

STRUCTURAL STUDIES OF SOLUTION-MADE HIGH ALKALI CONTENT BORATE GLASSES

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The glass forming range of alkali borates has been extended to $R=5.0$ (83 molar percent alkali oxide) using a solution method. This method involves the reaction between solutions of boric acid (H_3BO_3) and alkali hydroxide (MOH). Physical properties and NMR studies were performed on the intermediate and final glass products of this method. We have obtained results for the entire alkali borate system including lithium, sodium, potassium, rubidium and cesium. The structure of these invert glasses remain enigmatic.

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I. Introduction

Alkali borate glasses $[R(M_2O).B_2O_3]$, where M is the alkali metal] are generally made by fusing alkali carbonates and boric acid or boron oxide. The glass formation ranges of these glasses have been determined, even though the alkali content in the glass was limited due to carbon dioxide retention [1]. Using a newer solution method[2], we made glasses in the alkali borate system with R-values ranging from 0.2 to 5.0 and we determined their molar volumes and glass transition temperatures (T_g). In addition, we performed ^{11}B MAS NMR on samples of very high alkali concentrations.

This is an extension and completion of the study of potassium borates by Moeller *et al.*[3]. In the present study we extended the solution method to encompass all alkali borates

This solution method is not the first attempt to bypass carbon dioxide retention in alkali borate glasses. Royle *et al.*[4] prepared alkali borate glasses using alkali oxides which allowed formation of alkali borate glasses to higher R values than previously achieved using alkali carbonates. Royle made alkali borates up to about $R = 3.8$. However, this method was cumbersome as the starting materials were hygroscopic and the glass samples needed to be prepared under an inert environment. Another problem that they encountered was the loss of 10-15% of the initial alkali content when heated to 1000°C before quenching. Finally, not all the oxides were readily available. The solution method, on the other hand, needs an inert environment only in the last heating before quenching. This method is a successor method to the preparation of high alkali content borate glasses that uses alkali hydroxides instead of alkali oxides.

II. Experimental Procedure

The starting materials for $R(M_2O).B_2O_3$ are H_3BO_3 (ACS reagent, 99.5%+, Aldrich) and MOH (50% solution, Aldrich). While making the H_3BO_3 solution (1g H_3BO_3 /100g water), it was heated for 15 minutes during solution stirring as this facilitated quicker dissolving. After mixing the boric acid solution with alkali hydroxide in a Teflon beaker, we dried the solution at 130 °C for periods ranging from a day to a week. The high alkali content borate precipitate generally took 4-5 days to dry. A slight deviation in procedure occurred in lithium borates because LiOH (98%+ powder, Aldrich) is only available in powder and has to be made into a solution to be used efficiently.

The validity of this method was verified by producing low alkali content borate glasses to compare their properties against glasses produced using the conventional alkali carbonates and traditional melts. The low alkali content borate glasses were made in platinum crucibles by heating the precipitates two or three times in an electric muffle furnace at 1000 °C for 15 minutes. These melts were then plate quenched to form bulk, clear, colorless glass. Physical properties of these glasses were comparable to literature data.

Using earlier procedures for the preparation of glasses using alkali oxides[3], glasses of $R > 1.0$ were made in vitreous carbon crucibles as the sample started reacting noticeably with the platinum crucible. We used about 10-12 g of precipitate to yield sufficient glass for physical characterization tests. For cesium, potassium and rubidium samples, the first heating was done in air at 650°C for 10 minutes in an electric muffle furnace to remove most of the water from the precipitate. The second and third heatings were done in an inert N_2 environment at 900°C for maximal expulsion of moisture from the sample. These melts were then roller quenched to make bulk, clear, and colorless glass as plate quenching did not offer the rate of cooling needed to make these glasses. Since high alkali content borate glasses were hygroscopic, we performed

several heatings and then observed that most of the water was driven out in the first two heatings at 900°C. The water expulsion in the 3rd and 4th heatings was negligible. Lithium and sodium samples followed a slightly different sequence of heatings. The first heating was done in air at 650°C and the other heating was done at 900°C in an inert N₂ environment for 20 minutes. Since these glasses were easier to make than the heavier alkali borates, the melts were able to be plate quenched up to R = 3.0. The glasses beyond this molar ratio were roller quenched to make samples that contained more glass than crystal. Using the solution method and available means of rapid quenching, the glass formation for alkali borates ended at about R = 5.0.

