between 5-25 K/min and the relationship between cooling rate and fictive temperature[21] was used:

$$(\log q_1 - \log q_2) / ((1/T_{f1}) - (1/T_{f2})) = -\Delta H_A / 2.3R \quad \{2\}$$

The heat capacities of the glasses were determined as in [19]. Configurational heat capacity was estimated using DSC results just above and below the glass transition temperature:

$$C_{p,\text{conf}} = C_{p,\text{liquid}} - C_{p,\text{glass}}(T_g).$$

2.3 NMR spectroscopy

^{11}B MAS NMR spectra were collected on a Varian 14.1 T spectrometer at 192.4 MHz using a Varian/Chemagnetics T3 probe with 3.2 mm zirconia rotors spinning at 20 kHz, a recycle delay of 4 s and a pulse length of 0.3 μs , the later corresponding to a (solid) radiofrequency (rf) tip angle of about 30° . ^{11}B chemical shifts are reported in parts per million (ppm) relative to 1.0 M boric acid at 19.6 ppm. ^{27}Al MAS NMR spectra were collected on a Varian 18.8 T spectrometer at 208.4 MHz with a 0.2 s pulse delay and 0.275 μs pulse length, which corresponded to a 30° tip angle. ^{27}Al chemical shifts were referenced to 0.1 M $\text{Al}(\text{NO}_3)_3$ at 0 ppm. ^{27}Al NMR spectra were fit using DMFIT [22]. The partially resolved ^{41}Al , ^{45}Al and ^{67}Al peaks were fit using the CZSimple model with a critical exponent for the Czjzek distribution of 5, because this models the asymmetric lineshape of quadrupolar nuclei well. Each Al coordination environment was fit with one CZSimple peak, and Gaussian peaks were used for sidebands. To obtain the relative peak areas of ^{13}B and ^{10}B , ^{11}B NMR spectra were fit using several Gaussian peaks with no assigned structural significance. Component intensities in all spectra were corrected for the presence of satellite transition sidebands.

3. Results

3.1 Compositional effects on glass transitions and heat capacities

The glass transition temperatures of Ca, La and Y glasses with modifier oxide contents of about 43 mole % (equal oxygen basis as described above) and with varying r_{BS} from 0 to 1 are shown in Figure 1, including new data for low boron compositions, results for $r_{BS} = 0.5, 0.7$ from our recent study [1], and other data from the literature (see caption). For the latter, some compositions were interpolated a few mole percent; cooling rates ranged from 3 to 10 K/min but this has only a minor effect at the scale plotted. Note also that the experimental T_g of YAS-43_0 from this study is within the range of reported values from the literature for this composition, 880- 905 °C [23, 24]. Two well-known trends were observed. For each modifier cation, T_g decreased as r_{BS} increased. Secondly, T_g increased with increased modifier cation field strength from Ca^{2+} to La^{3+} to Y^{3+} . Heat capacities (Table 2) do not show a systematic change with either cation field strength or r_{BS} . Note that while it is unusual for C_{pg} to be slightly above 3R/g-atom, as is the case for YABS-43_0.1, the classical Dulong-Petit “vibrational limit” applies strictly to C_v ; C_p depends also on thermal expansion and the highest T_g is indeed for YABS-43_0.1. For instance, CABS-43_0.1 has a significantly lower $C_{p,conf}$ than does CABS-43_0.5, but there is less change between YABS-43_0.1 and YABS-43_0.5. LABS-43_0.1 has the highest $C_{p,conf}$ of the $r_{BS}=0.1$ glasses.

3.2 Variation in network cation coordination with temperature

In Figure 2, we have shown the 18.8 T ^{27}Al MAS NMR spectra of La- and Y- aluminoborosilicate glasses with r_{BS} varying from 0 to 1. In each spectrum, there are three

partially resolved components centered at around 60, 35 and 0 ppm, which correspond to four, five, and six-coordinated Al ($^{[4]}\text{Al}$, $^{[5]}\text{Al}$ and $^{[6]}\text{Al}$), respectively.[25-27] The relative percentages of each component are presented in Table 3. Data are shown for each glass with two different cooling rates.

