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# Structural Studies of Solution- Made High Alkali Content Borate Glasses

**Joy Banerjee, Greg Ongie, Jacob Harder, Trenton Edwards, Chris Larson,  
Scott Sutton, Anthony Moeller, Abhirup Basu, Mario Affatigato,  
Steve Feller**

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

**Masao Kodama**

*Department of Applied Chemistry, Sojo University, 4-22-1 Ikeda,  
Kumamoto, 860-0082, Japan*

**Scott Kroeker**

*Department of Chemistry, University of Manitoba, Winnipeg, MB, Canada R3T  
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# Abstract

*The glass forming range of alkali borates has been extended to  $R=5.0$  (83 molar percent alkali oxide) using the solution method devised by Kodama. 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 the glass remains enigmatic.*

# 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. Using the solution method, we made glasses in the alkali borate system with R-values ranging up to 5.0, where R is the molar ratio of alkali oxide to boron oxide in the glass, and we determined their densities and glass transition temperatures. Molar volumes and packing fractions of these glasses were then ascertained using the density data and ionic radii.  $^{11}\text{B}$  MAS NMR studies were also carried out on the samples. This is a continuation and completion of the study of potassium borates by Moeller *et al.*

# Introduction continued

The solution method is not the first attempt to bypass carbon dioxide retention in alkali borate glasses. Royle *et al.* prepared alkali borate glasses using alkali oxides which allowed for extension of the composition of alkali borate glasses beyond those previously achieved using alkali carbonates. Royle made alkali borates up to  $R=3.8$ . However, this method was cumbersome as the starting materials were very 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. These advantages of using alkali hydroxides instead of alkali oxides makes the solution method is an ideal successor to the preparation of high alkali content borate glasses.

# The Basics

In this method, **alkali hydroxide** is used to introduce alkali oxide into the glass. This reduces the amount of CO<sub>2</sub> retention in the glass which makes it easier to make glass.

**Teflon beakers** are used instead of glass beakers to dry the solutions because the precipitates stick to the glass surface and are tough to extract.

**Vitreous carbon crucibles** are used for higher end alkali borate glasses ( $R > 1$ ) because the alkali metal reacts with the platinum crucibles. They have a maximum service temperature of  $\sim 3000^{\circ}\text{C}$ .

Since high R-value glasses are extremely hygroscopic, the glasses are made in an **N<sub>2</sub>-environment glove box** to prevent contact of the glass with moisture and CO<sub>2</sub> in the air.

# Making the Solution and Precipitate



where M is the alkali metal and  $a > n$

1. The process is started by mixing boric acid in Nanopure<sup>®</sup> distilled water for 15 minutes in a glass beaker using a magnetic stirrer while heating. The amount of boric acid used depends on the R-value of the glass.
2. The required amount of alkali hydroxide is measured into a Teflon beaker. In most of the compositions, 20 g of the alkali hydroxide produces about 10 g of precipitate.
3. The boric acid solution is then poured into the Teflon beaker which contains the alkali hydroxide and is mixed with a magnetic stirrer again for 15 minutes.
4. The beaker is then covered with a watch glass and put into the drying oven which is preset at  $\sim 130^\circ\text{C}$ . The waiting period for the dried precipitate varies from one day to one week. The precipitates for the high R alkali borates take the most time to dry.
5. The dried precipitate is placed in a bottle and parafilmed.

# Making the Glass

1. We begin by weighing the amount of precipitate needed for a good glass yield in a carbon crucible. This typically ranges from 10 to 12 g.
2. The sample is heated in a furnace in air set at 650°C for 10 minutes. This heating is used to drive off excess water from the sample.
3. The sample is heated again in an electric muffle furnace at 900°C for 10 minutes. The furnace is located in a N<sub>2</sub>-glove box. After removing the crucible from the furnace, it is placed in a small jar, parafilm and transported to the balance and weighed. This produces the second weight loss.
4. After reheating the sample in the 900°C furnace in a N<sub>2</sub>-glove box for 10 minutes, the melt is roller quenched or plate quenched in the glove box. The glass is then placed in pans for T<sub>g</sub> analysis using a Perkin Elmer DSC 7 or canister for density measurement using a Quantachrome pycnometer.