The densities of the glasses were measured using a Quantachrome Ultrapycnometer 1000 and an analytical balance. Multiple runs were averaged to obtain a reliable density. The sample pycnometer runs were sandwiched between two high purity aluminum runs for calibration purposes. The error is estimated to be ±1%. The T_gs were obtained using a Perkin Elmer Differential Scanning Calorimeter 7 (DSC). The samples were heated at 40°C/min from 50°C to 600°C and the T_g was found using the onset method. The error achieved was ±5°C.

¹¹B MAS NMR spectra were obtained on a Bruker AMX 500 NMR spectrometer operating at 160.465 MHz (11.7 T) or an INova 600 NMR spectrometer operating at 192.558 MHz (14.1 T). Samples were spun in the frequency range 6 to 8.5 KHz. Glass samples were crushed and packed into a rotor. A typical experiment involved excitation of the sample spinning at 8kHz by a 1μs rf pulse which was short enough to excite all ¹¹B nuclei. Signal average of 64 transients collected with a relaxation delay of about 4 s. The time domain signals were Fourier transformed to produce the frequency spectra used in the analysis and paper. ¹¹B chemical shifts are reported relative to a 0.1 m aqueous boric acid. Appropriate corrections for finding the N₄ fraction were made for finite spinning speeds and applied magnetic fields according to the method of Massiot *et al* [5].

III. Results

In this study, we obtained glasses and densities for low R (0.0 ≤ R ≤ 0.5) and high R (2.0 ≤ R ≤ 5.0) alkali borates, from which we determined the molar volume (Figure 1). In addition to density, we also measured glass transition temperatures (T_gs). At low alkali content these measurements provided additional quality checks on the sample concentration. The full set of results may be found in another paper by Banerjee *et al.*[6] that focuses on the physical properties of these glasses.

Figures 2-4 depict ¹¹B MAS NMR results from potassium borates as examples of both the solution method hydrated precursors and the resulting glasses. Figure 5 shows an ¹¹B MAS NMR spectrum from a solution method sodium borate glass with R = 2.5. Table 1 presents the quadrupole, chemical shift, and N₄ results that were obtained from the data.

IV. Discussion

In Figure 1, lithium borate and sodium borate glasses show a monotonic decrease in the molar volume due to the formation of tetrahedral units, which are more compact than three coordinated trigonal planar units until x = 0.5, where x is the molar fraction of alkali oxide in the glass. Beyond x = 0.5, although four-coordinated boron back converts to three-coordinated borate units with one non-bridging oxygen, three-coordinated borate units with two non-bridging oxygens, and three-coordinated borate units with three non-bridging oxygens, there are increasing amounts of lithium and sodium ions in the glass structure per mole, and since these ions are small and interstitial, the molar volume keeps decreasing, but at a lesser rate. However, in cesium, rubidium, and potassium borate glasses, there is an initial nearly constant molar volume in the composition range where tetrahedral boron formation takes place followed by

monotonic increase because the larger size of the ions dominates the molar volume with increase in cesium, rubidium and potassium content.

The ^{11}B MAS NMR spectra from the solution method for high content potassium borate glasses are quite distinctive in some respects, see Figures 2 and 3. The spectra primarily exhibit a powder pattern from trigonal borons with large quadrupole coupling constants (Q_{cc}) and asymmetry parameters (η), see Table 1 [7]. Work by Bray and coworkers demonstrated that such quadrupole parameters are associated with the trigonal borate groups with one or two non-bridging oxygens [8]. Based on the extremely high alkali concentration ($R = 3.0$ and 3.5) it is likely that the unit contains two non-bridging oxygens per boron. However, this still implies that the glasses appear, from the NMR spectra, to be undermodified since the asymmetric trigonal unit with two non-bridging oxygens per boron has a composition of $R = 2$.