In our previous study of previous high r_{BS} ($r_{\text{BS}}=0.5, 0.7$) Ca, La and Y aluminoborosilicates of the same modifier and alumina contents [1], we observed increasing proportions of $^{[5]}\text{Al}$ and $^{[6]}\text{Al}$, and thus increasing mean Al coordination number, with decreasing fictive temperature. By expanding the compositional range of r_{BS} under investigation, we have now found that as r_{BS} decreases to much lower values, the direction of the change in Al coordination with temperature can actually reverse (Figure 2). In aluminosilicates and low- r_{BS} aluminoborosilicate compositions, the mean Al coordination number clearly increases ($r_{\text{BS}}= 0$) or remains nearly constant ($r_{\text{BS}}= 0.1$) as fictive temperature increases, contrasting markedly with the high- r_{BS} compositions. As discussed below, this reversal in trend with a single compositional variable greatly clarifies seemingly disparate results in the literature for boron-rich vs. boron-free glasses.

The effects of fictive temperature on B coordination are shown in the ^{11}B spectra (Figure 3) for two representative glasses: a previously studied $r_{\text{BS}}=0.5$ Y aluminoborosilicate [1] and the comparable glass with $r_{\text{BS}}=0.1$. There are two resolved components, well known to be the major $^{[3]}\text{B}$ species centered at around 12 ppm, and the minor $^{[4]}\text{B}$ species at around 1 ppm. The relative proportions of these coordinations for new samples and others from our recent studies are given in Table 3. In the figure, data are shown for each glass with two different cooling rates. Although the direction of the change in B coordination with temperature is the same in both cases, the

magnitude of the change in B coordination with temperature is much smaller for the $r_{BS}=0.1$ glass than for the $r_{BS}=0.5$ glass.

3.3 Variation in network coordination with composition

In Figure 4, we show the effect of modifier cation field strength on Al coordination for Ca, La, and Y $r_{BS}=0.1$ glasses, cooled at 10 K/min. The proportions of $^{[5]}Al$ and $^{[6]}Al$ increase markedly with increasing field strength, as has been seen in a number of previous studies. In contrast, the effect of modifier cation field strength on B coordination is small. From Table 3, there is less $^{[4]}B$ in CABS-43_0.1M (5.6 ± 0.5 %) than in LABS-43_0.1M (8.2 ± 0.5 %). Within uncertainty, however, LABS-43_0.1M and YABS-43_0.1M have the same concentrations of $^{[4]}B$.

Al coordination also dramatically increases with higher boron to silicon ratio, as shown in Figure 5 for representative Y glasses with r_{BS} ranging from 0 to 0.7. The Y aluminoborate endmember ($r_{BS}=1$) was studied by Eckert and co-workers with ^{27}Al NMR at 11.7 T (their sample “Y20”) instead of 18.8 T field, and so the spectra are not directly comparable. However, those authors report even less $^{[4]}Al$ (34%) in that composition than we observe in our $r_{BS}=0.7$ glass.[11] In bismuth aluminoborosilicate glasses, increased $^{[5,6]}Al$ was also observed as r_{BS} increased.[28]

As shown by the Al speciation data in Table 3, this trend is also followed for both Ca and La. Note also that a CAB-40_1.0 glass with $CaO:Al_2O_3:B_2O_3$ of 40:20:40 mol % (Ca-II) was reported to contain $80 \pm 5\%$ $^{[4]}Al$ [5], comparing well to our similar low-silica glass CABS-43_0.7M with $80.6 \pm 1.7\%$ $^{[4]}Al$. Furthermore, a CAS-44_0 glass with $CaO:Al_2O_3:SiO_2$ of

44:14:42 mol % (CA42.14) was reported to have 92.4 % $^{[4]}\text{Al}$ [29], which is in excellent agreement with our comparable low boron glass CABS-43_0.1F, with $92.1 \pm 1.7\%$ $^{[4]}\text{Al}$. Additionally, a composition close to LAS-43_0 had 90.4% $^{[4]}\text{Al}$, which is in excellent agreement with our comparable low boron glass LABS-43_0.1F, with 86.2%. [30]

To separate out compositional from temperature effects on Al coordination, an isothermal plot was constructed by extrapolating or interpolating data for $^{[4]}\text{Al}$ contents for glasses with different T_f to 700 °C (Figure 6). The qualitative trend of increasing $^{[5,6]}\text{Al}$ with increasing r_{BS} , as seen in the as-quenched glasses, is robustly conserved. Note that for data points involving temperature extrapolation rather than interpolation, error bars have been increased here relative to [1] in order to better reflect estimated uncertainties. The isothermal comparison confirms that for Ca, La and Y glasses, as r_{BS} increases, the amount of $^{[4]}\text{Al}$ decreases. For comparison, $^{[4]}\text{Al}$ contents at 700 °C are included for two Ca aluminoborosilicate glasses from our previous publication [4, 19] that have less modifier oxide (20 mol% CaO) and correspondingly less non-bridging oxygen (NBO). The data points from the previous study [19] are similar within uncertainty, which is consistent with the narrower range of r_{BS} ($r_{\text{BS}} = 0.1$ and 0.3) explored in that study.