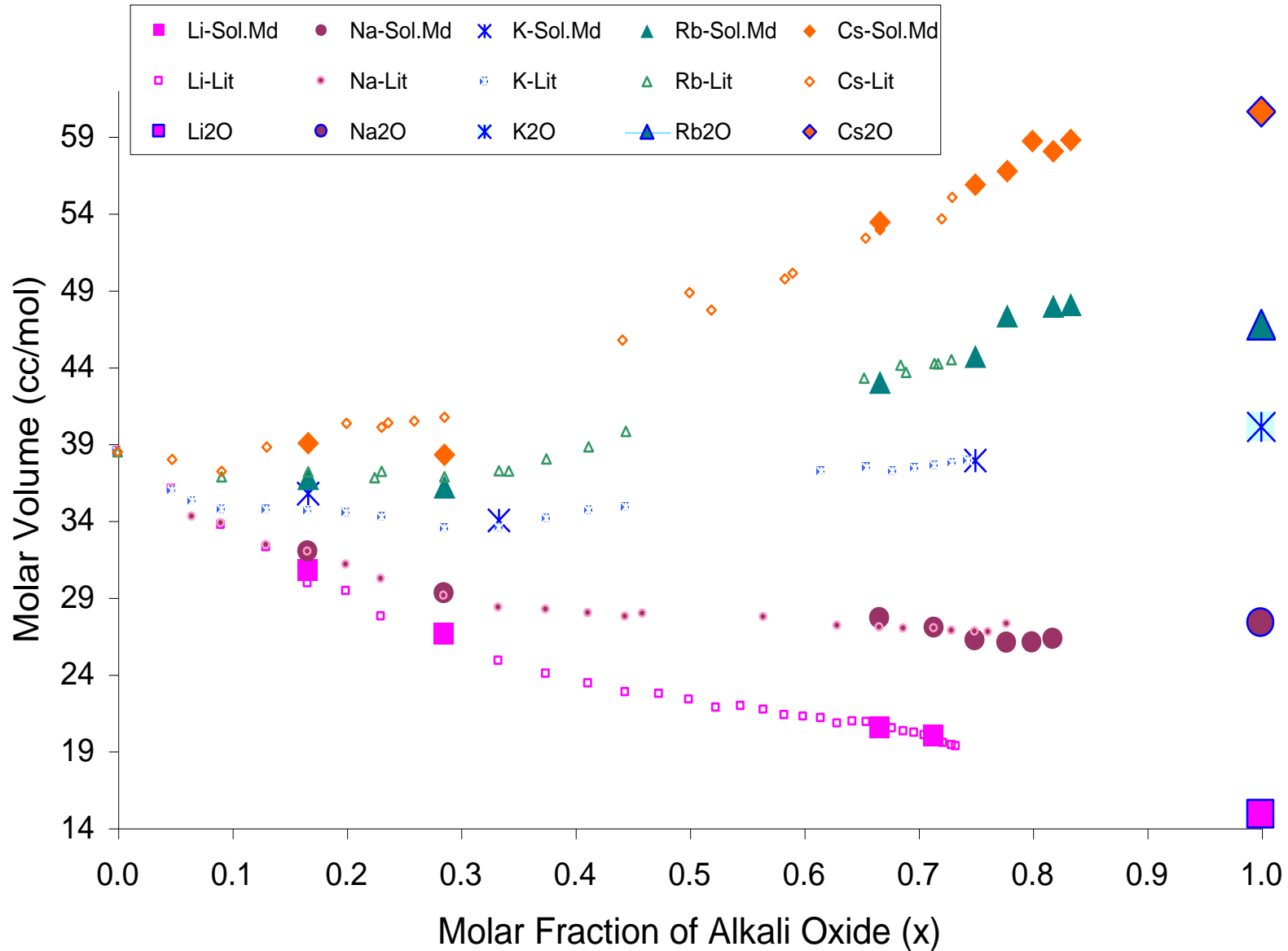
# NMR Procedure

$^{11}\text{B}$  MAS NMR spectra were obtained on a Bruker AMX 500 MAS-NMR spectrometer operating at 160.465 MHz (11.7 T) or an INova operating at 192.558 MHz (14.1 T). Samples were spun in the frequency range 6 to 8.5 KHz.



# Results

## Molar Volume of Alkali Borates



Another indicator of structural information is the packing fraction, defined as the volume of the ions present divided by the total volume of the glass, including empty space. The packing fraction,  $p$ , is calculated using:

$$p = \text{density} * \sum \frac{\left(\frac{4}{3} \pi r_i^3 n_i\right)}{\text{MolWt}}, \quad (2)$$