Figure 4 shows the spectrum for a representative borate precursor material formed upon drying the reacted solutions; this spectrum corresponds to a potassium borate sample with $R = 3.0$. The trigonal borons have similar quadrupole parameters to the finished glass indicating similar asymmetry in the trigonal unit of both the glass and the precursor material. However, the fraction of four-coordinated borons is 0.38 in the precursor; this is substantially larger compared with the glass ($N_4 = 0.035$), see Table 1. Since this fraction is drastically reduced upon heating to form the glass this implies that water is playing the role of a modifying cation in the solution reacted glass precursor, a role similar to that played by the alkalis at lower alkali content.

Earlier ^{11}B NMR studies of rubidium borate glasses prepared directly from alkali oxide yielded similar quadrupole parameters and N_4 values compared with the present solution made potassium borate glasses [9], see Table 2. This indicates that the rubidium and potassium glasses form a similar glass structure, one composed mainly of trigonal borons with two non-bridging oxygens. Also, the cesium borate glasses prepared from Cs_2O were also examined by ^{11}B NMR and essentially the same NMR results were obtained as for rubidium and potassium [10]. It is perhaps surprising that there is no indication of the fully modified trigonal borons with three non-bridging oxygens in any of these glasses.

Another surprise occurs when Raman spectra were examined from these heavily modified rubidium and cesium glasses [9]. The Raman spectra displayed prominent peaks near 345 cm^{-1} , 376 cm^{-1} , 612 cm^{-1} and $675\text{-}700\text{ cm}^{-1}$. These features are not observed in other borate systems and imply new short-range environments may be present. Kamitsos has hypothesized that such features are consistent with the formation of and symmetry displayed by tetrahedral borons with two non-bridging oxygens. The evidence from NMR, however, does not seem to support this hypothesis as a much smaller Q_{cc} would be expected for borons tetrahedrally bonded. Thus the structure remains enigmatic.

The spectrum from the examined solution-made sodium borate glass with $R = 2.5$ displays primarily the signature of an asymmetric boron with two non-bridging oxygens, see Figure 6 and Table 1. This is entirely consistent with the potassium and rubidium glasses described above although the composition is somewhat lower in alkali. The small fraction of tetrahedral borons (0.02) is consistent with the other systems as well as the lithium system [11] prepared from carbonates at similar compositions; the lithium system is known not to retain significant carbon dioxide below $R = 3$ [1].

V. Conclusion

The formation of alkali borate glasses has been extended to $R=5.0$ (83 mol% alkali oxide) using a solution method employing alkali hydroxides. The densities and T_g s of these glasses were measured.

The solution method is similar to using alkali oxides though the solution method utilizes alkali hydroxides instead. Solutions of alkali hydroxides are easier to use as they are stable in air as opposed to the hygroscopic nature of alkali oxides. Since the methods are similar and produce glasses without CO₂ retention, these data have been compared to draw conclusions about glass structure.

The ¹¹B NMR spectra indicate boron in these high alkali content glasses is primarily three-coordinate with two non-bridging oxygens per boron. The N₄ fraction is approximately zero in all glasses. In contrast the solution method precursor which remains after the solution is reacted and dried contains sizable N₄ fractions near 0.4.

VI. Acknowledgments

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System	R	Qcc (MHz)	η	Isotropic Chemical Shift (ppm)	N_4 (± 0.01)	Tetrahedral Boron Chemical Shift (ppm)
Potassium (glass)	3.0	2.53	0.57	21.0	0.035	1.9
Potassium (glass)	3.5	2.48	0.68	21.4	0.00	----
Potassium (precursor)	3.0	2.4	0.68	18.5	0.38	2.1
Sodium (glass)	2.5	2.57	0.62	21.2	0.02	1.9

Table 1: NMR parameters from representative solution made samples. Qcc, η and isotropic chemical shift values refer to the trigonal boron site.