Higher r_{BS} also generally leads to higher percentages of $^{[4]}\text{B}$, as previously reported in bismuth aluminoborosilicates.[28] Direct examples from Table 3 include CABS-43_0.1M ($5.6 \pm 0.5\%$ $^{[4]}\text{B}$) vs. CABS-43_0.7M ($17.1 \pm 1.0\%$ $^{[4]}\text{B}$) and LABS-43_0.1M ($8.2 \pm 0.5\%$) vs. LABS-43_0.7M ($15.7 \pm 1.0\%$). An isothermal comparison at 700°C further supports this qualitative trend (Figure 7, Table 4). Note that for data points involving temperature extrapolation rather than interpolation, error bars have been increased in this publication relative

to [1] in order to better reflect estimated uncertainties. In the isothermal comparison, however, it becomes apparent that the $r_{BS}=0.5, 0.7$ glasses listed in Table 3 have similar $^{[4]}B$ contents within uncertainty. For comparison, Figure 7 includes data for two Ca aluminoborosilicate glasses that have less modifier oxide (20 mol% CaO) and correspondingly less NBO, that is CABS7 and CABS21 [4, 19]. For these CABS-20 glasses, the trend in boron speciation with r_{BS} is confirmed. Indeed, $^{[4]}B$ increases more dramatically with r_{BS} than for the CABS-43 glasses, perhaps because there is lower total $^{[4]}B$ in the latter.

4. Discussion

4.1 Compositional effects on glass transitions and heat capacities

Glasses in this study with higher field strength modifiers have higher T_g , following a trend that is well established in the literature [23]. Many glasses follow the trend seen in this study of decreasing T_g with increasing r_{BS} . [31]. The changes in configurational heat capacity as composition is varied in five component aluminoborosilicate systems are complex, as seen in earlier work in aluminoborosilicate systems. [1, 4] This may not be surprising, given the known complexity of interactions of composition and network cation coordinations and connectivities.

4.2 Network cation coordination and fictive temperature

Previous work in ternary aluminosilicate [9, 15-17] and aluminoborate [18] glasses suggested the possibility of a reversal of the direction of Al coordination change with temperature as the relative proportions of boron and silicon in the network are varied. *In-situ*, high temperature NMR studies of boron-free Ca [16], and La and Y [9] aluminosilicate liquids, as well as fictive temperature studies of ambient pressure Ca aluminosilicate glasses [15, 17],

demonstrated that Al coordination increased with increased temperature and that the magnitude of this change depends on composition. A commercial “E-glass” composition (primarily Ca-aluminoborosilicate, $r_{BS}=0.17$) also had a higher $^{[5]}Al$ content at higher T_f , enhanced in very rapidly cooled small-diameter fibers.[32] In peraluminous Li aluminoborate glasses, however, Al coordination decreased with increased fictive temperature.[18] Furthermore, although in previously studied Ca aluminoborosilicate glass CABS-20_0.1, Al coordination changes with fictive temperature were small, in CABS-20_0.3 Al coordination did decrease with increased fictive temperature.[4, 19] Despite previous suspicions of a role in boron content in controlling this structural change with temperature, this key compositional variable has apparently not been previously systematically investigated. The new results presented here thus serve to significantly clarify what could seem to be disparate results.

The directions and sizes of the fictive temperature effects on mean B coordination number observed here are also consistent with previous studies, in which borate, aluminoborate, borosilicate and aluminoborosilicate glasses all have decreasing B coordination with increasing fictive temperature when the effect is large enough to detect. While the magnitude of the fictive temperature effect is small for the $r_{BS}=0.1$ glasses in this study, this finding is unsurprising for this composition. In several previous studies, we used observed changes in boron speciation, together with NBO concentrations, to estimate ΔH values for reaction 1[4, 19]. Estimating ΔH would be very imprecise given small temperature effects on $^{[4]}B\%$ seen in the $r_{BS}=0.1$ compositions studied here, but we can check whether our data are consistent with a reasonable ΔH for {1}. We thus assume a value of ΔH of 24 kJ/mol (c.f. data for CABS-20_0.1 give $\Delta H=24\pm 8$ kJ/mol [19]), and use the following equation to calculate NBO:

$$\text{NBO} = 2 * ([\text{CaO}] - \text{N}_4 * [\text{B}_2\text{O}_3] - \text{Al}_4 * [\text{Al}_2\text{O}_3]) / ([\text{CaO}] + 3 * [\text{B}_2\text{O}_3] + 3 * [\text{Al}_2\text{O}_3] + 2 * [\text{SiO}_2]) \quad \{3\}$$

