

Dependence of N_4 upon alkali modifier in binary borate glasses

W. J. Clarida, J. R. Berryman, M. Affatigato, S. A. Feller¹

Physics Department, Coe College, Cedar Rapids, IA 52402, USA

S. C. Kroeker

Department of Chemistry, University of Manitoba, Winnipeg, MB, Canada

J. Ash, J. W. Zwanziger

Department of Chemistry, Indiana University, Bloomington, IN, USA

B. Meyer, F. Borsa & S. W. Martin

Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011, USA

In this paper we re-examine the alkali dependence of the fraction of four-coordinated borons (N_4) in two series of glasses: alkali borates ($0.4M_2O.B_2O_3$) and mixed lithium caesium borates ($0.4(xLi_2O+(1-x)Cs_2O).B_2O_3$). High field ^{11}B MAS-NMR experiments were performed to maximise the accuracy of the present results. We found no evidence for an alkali dependence on N_4 in either system. In each case N_4 closely followed the relation $N_4=R$ where R is the molar ratio of alkali to boron.

One of the most extensively studied areas in glass science is the short range order of alkali borate glasses. Despite several comprehensive studies done on the short range order of these glasses there are still unresolved questions.⁽¹⁻³⁾ One of the more important of these is the role that the four-coordinated boron units (fractionally given by N_4) play in these glasses.

One component of that question is what role does the alkali modifier play in tetrahedral boron formation? It is known that the borate glass must have a cationic modifier to form the N_4 unit but the extent of the role of the the specific kind of modifier is not precisely known beyond that. In the original ^{11}B NMR study of alkali borates by Bray & O'Keefe,⁽¹⁾ alkali independence was noted for N_4 as shown in Figure 1. Based upon a 1989 paper by Zhong & Bray,⁽³⁾ however, the most accepted idea is that there is a significant role that the modifier plays in the glass. They determined that the fraction, N_4 , in a glass is not only dependent on the amount of alkali metal but also on the specific metal being used. Their results showed a

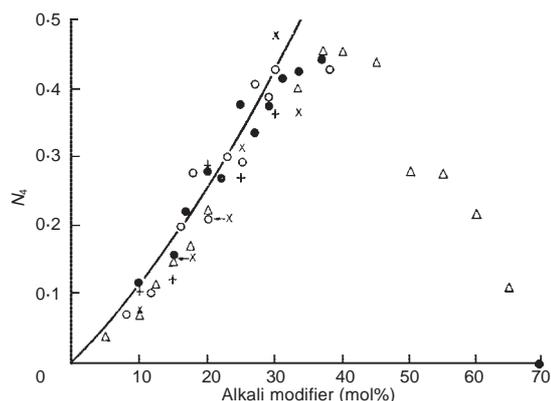


Figure 1. Fraction of four coordinated borons in alkali borate glasses after Bray & O'Keefe⁽¹⁾

● Na_2O ○ K_2O △ Li_2O + Rb_2O × Cs_2O

divergence of N_4 amounts commencing around $R=0.25$ with the maximum divergence occurring around $R=0.65$, where R is the molar ratio of alkali oxide to boron oxide, displayed in Figure 2. The data they obtained also indicated a greater value for N_4 in glasses with smaller alkali ions.

NMR has made several significant advances since 1989, one of the largest being the common availability of MAS-NMR (magic angle spinning), which provides enhanced sensitivity and resolution than previous static NMR experiments could achieve. By using this precision MAS-NMR we were able to obtain spectra of all the alkali borates near the N_4 maximum ($R=0.4$) with a signal to noise ratio of about 1000:1. When we compared the N_4 amounts in each glass we found no significant variance between the glasses. Interestingly this result is in excellent accord with the earlier studies on alkali borates by Bray & O'Keefe.⁽¹⁾

¹ Author to whom correspondence should be addressed. (email: sfeller@coe.edu)