System	R	R _{eff}	Q _{cc} (MHz)	Average η	N ₄ (± 0.05)
Rubidium (glass)	2.0	1.7	2.36	0.62	0.14
Rubidium (glass)	3.0	2.3	2.40	0.63	0.00
Rubidium (glass)	3.5	2.6	2.40	0.63	0.02
Rubidium (glass)	3.8	2.9	2.44	0.62	0.01

Table 2: ¹¹B NASP NMR data from high alkali content rubidium borate glasses[10]. The best fits were performed using weighted average of sites who weighted average Q_{cc} and η values are reported above.

Molar Volume of Alkali Borates

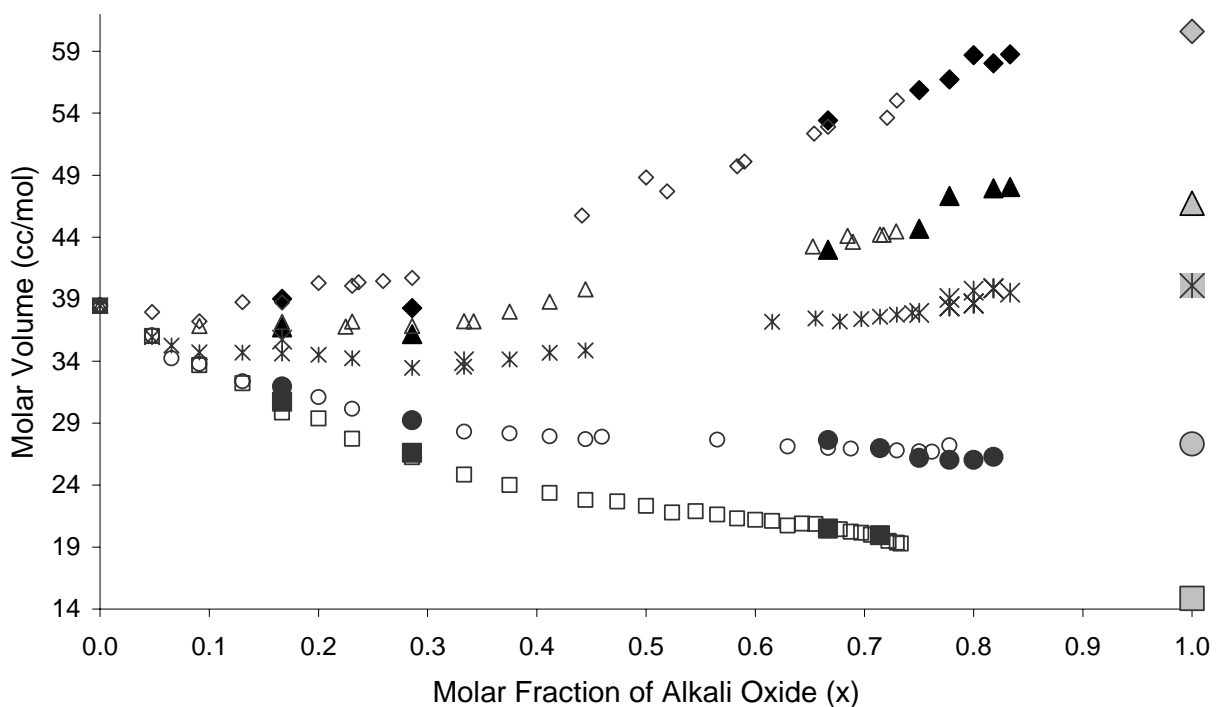


Figure 1: Molar volume of alkali borates in cc/mole given as a function of the molar fraction of alkali oxide (x), where the small open symbols are the alkali carbonate values for the system, and the filled large points are the current solution method experimental data. The ◆'s represent the cesium system, the ▲'s represent the rubidium system, the ✱'s represents the potassium system, the ●'s represents the sodium system, and the ■'s represents the lithium system. Also, the large symbols with gray background at x=1 are values deduced from alkali oxide crystals. The error in the data points are comparable to the size of the data points.