Because defining NBO is most obvious when contents of ^[5,6]Al are small, we calculated NBO for CABS-43_0.1. We then used the literature ΔH for CABS-20_0.1 in the van t'Hoff equation to predict the ^[4]B% at one fictive temperature using the ^[4]B% at another fictive temperature. The calculated difference in ^[4]B% between the two temperatures ranged from 0.8-1.4% depending on uncertainty in ΔH , whereas the experimental change in ^[4]B% was >0 to 1.4% based on uncertainty in determining relative areas. Both the calculation and the experiment are consistent with small, and thus potentially difficult to observe, changes in ^[4]B% as T_f varies. Furthermore, the calculation suggests that the small changes in ^[4]B contents with T_f are simply a consequence of the low total amount of ^[4]B and small changes in the high NBO concentration that were calculated for the $r_{\text{BS}}=0.1$ glasses, not to any fundamental difference in the structural response to temperature. This echoes earlier findings of effects of T_f on boron speciation that were too small to be quantified in glasses that have low NBO contents [14] [13], and supports the role of reaction { 1 } in controlling speciation. Just as glasses that contain low contents NBO do not show much change in ^[4]B% with temperature, glasses containing only small concentrations of ^[4]B% and large amounts of NBO are not be predicted to show much change in ^[4]B% with temperature.

4.3 Interactions among boron and aluminum speciation

The strong effect of boron content (at least as captured here in r_{BS} variations) on the sign of the temperature effect on Al coordination suggests some kind of interplay between B and Al speciation. To explore these interactions, we calculate the moles ^[4]B and ^[4]Al per formula unit on a (La,Y)_{2/3}O-Al₂O₃-B₂O₃-SiO₂ basis (per 100 mol of oxide components), as in our previous

contribution [1], and compare their co-variations at different values of T_f . In Figure 8, we show these previous data along with new results for the two La aluminoborates. Intriguingly, the changes in $^{[4]}\text{Al}$ versus $^{[4]}\text{B}$ for various temperatures can all be fit with slopes of about -1.5, with a range of about ± 0.5 [1]. Corresponding results for temperature effects on the CABS glasses in this temperature and composition range are considerably less precise, particularly because of their lower contents of $^{[5,6]}\text{Al}$, and are thus not plotted. In the previous paper, we included a possible equilibrium among species that would result in a slope of -1.5, i.e. 1.5 moles of $^{[5]}\text{Al}$ converted to $^{[4]}\text{Al}$ at higher temperature for each mole of $^{[4]}\text{B}$ converted to $^{[3]}\text{B}$, at roughly constant NBO content, one of several that can be imagined that give slopes in this range. Since that equilibrium included Si species, we suggest here a related reaction that could be applied to Si-free compositions. As previously, the subscripts are the inverses of the cation coordination numbers to allow proper bond counting:

As before [1], we emphasize that in multicomponent oxide liquids there will be many equally valid competing equilibria and reactions that describe them; the intriguing net result does seem to be some kind of consistent compensation of changes in B coordination by changes in Al speciation.

More complex NMR methods have the potential to more directly address changes in boron-aluminum interactions with changing T_f . For example, Eckert and co-workers used double resonance NMR of ^{11}B and ^{27}Al (methods such as REDOR and CPMAS-HETCOR) to investigate whether preferential interactions exist among Al and B network species in aluminoborates, i.e. whether there are non-random associations of the cations in their different

coordination states [5, 11, 33, 34]. In compositions close to those studied here ($\text{CaO}:\text{Al}_2\text{O}_3:\text{B}_2\text{O}_3$ 40:20:40 mol% or Ca-II [5] and $\text{Y}_{2/3}\text{O}:\text{Al}_2\text{O}_3:\text{B}_2\text{O}_3$ 43:14:43 mol% [11] or Y20), statistical bonding distributions were observed, but T_f was not varied. Such types of methods may hold real promise for future studies of temperature effects on network structure.