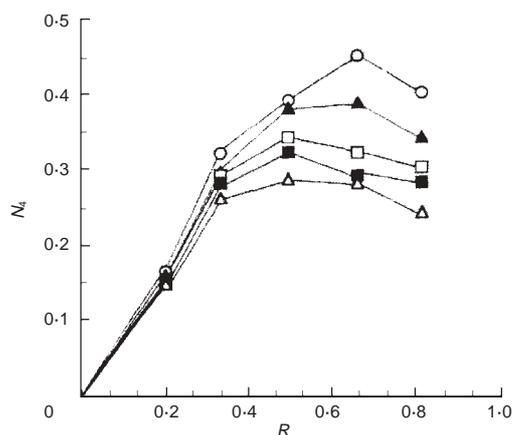


Figure 2. Fraction of four coordinated borons in alkali borate glasses after Zhong & Bray⁽³⁾

○ LB ▲ NB □ KB ■ RB △ CB

Experimental details

Glasses were primarily made in the following families: $0.4M_2O \cdot B_2O_3$ and $0.4(xLi_2O + (1-x)Cs_2O) \cdot B_2O_3$. Some caesium borate glasses ($R=0.3$ and 0.475) were also prepared for comparisons with other alkali borates at other compositions. Samples were prepared with reagent grade chemicals, and 5–8 g well mixed batches were prepared and heated for 10 min at $1000^\circ C$ in platinum crucibles. Two things were done to ensure that we had the correct composition of glass. We recorded the mass before and after heating to check that the weight loss was close to the predicted value. No glass was used with a weight loss error greater than 2% from the expected value. Also, all glasses were run in a Perkin Elmer DSC 7 to determine their T_g and to compare to literature values. All glasses used were within $7^\circ C$ of previously reported values.⁽⁴⁾

Once all the glasses had been prepared they were taken to Indiana University (J. Ash), sent to Stanford University (S. Kroeker) or brought to Iowa State University (B. Meyer, S. Martin and F. Borsa) for the NMR experiments. At Indiana the ^{11}B NMR spectra were recorded on a Bruker Avance 400 (9.4 T) spectrometer at a resonant frequency of 128.38 MHz using a 4 mm MAS probe. The samples were spun at 12 kHz. A short pulse, chosen to be approximately $1/8$ of the 'solution $\pi/2$ ' pulse length, was used to ensure consistent excitation of all B sites. A supersaturated boric acid solution was used to calibrate this pulse length as well as to set the reference. The single aqueous boric acid peak was set to 19.6 ppm so that the primary reference, $BF_3 \cdot O(CH_2CH_3)_2$, would resonate at 0 ppm. A recycle delay of 5 s was used between scans. In order to remove the ^{11}B background signal caused by the boron containing ceramic coil housing of the probe, a background B spectrum was recorded under identical conditions using an empty rotor. These spectra were convolved and typically present in each spectrum was a quadrupolar broadened powder pattern associated with trigonal borons (N_3) that appeared with a much narrower peak associated with the tetrahedral borons (N_4). Because of this simple curve fitting could not be used; instead quantification of N_4 was achieved by

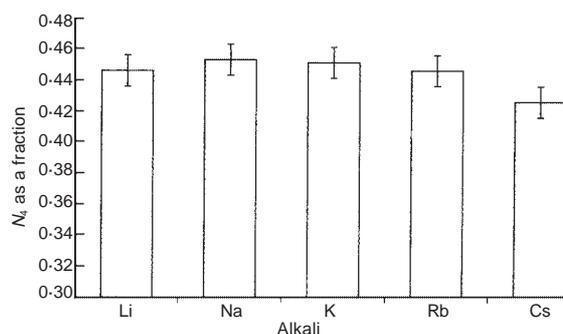


Figure 3. Fraction of four coordinated borons in alkali borate glasses at $R=0.4$, present work

simulating the spectra using Xedplot. The spectra obtained at 9.4 T were simulated using a quadrupole coupling constant (Q_{cc}) = 2.5 MHz and an asymmetry parameter, η , of 0.2 for the BO_3 sites and a much smaller Q_{cc} for BO_4 (about 500 kHz). The resulting error in N_4 is ± 0.01 .