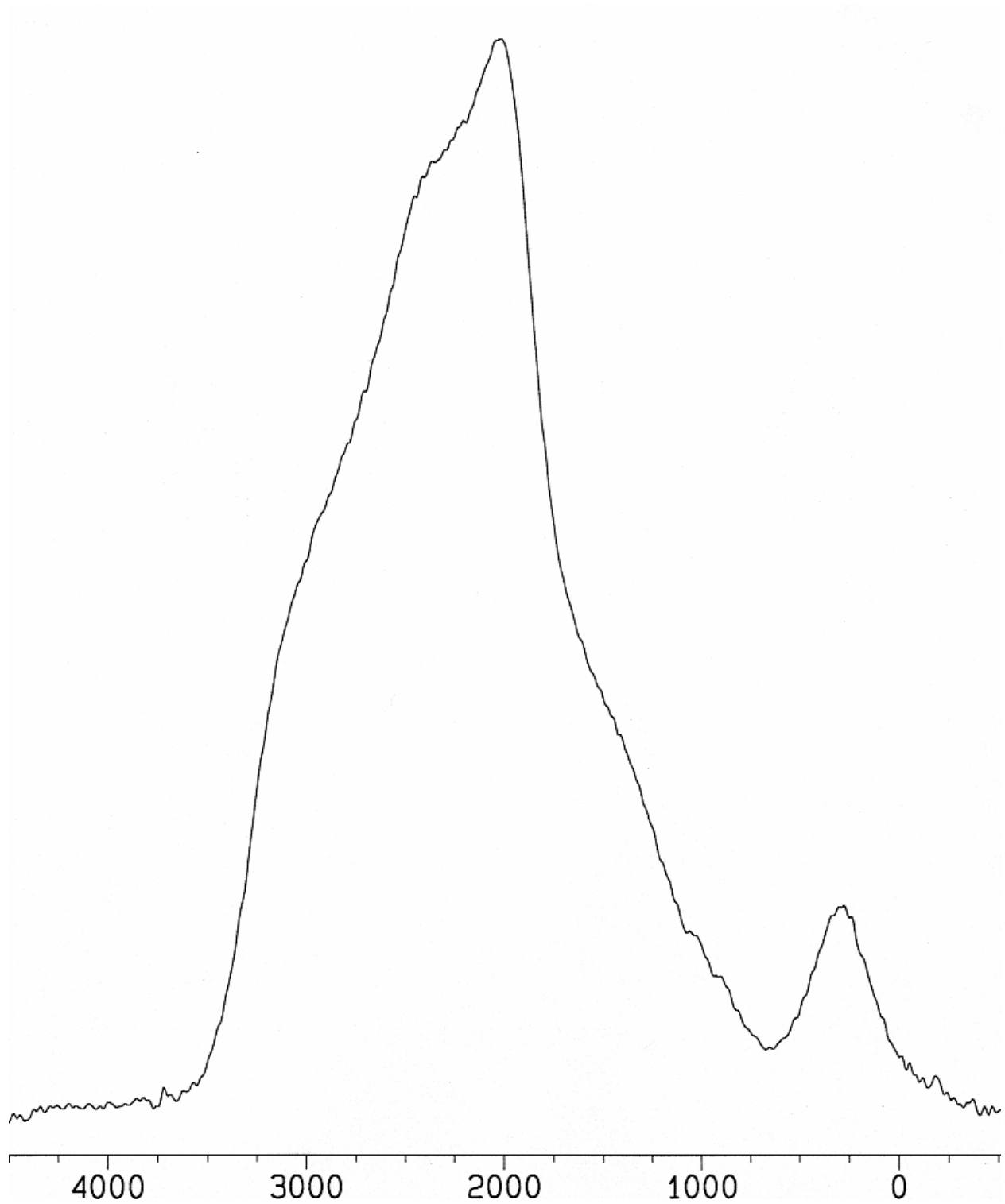


Figure 2

Figure 2: ^{11}B MAS NMR spectrum for R = 3.0 potassium borate glass prepared by the solution method.