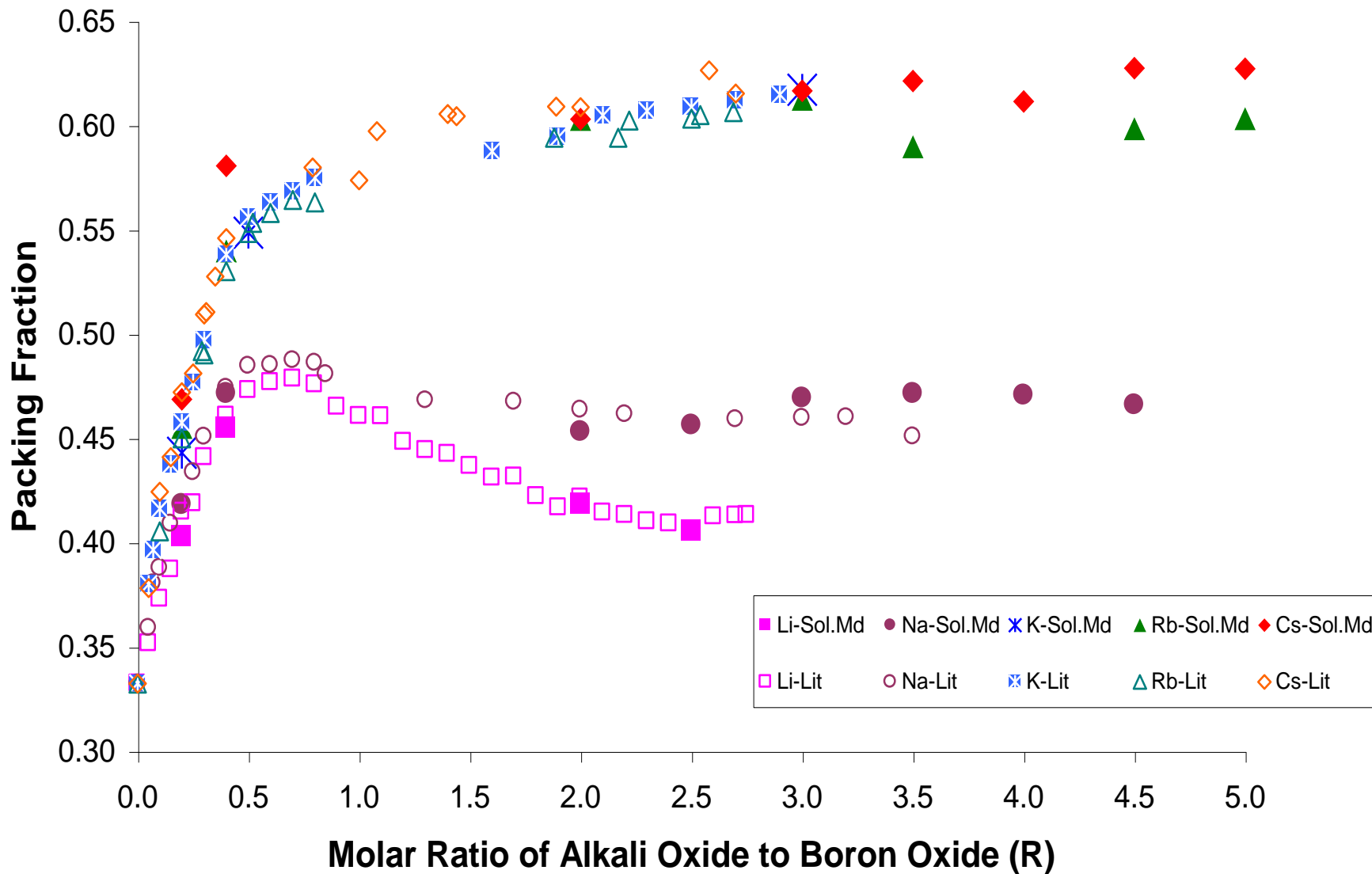
where  $r_i$  is the radius of the  $i^{\text{th}}$  ion, and  $n_i$  is the amount of that ion present in the structural formula. In our calculations, Shannon radii were used for the alkali ions, while all other radii were obtained from x-ray and neutron scattering results.

The ionic packing dominated by alkali ions have a much higher packing fraction than the covalent packing oxygen network, approaching the packing of random spheres ( $\approx 64\%$ ). In the region,  $0 \leq R \leq 0.4$ , each packing trend shows a sharp increase as the triangular planar  $f_1$  units convert into compact tetrahedral  $f_2$  units.