4.4 Effect of cation field strength on structure

With increasing modifier cation field strength, Al coordination increases. This trend has been documented in La and Y aluminosilicates [6-9], in alkali and alkaline earth aluminosilicates [35, 36], in Ca, La and Y aluminoborosilicates with $r_{\text{BS}}=0.5, 0.7$ [1], and in Na, Ca, Mg aluminoborates[5]. Smaller, more highly charged modifiers are better able to compete with Al for short, strong bonds to oxygen, driving the formation of $^{[5,6]}\text{Al}$ in compositions containing high cation field strength modifier cations.[7]

Conversely, the data do not support a simple, consistent trend in B coordination with modifier cation field strength, which can, however, be clearly seen in other compositional ranges, especially when comparing alkali and alkaline earth modifiers in aluminoborosilicates and borosilicates [4] [37]. Depending on the cations being compared and other compositional variables, B coordination can decrease, increase or remains constant with changes in field strength. For example, while CABS-43_0.1M has a lower $^{[4]}\text{B}$ content than higher field strength LABS-43_0.1M, compositionally distinct CABS-20_0.1 has less $^{[4]}\text{B}$ than its lower cation field strength Ba analog (CABS-20_0.1 has an 17% $^{[4]}\text{B}$ % at 700°C whereas its Ba analog has 39% $^{[4]}\text{B}$ % at 700°C).[4] Multicomponent aluminoborosilicate glasses showed decreased $^{[4]}\text{B}$ as cation field strength increased from La to Y to Lu.[3] Conversely, in this study, LABS-43_0.1M and YABS-43_0.1M have similar $^{[4]}\text{B}$ contents despite differing cation field strengths.

Even in compositionally simple binary borate systems, complex trends in $^{[4]}\text{B}$ contents can be seen with varying cation field strength. As modifier oxide concentration increases, the NBO term in equation 1 increases. Among Li, Na, K, Rb, Cs borate glasses containing NBO, lithium borate glasses have the highest contents of $^{[4]}\text{B}$, perhaps because $^{[4]}\text{B-O-}^{[4]}\text{B}$ linkages are less disfavored for small cations as a result of reduced cation-cation repulsion.[38] An isothermal comparison among Na, Ba and Ca borates indicated that in compositions with less than 40 mol% modifier and correspondingly low NBO concentrations, $^{[4]}\text{B}$ decreased as modifier cation field strength increased [39]. As modifier oxide concentration, and thus NBO content, increased, however, the rate at which $^{[4]}\text{B}$ decreased varied for Na, Ba and Ca cations. At intermediate modifier concentrations between 50 and 70 mol%, Ba and Ca borate have similar $^{[4]}\text{B}$ contents. At high modifier concentrations above 70 mol%, however, Ca borate has higher $^{[4]}\text{B}$ than Ba borate, perhaps because the smaller Ca cation is better able to compensate $^{[4]}\text{B-O-}^{[4]}\text{B}$ than the larger Ba cation due to its smaller size and correspondingly decreased cation-cation repulsions.[39] This complexity, seen even in the binary borates, may account for the complexity in the quaternary system. The preference for $^{[4]}\text{B}$ versus NBO appears to depend on composition, as well as cation size and charge, thus obscuring effects of modifier cation field strength. As glass formation regions are limited in quaternary systems, especially with higher cation field strengths (for instance, LABS-20_0.1 phase separates [1]), it is difficult to generate a complete picture of the effects of this important variable on boron coordination.

4.5 Effects of boron vs. silicon content on structure

As r_{BS} increases, $^{[4]}\text{Al}$ is systematically converted to $^{[5,6]}\text{Al}$. The increased Al coordination may be a consequence of the increase in the overall proportion of network forming cations that

occurs as r_{BS} increases, as one mole of B_2O_3 is substituted for one mole of SiO_2 . Both B and Si have larger cation field strengths than Al. Therefore, B and Si are more likely to secure short, strong bonds to oxygen than Al. As the total number of B and Si atoms increases as r_{BS} increases, some Al is forced into higher coordination. In addition to having higher Al coordination, glasses with higher r_{BS} have slightly higher mean B coordination numbers. Both increased Al coordination and increased B coordination have also been observed for bismuth aluminoborosilicate glasses as r_{BS} increased [28], consistent with our results.

A comparable effect is not obviously seen in the Si-free ternary aluminoborate systems. In high field, high-resolution NMR studies of bismuth [28] and lead [40] aluminoborates with 2 to 8 % Al_2O_3 , decreases in $^{[4]}B$ content and lack of large changes in Al speciation were seen when Al_2O_3 was substituted for B_2O_3 . An earlier study of alkaline earth borates that covered a wider compositional range (but with lower precision because of lower resolution spectra and Gaussian curve fitting), also did show systematic effects on B coordination of B/Al, but not on Al coordination [41].