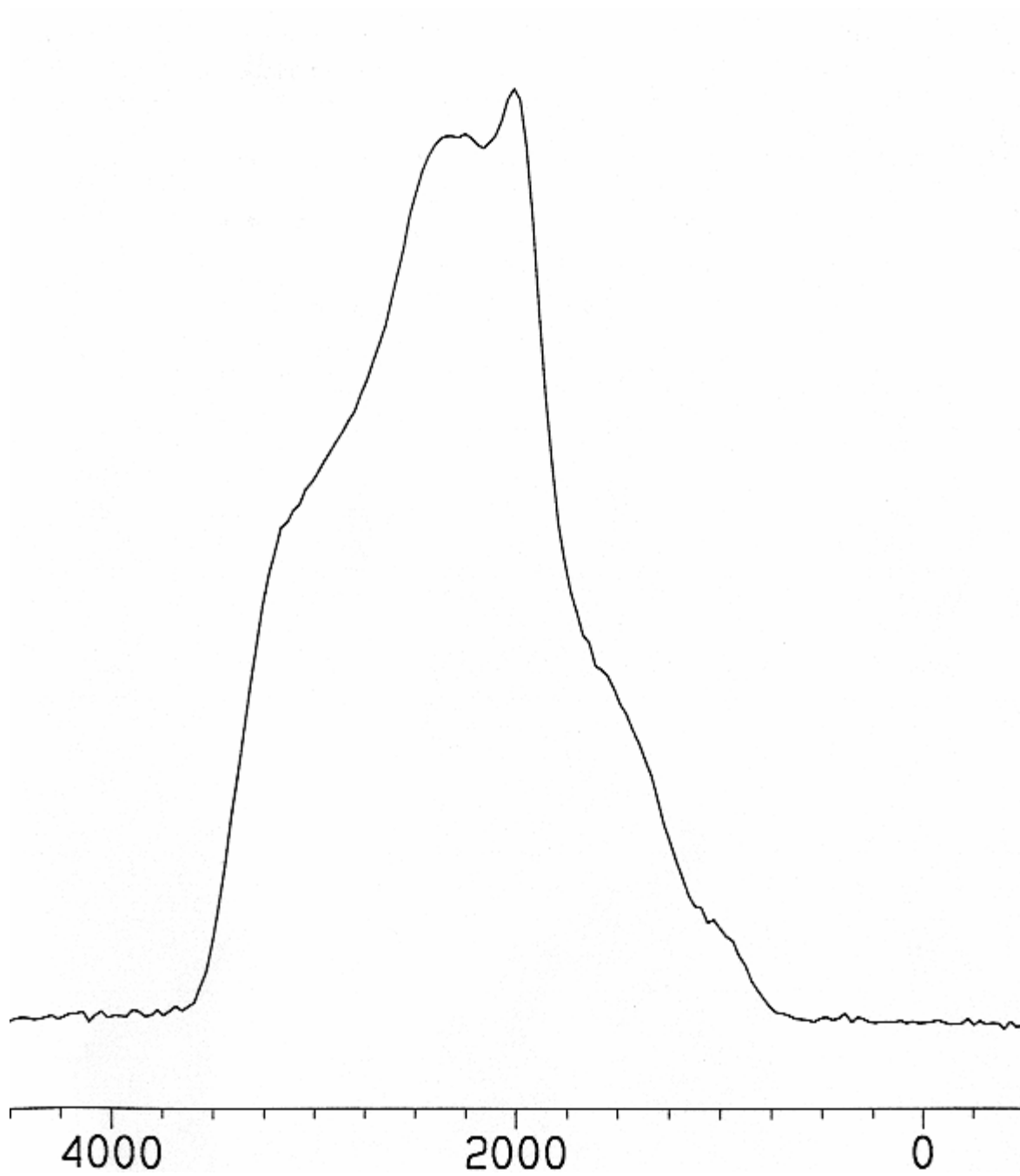


Figure 3

Figure 3: ^{11}B MAS NMR spectrum for R = 3.5 potassium borate glass prepared by the solution method.