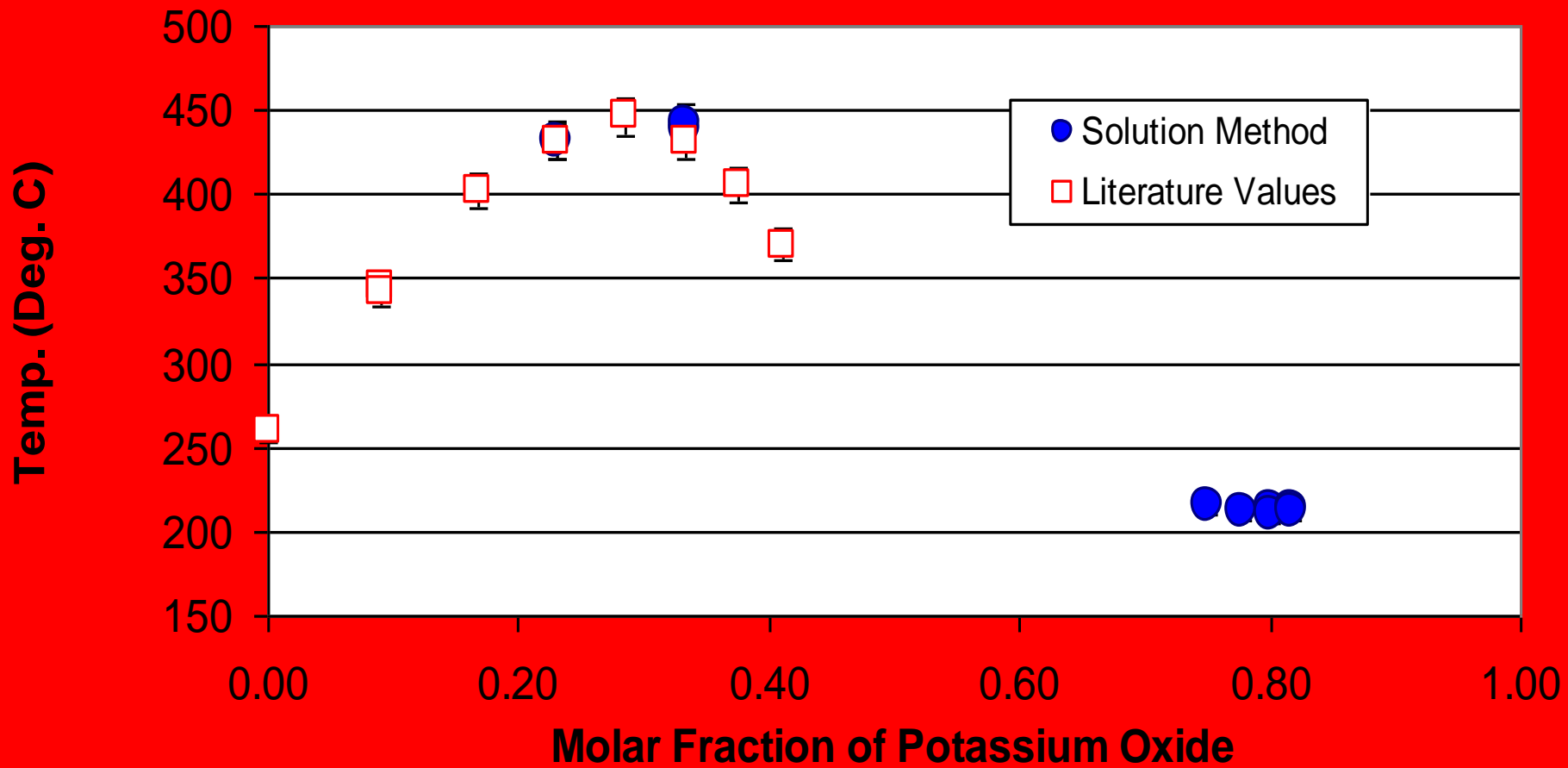
Following this region, the packing divides into the two kinds of packing given above. Cesium, rubidium, and potassium borates, having alkali with Shannon radii larger than the oxygen radius, pack ionically; sodium and lithium borates, having alkali with Shannon radii smaller than the oxygen radius, pack covalently.