5. Conclusions

Our new data confirm that in aluminosilicate and B-poor aluminoborosilicate glasses, average Al coordination increases or remains constant at higher fictive temperatures, but in aluminoborates and B-rich aluminoborosilicates, this temperature effect is reversed. Interactions among B and Al species may be responsible for this behavior, and could be investigated in future work using double resonance NMR and other advanced methods. A decrease in B coordination with increasing fictive temperature is observed across the entire range of boron oxide to silica ratios studied, and the magnitude of this effect depends on the composition, consistent with

simple thermodynamic treatments of the speciation. In aluminoborosilicates with the lowest such ratio, however, this change can be difficult to detect simply because of species proportions. In general, observation of changes in the magnitude of Al coordination with changes in fictive temperature is easier in high field strength, high B glasses with more ^[5,6]Al than in low field strength, low B glasses with less ^[5,6]Al, although the maximum occurs with intermediate composition LABS-43_0.7 rather than with the highest field strength and boron content. Here, we confirm a systematic correlation between decreasing Al and B coordinations at higher temperature. There is higher Al coordination in glasses with higher modifier cation field strength, because smaller, more highly charged cations are better able to compete with Al for short, strong bonds to oxygen, forcing Al into higher coordination. There is also higher mean Al coordination in glasses with high boron oxide to silica ratios, because the total number of network forming B and Si atoms is greater, and B and Si atoms again compete with Al for short, strong bonds to oxygen. Fictive temperature should be carefully constrained in studies of aluminoborate and boron-rich aluminoborosilicate glasses, to allow more clear separation of effects of temperature and composition on structure.

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Figure Captions

Figure 1: Glass transition temperatures for glasses with 43 mol% modifier oxide on an equal oxygen basis; Ca is represented with circles, La with triangles and Y with squares. Data from this work are represented with filled symbols, whereas literature T_g are represented with open symbols: Ca [42] and La [43, 44] aluminosilicates; Ca, La and Y aluminoborosilicates with $r_{BS}=0.5, 0.7$ [1]; and Ca [45], La [12] and Y [11] aluminoborates. Error bars are smaller than the symbols.

Figure 2: The 18.8T ^{27}Al NMR spectra of glasses with a range of r_{BS} from 0 to 1 are stacked and each composition is labeled. Spectra for two cooling rates are included for each glass: fast (dotted) and medium (solid). The arrowhead points in the direction of increasing fictive temperature. The spectra of two glasses were taken from [1]: YABS-43_0.5 (Y1 in [1]) and LABS-43_0.7 (La2).

Figure 3: The 14.1 T ^{11}B NMR spectra of Y aluminoborsilicate glass YABS-43_0.1 from new data is compared to YABS-43_0.5 from [1], which was referred to as Y1 there. For each glass, two cooling rates are included: fast (dotted) and medium (solid). The arrowhead points in the direction of increasing fictive temperature.

Figure 4: The 18.8T ^{27}Al NMR spectra of Ca, La and Y glasses with $r_{BS}=0.1$, which were all cooled at 10K/min (medium cooling rate “M”), are shown.

Figure 5: The 18.8T ^{27}Al NMR spectra of glasses with 43 mol% $\text{Y}_{2/3}\text{O}$ are overlaid and r_{BS} is labeled. All spectra are of glasses cooled at 10K/min (medium cooling rate “M”). The spectra of

Y glasses with $r_{BS}=0.5$ and $r_{BS}=0.7$ are taken from [1], where they are referred to as Y1 and Y2, respectively.

Figure 6: An isothermal plot ($T=700^{\circ}\text{C}$) of $^{[4]}\text{Al}\%$ versus r_{BS} . Filled symbols are used to represent data from the current publication with 43 mol% modifier on an equal oxygen basis, and circles are used for Ca, triangles for La and squares for Y. Data from previous publications are represented with open symbols: hexagonal symbols for Ca glasses with 20 mol% modifier on an equal oxygen basis are included [4, 19]; and circles for Ca, triangles for La and squares for Y glasses with 43 mol% modifier on an equal oxygen basis [1].

Figure 7: An isothermal plot ($T=700^{\circ}\text{C}$) of $^{[4]}\text{B}\%$ versus r_{BS} . Filled symbols are used to represent data from the current publication with 43 mol% modifier on an equal oxygen basis, and circles are used for Ca, triangles for La and squares for Y. Data from previous publications are represented with open symbols: hexagonal symbols for Ca glasses with 20 mol% modifier on an equal oxygen basis are included [4, 19]; and circles for Ca, triangles for La and squares for Y glasses with 43mol% modifier on an equal oxygen basis [1].