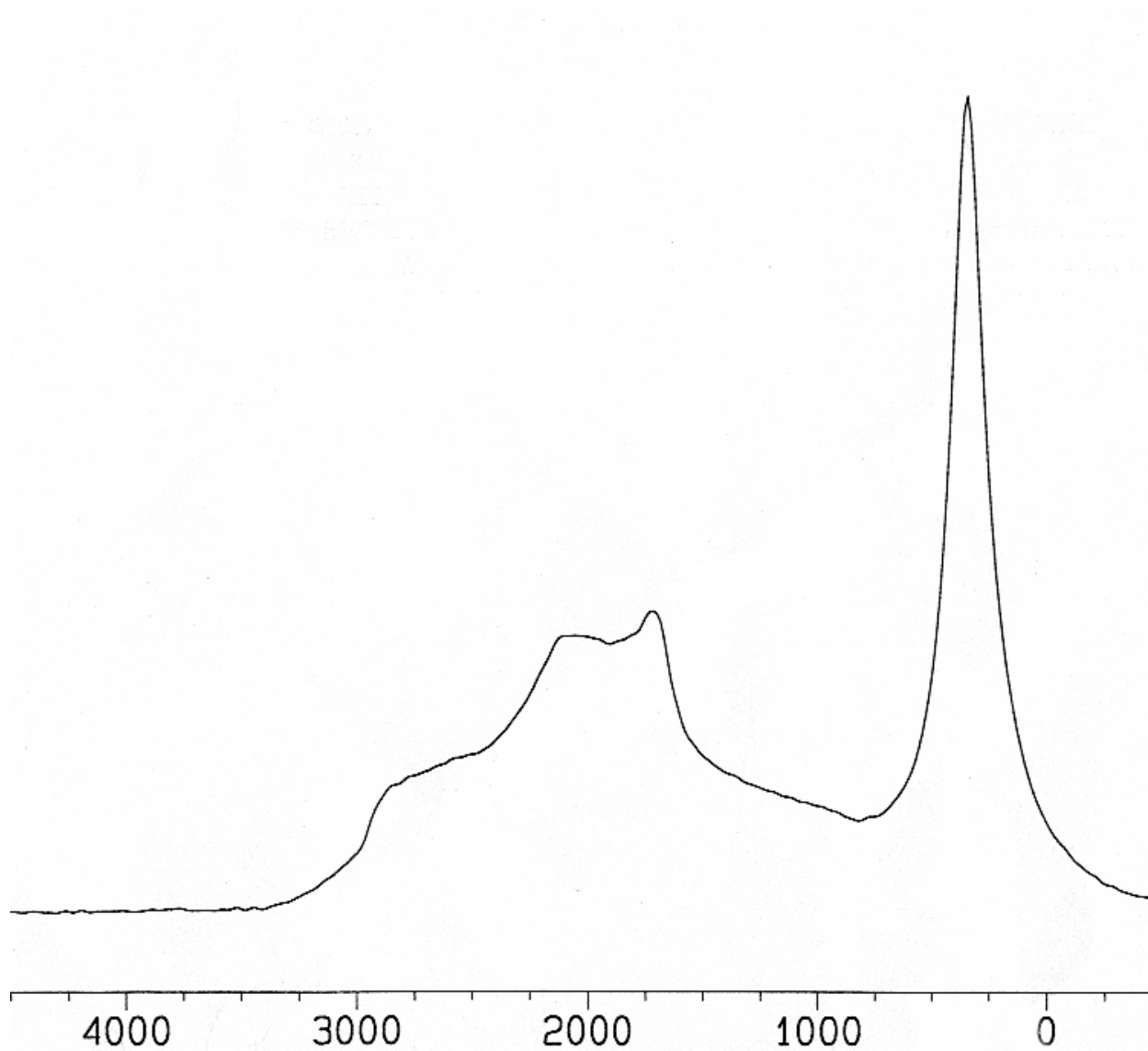


Figure 4

Figure 4: ^{11}B MAS NMR spectrum for R = 3.0 potassium borate precursor from the solution method.