# Results - II

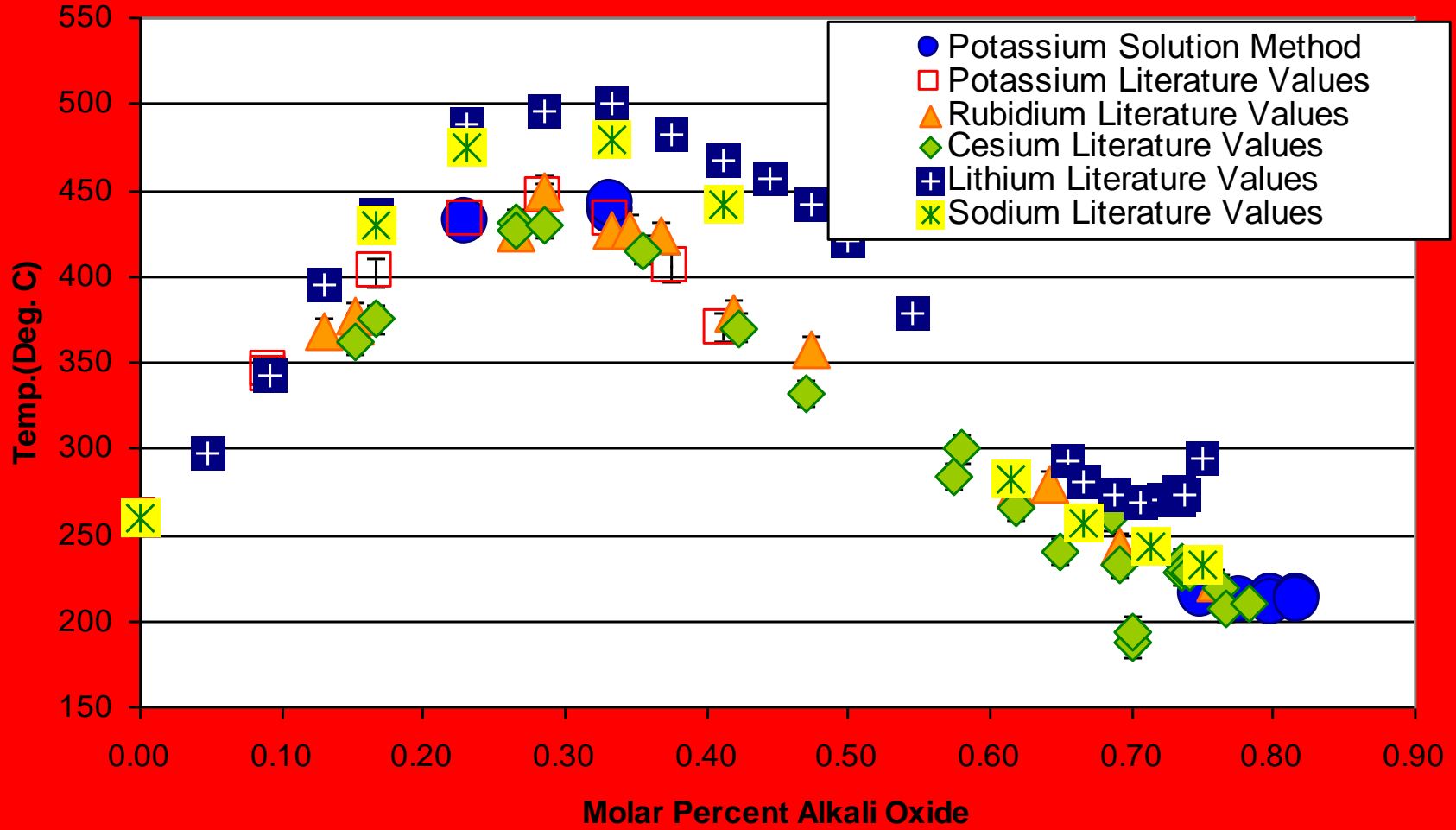
## Packing Fractions of Alkali Borates



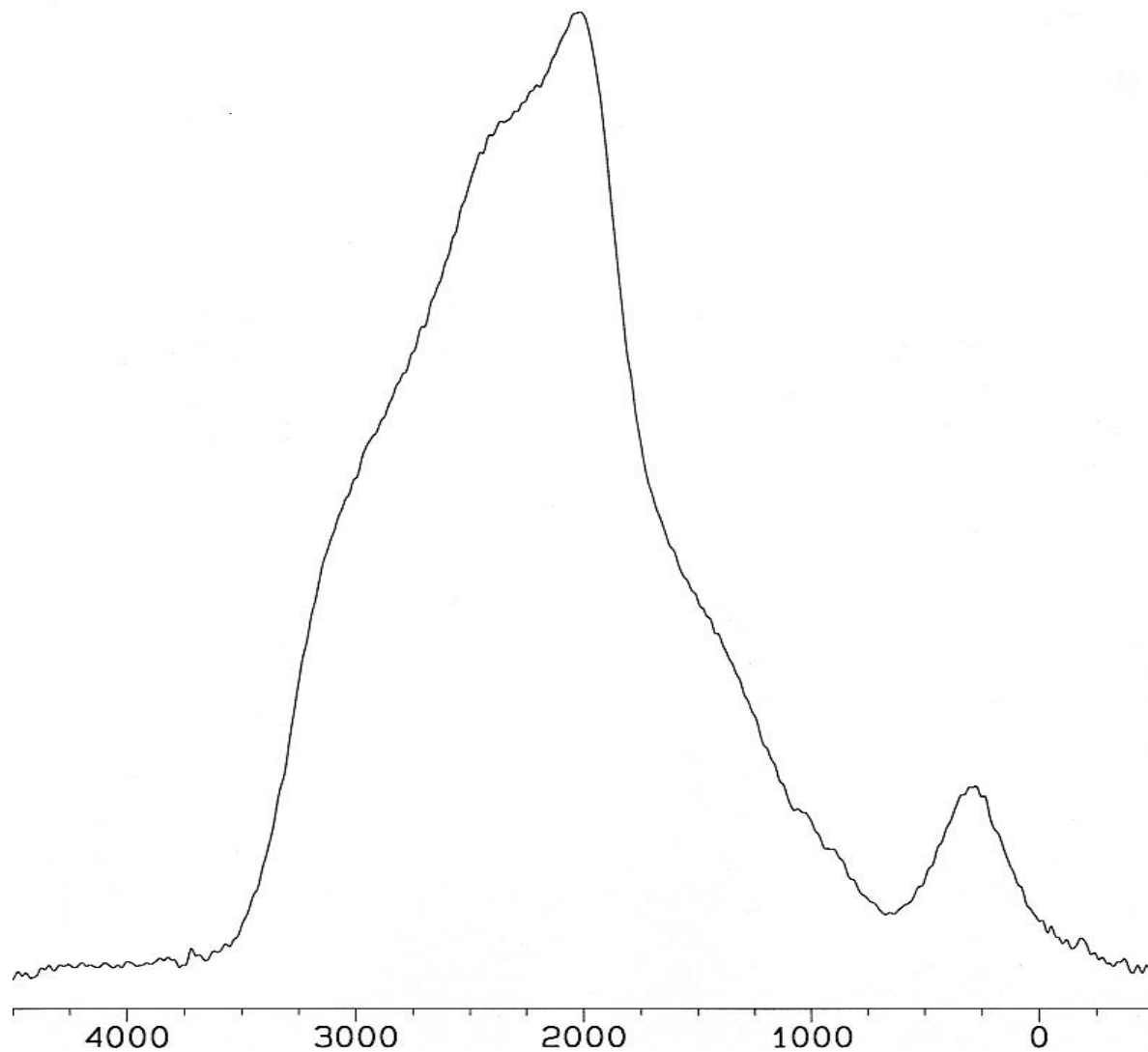
## Tg of Potassium Borates



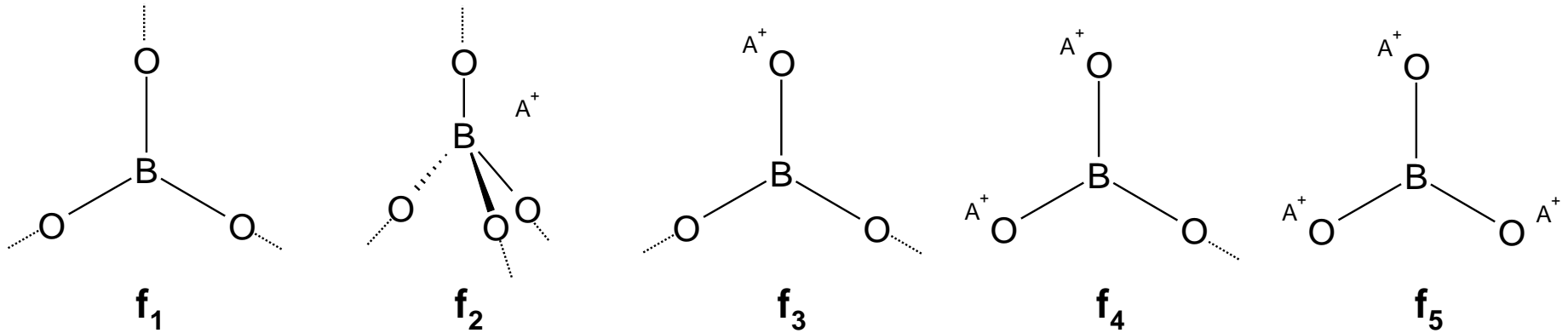
### Alkali Borate Tg



# Potassium Borate, $R = 3.0$



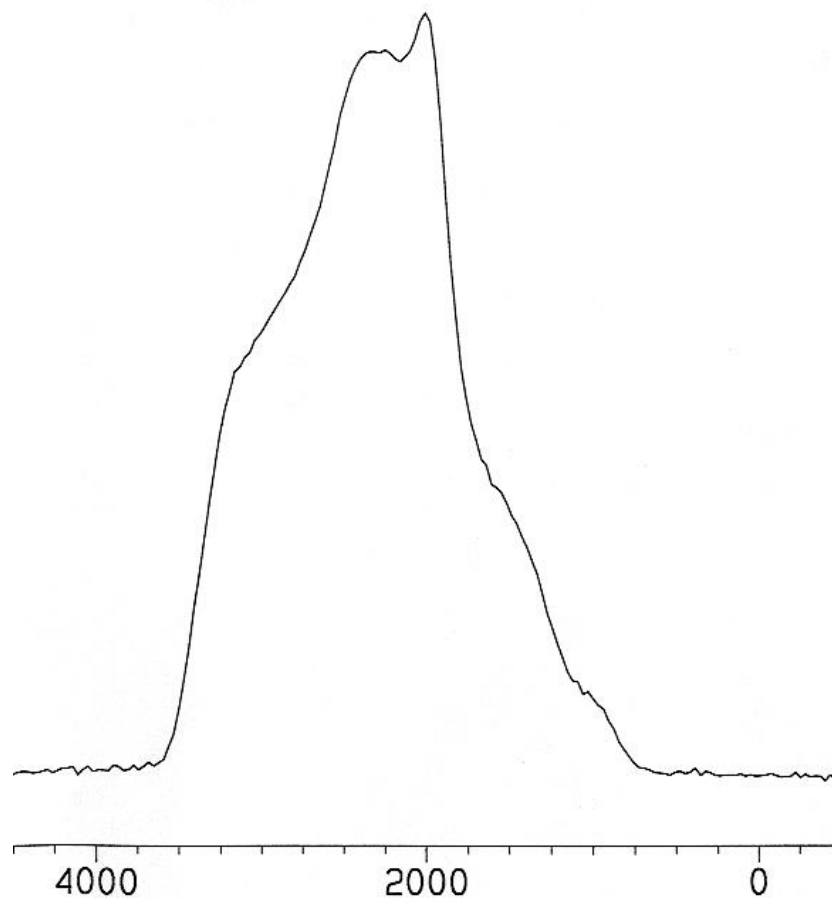