Figure 8: As described in the text, the amount of $^{[4]}\text{Al}$ per formula unit is plotted against the amount of $^{[4]}\text{B}$ for glasses with high B/Si ratios. As a guide for the eye, lines with a slope of -1.5, whose arrow heads point toward increasing fictive temperature, are drawn. New data are represented with filled symbols, and LAB-47_1 is represented with an isosceles triangle, whereas LAB-33_1 is represented with an equilateral triangle. Data from a previous publication [1] are represented with open symbols: YABS-43_0.5 (Y1) is a square, LABS-43_0.5 (La1) is a circle, YABS-43_0.7 (Y2) is a diamond and LABS-43_0.7 (La2) is a hexagon.

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567

Tables

Table 1: Glass compositions in mol% where “M_nO” denotes CaO, Y_{2/3}O or La_{2/3}O for glasses whose labels contain “C”, “Y” or “L,” respectively

Label	field strength	Composition				572
		M _n O	Al ₂ O ₃	B ₂ O ₃	SiO ₂	
$r_{BS}=0^{\delta}$						
YAS-43_0°	0.57	43	14	0	43	
$r_{BS}=0.1$						
CABS-20_0.1†	0.36	20	8	7	65	
$r_{BS}=0.1$						
CABS-43_0.1	0.36	43	14	4	38	
LABS-43_0.1	0.50	43	14	4	38	
YABS-43_0.1	0.57	43	14	4	38	
$r_{BS}=0.3$						
CABS-20_0.3††	0.36	20	8	21	51	
$r_{BS}=0.5$						
CABS-43_0.5*	0.36	43	14	21	21	
LABS-43_0.5*	0.50	43	14	21	21	
YABS-43_0.5*	0.57	43	14	21	21	
$r_{BS}=0.7$						
CABS-43_0.7**	0.36	43	14	28	14	
LABS-43_0.7**	0.50	43	14	28	14	
YABS-43_0.7**	0.57	43	14	28	14	
$r_{BS}=1.0$						
LAB-33_1.0	0.50	33	12	56	0	
LAB-47_1.0	0.50	47	16	36	0	

$$\delta r_{BS} = [B_2O_3] / ([B_2O_3] + [SiO_2])$$

° sample YAS226, originally synthesized in [7]

† sample CABS7 from [4]

†† sample CABS21 from [4]

* samples Ca1, La1, Y1 from [1]

** samples Ca2, La2, Y2 from [1]

581 Table 2: Glass properties
582

Label	Heat Capacity		T_f^δ		ΔH_f^δ (kJ/mol)
	$C_{p,conf}$ (Jg-atom ⁻¹ K ⁻¹)	$C_{pg}(T_g)/3R$	M (T _g) (±3°C)	F (±20°C)	
$r_{BS}=0$					583
YAS-43_0°	n.d.	n.d.	888	n.d.	586
$r_{BS}=0.1$					587
CABS-20_0.1†	6.0	0.93	700	770	588
$r_{BS}=0.1$					589
CABS-43_0.1	9.9	0.93	741	813	590
LABS-43_0.1	14.0	0.97	805	864	591
YABS-43_0.1	11.7	1.04	850	920	592
$r_{BS}=0.3$					593
CABS-20_0.3†	8.0	0.87	658	717	594
$r_{BS}=0.5$					595
CABS-43_0.5*	12.1	0.98	633	685	596
LABS-43_0.5*	NA	NA	703	750	597
YABS-43_0.5*	11.4	0.90	763	813	598
$r_{BS}=0.7$					599
CABS-43_0.7**	12.3	0.98	620	667	600
LABS-43_0.7**	13.1	0.87	680	735	601
YABS-43_0.7**	13.0	0.94	736	808	602
$r_{BS}=1.0$					603
LAB-33_1.0	n.d.	n.d.	n.d.	n.d.	604
LAB-47_1.0	n.d.	n.d.	662	n.d.	605

610 ° sample YAS226, originally synthesized in [7]

611 † sample CABS7 from [4]

612 †† sample CABS21 from [4]

613 * samples Ca1, La1, Y1 from [1]

614 ** samples Ca2, La2, Y2 from [1]

615 δ Here “M” refers to a medium cooling rate of 10K/min and “F” to a fast cooling rate of 100 K/s, and n.d.
616 is short for “not determined”