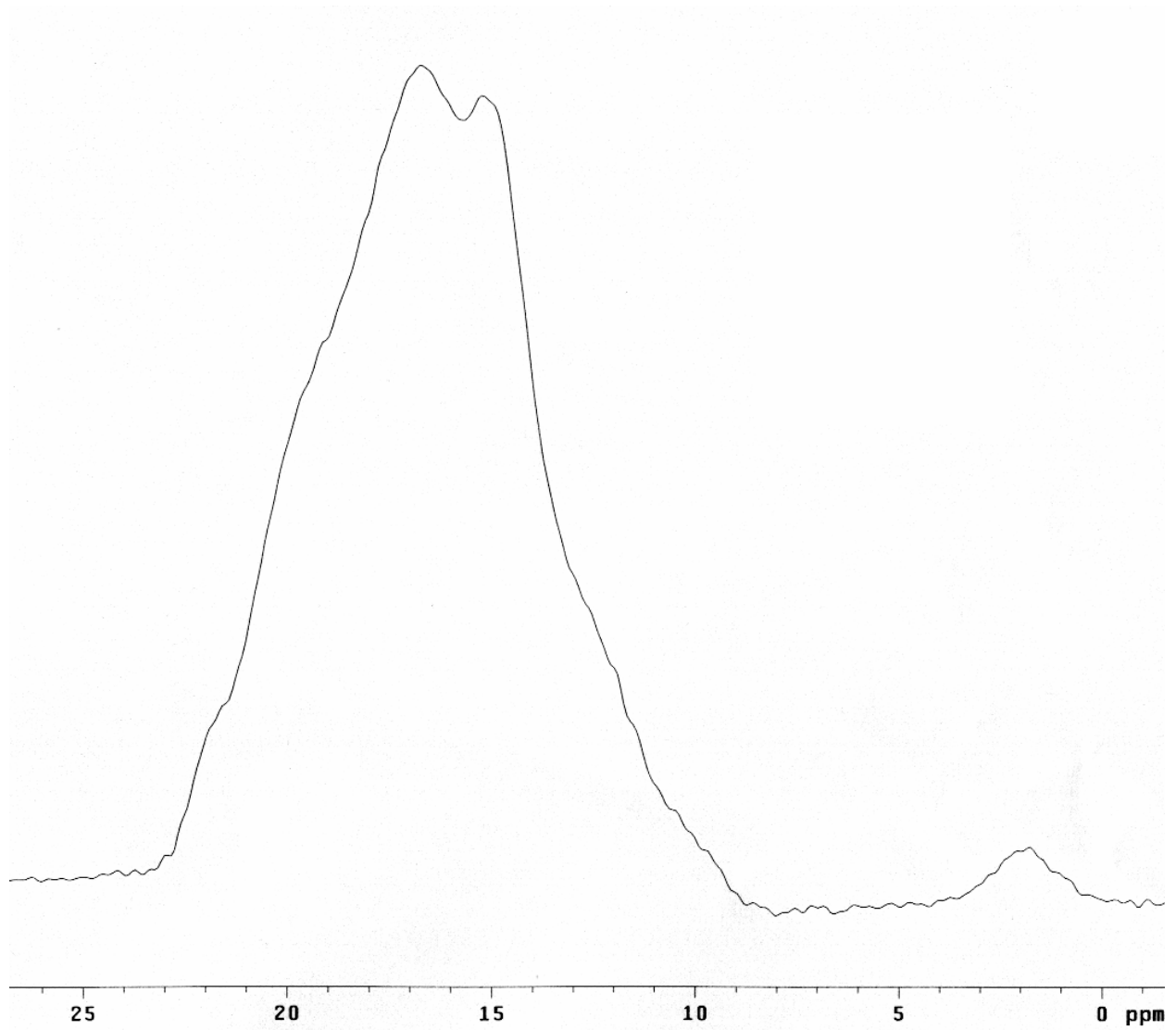


Figure 5

Figure 5: ^{11}B MAS NMR spectrum for R = 2.5 sodium borate glass from the solution method.

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