# Structures of Borate Units



$A^+$  - Alkali ion

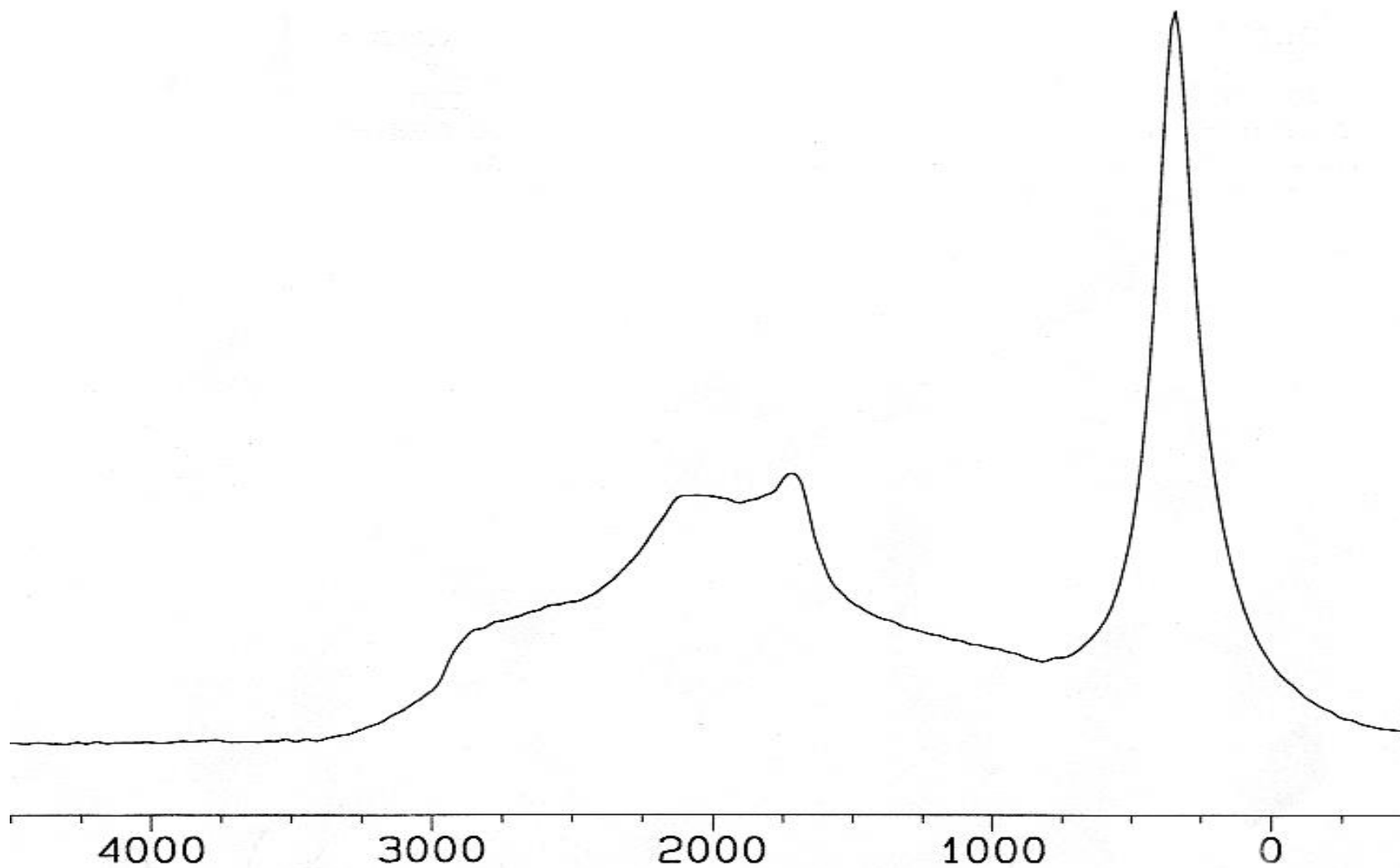
- $f_1$  – three coordinated trigonal planar borate unit with three bridging oxygens
- $f_2$  - four coordinated tetrahedral borate unit with four bridging oxygens
- $f_3$  - three coordinated trigonal planar borate unit with one non-bridging oxygen
- $f_4$  - three coordinated trigonal planar borate unit with two non-bridging oxygens
- $f_5$  - three coordinated trigonal planar borate unit with three non-bridging oxygens