The $R=0.3$ and 0.475 caesium borate samples were run at Stanford using MAS-NMR at 14.1 T and a sample spinning rate of 16 kHz with a Varian INOVA 600. We obtained accurate values of N_4 by the relative area method (within ± 0.01) because at such a high field the peaks associated with trigonal and tetrahedral borons are completely separated. Each glass was signal averaged with 512 runs and a relaxation delay of 1 s and very short pulse durations of less than $1/12 \pi$ to ensure that the boron was all excited equally. Measured peak areas were corrected for spinning speed and applied field effects according to the procedure of Massiot *et al.*⁽⁵⁾

Static ^{11}B NMR measurements were performed on the mixed alkali samples at Iowa State using a 4.7 T Oxford superconducting magnet. Glass samples were crushed into fine powders and loaded into quartz tubes using a nitrogen filled glove bag. The tubes were then sealed with Teflon tape, removed from the glove bag and placed inside the RF coil in the probe. The signal then was acquired following a $\pi/8$ pulse. Each measurement was averaged over 400 scans with 5 s delay in between each scan. The Fourier transformed frequency spectra were then analysed for N_4 by using the usual area method of Bray⁽²⁾ and a program developed by Sills.⁽⁶⁾ These N_4 have an error of 5%.

Results and discussion

Figure 3 presents a plot of N_4 for the alkali borate glasses at $R=0.4$. As can be seen the fraction, N_4 , in the glass does not show the relationship with alkali cation, previously reported by Zhong & Bray have reported before.⁽³⁾ If such alkali dependence existed we would see a steady decrease in N_4 as the cation became large. Our data agree much more closely with the data that were presented by Bray & O'Keefe,⁽¹⁾ see Figure 1. Because the wideline NMR technique employed in the early sixties had a relatively large error they could not state anything conclusively about the N_4 dependence on alkali cation, but the data they obtained did seem to indicate that there was no dependence. The error with modern NMR techniques is substantially less and

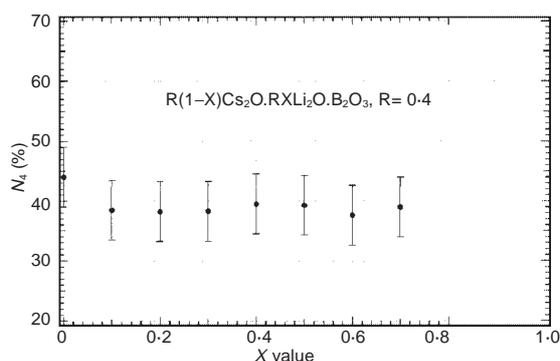


Figure 4. Fraction of four coordinated borons in a series of mixed lithium caesium borate glasses at $R=0.4$

we can now see that there is very little fluctuation in the N_4 amounts across alkali metals.

Along with the MAS-NMR experiments we ran two other experiments to provide additional evidence that there is no dependence on alkali metal. Static NMR was performed on ten lithium-caesium mixed alkali borate samples. The composition was again $R=0.4$ and the glasses ranged from 100% lithium to 100% caesium for the alkali content. When the N_4 data for each glass are compared again there is no observable change, outside of the experimental error as alkali content changes, see Figure 4. This is also in disagreement with the results obtained by Zhong & Bray who observed in mixed alkali borates lower values for the N_4 amounts than either of the individual alkali borate glasses.⁽²⁾

High field NMR measurements (14.1 T at Stanford University) of caesium borate glasses were performed and compared with previous values obtained for lithium borate glasses. Because of the high magnetic field used, we are able to obtain very accurate values for N_4 values of the caesium samples. These fractions were then compared with previous NMR studies of lithium borate glasses⁽²⁾ done using wide line NMR and computerised area comparisons. The two caesium

samples had N_4 values of 0.32 ± 0.01 and 0.40 ± 0.01 for $R=0.30$ and 0.475 , respectively whereas the lithium N_4 values, found from least squares analyses of a raft of lithium glasses were 0.30 ± 0.03 and 0.41 ± 0.03 for the same compositions.⁽²⁾ Close agreement was found again for these cases where the Zhong & Bray results indicated a difference of about 0.06 and 0.11, respectively.⁽³⁾ Additionally the present caesium results are in excellent agreement with a study of a large number of caesium borate glasses recently reported by Berryman *et al.*⁽⁷⁾

Conclusions

We have not seen any substantial change in the fraction of four-coordinated boron atoms, N_4 , in a series of alkali borate and mixed alkali borate glasses by the change of modifying alkali cation. In three separate projects the NMR results agree that N_4 changes only with the amount of alkali modifier and not with the actual alkali used.

Acknowledgments

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