617

618 Table 3: Al and B speciation
619

Label	Cooling Rate (K/s)	T _f (°C)	^[4] B ± 0.5 %	^[4] Al ± 1.7 %	^[5] Al ± 1.2 %	^[6] Al ± 1.2 %
<i>r_{BS}</i> = 0						
YAS-43_0F°	Unk		-	72.9	22.1	5
YAS-43_0M	0.167	888	-	74.6	21.2	4.2
<i>r_{BS}</i> = 0.1						
CABS-20_0.1F†	100	770	13	94	~6	~0
CABS-20_0.1M†	0.167	700	17	94	~6	~0
<i>r_{BS}</i> = 0.1						
CABS-43_0.1F	100	813	5.2	92.1	6.1	1.6
CABS-43_0.1M	0.167	741	5.6	92.4	5.4	2.2
LABS-43_0.1F	100	864	7.5	86.2	11.6	2.2
LABS-43_0.1M	0.167	805	8.2	86.2	11.3	2.4
YABS-43_0.1F	100	920	8.2	72.9	22.1	4.9
YABS-43_0.1M	0.167	850	8.5	73.4	21.2	5.3
<i>r_{BS}</i> = 0.3						
CABS-20_0.3F††	100	717	21	~91	~9	~0.3
CABS-20_0.3M††	0.167	658	24	89.3	10	0.7
<i>r_{BS}</i> = 0.5						
CABS-43_0.5F*	100	685	14.5	82.3	13.9	3.7
CABS-43_0.5M*	0.167	633	15.5	81.7	13.9	4.0
LABS-43_0.5F*	100	750	11.5	72.7	21.2	6.1
LABS-43_0.5M*	0.167	703	12.5	69.4	23.1	7.5
YABS-43_0.5F*	100	813	10.5	65.9	27.1	7.1
YABS-43_0.5M*	0.167	763	11.5	62.1	30.0	8.4
<i>r_{BS}</i> = 0.7						
CABS-43_0.7F**	100	667	13.5	80.6	15.5	3.9
CABS-43_0.7M**	0.167	620	17.1	79.3	15.7	5.0
CABS-43_0.7S**	0.0017	594	18.2	78.9	15.8	5.2
LABS-43_0.7F**	100	735	14.1	65.9	26.2	8.0
LABS-43_0.7M**	0.167	680	15.7	61.9	27.6	10.5
LABS-43_0.7S**	0.0017	649	17.0	60.2	27.7	12.6
YABS-43_0.7F**	100	808	13.0	57.7	32.2	10.1
YABS-43_0.7M**	0.167	736	14.2	55.7	32.6	11.8
YABS-43_0.7S**	0.0017	708	14.5	53.8	33	13.3

$r_{BS} = 1.0$

LAB-33_1.0F	100		22.6	57	33	10
LAB-33_1.0M	0.167		25	50	36.5	13.5
LAB-47_1.0F	100		15.4	63	28	9
LAB-47_1.0M	0.167	662	16.6	60	29	11

620 ° sample YAS226, originally synthesized in [7]

621 † sample CABS7 from [4]; uncertainty in $^{[4]}\text{B}\%$ is ± 1.0 †† sample CABS21 from [4]; uncertainty in $^{[4]}\text{B}\%$
622 is ± 1.0

623 * samples Ca1, La1, Y1 from [1]

624 ** samples Ca2, La2, Y2 from [1]; uncertainty in $^{[4]}\text{B}\%$ is ± 1.0 ; slow cooling rate samples, “S”, have a
625 cooling rate of 6 K/h

626

627 Table 4: Isothermal Comparisons at 700°C

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Label	Isothermal T (°C)	^[4] Al%	^[4] B%
YABS-43_0.1	700	74.7± 3.0	9.3± 1.0
YABS-43_0.5*	700	57.3±3.0	12.8±2.0
YABS-43_0.7**	700	53.1±1.7	14.7±1.0
LABS-43_0.1	700	86.5± 3.0	9.4± 1.0
LABS-43_0.5*	700	69.2±1.7	12.5±0.5
LABS-43_0.7**	700	63.5±1.7	15.2±1.0
CABS-43_0.1	700	93.0± 1.7	6.0± 0.5
CABS-43_0.5*	700	82.4±3.0	14.2±2.0
CABS-43_0.7**	700	81.3±3.0	12.4±2.0

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630 † sample CABS7 from [4]

631 †† sample CABS21 from [4]

632 * samples Ca1, La1, Y1 from [1]

633 ** samples Ca2, La2, Y2 from [1]

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635 Figure 1
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639 Figure 2
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