# Potassium Borate, $R = 3.5$

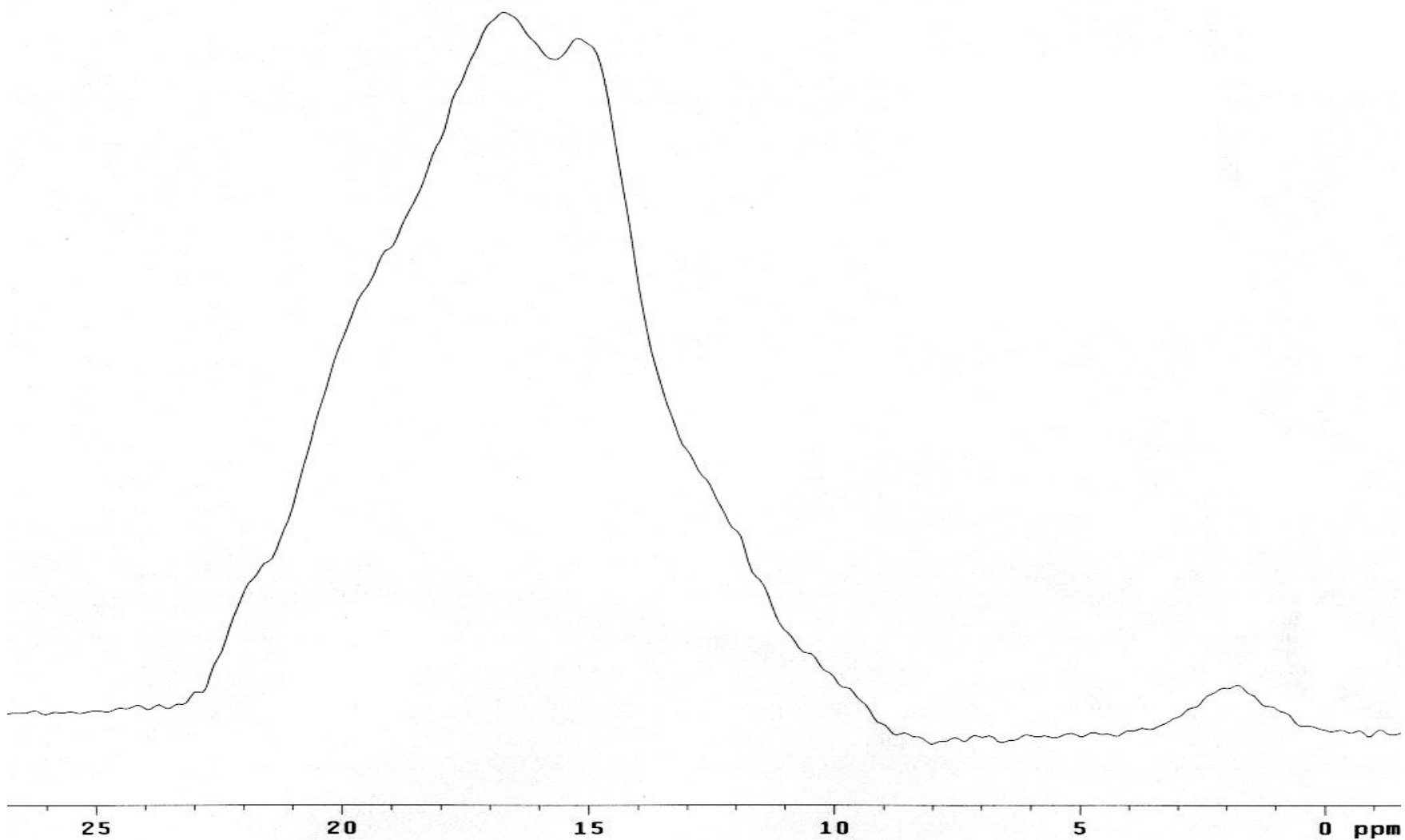




# Potassium Borate Precursor, R = 3.0



# Sodium Borate, $R = 2.5$



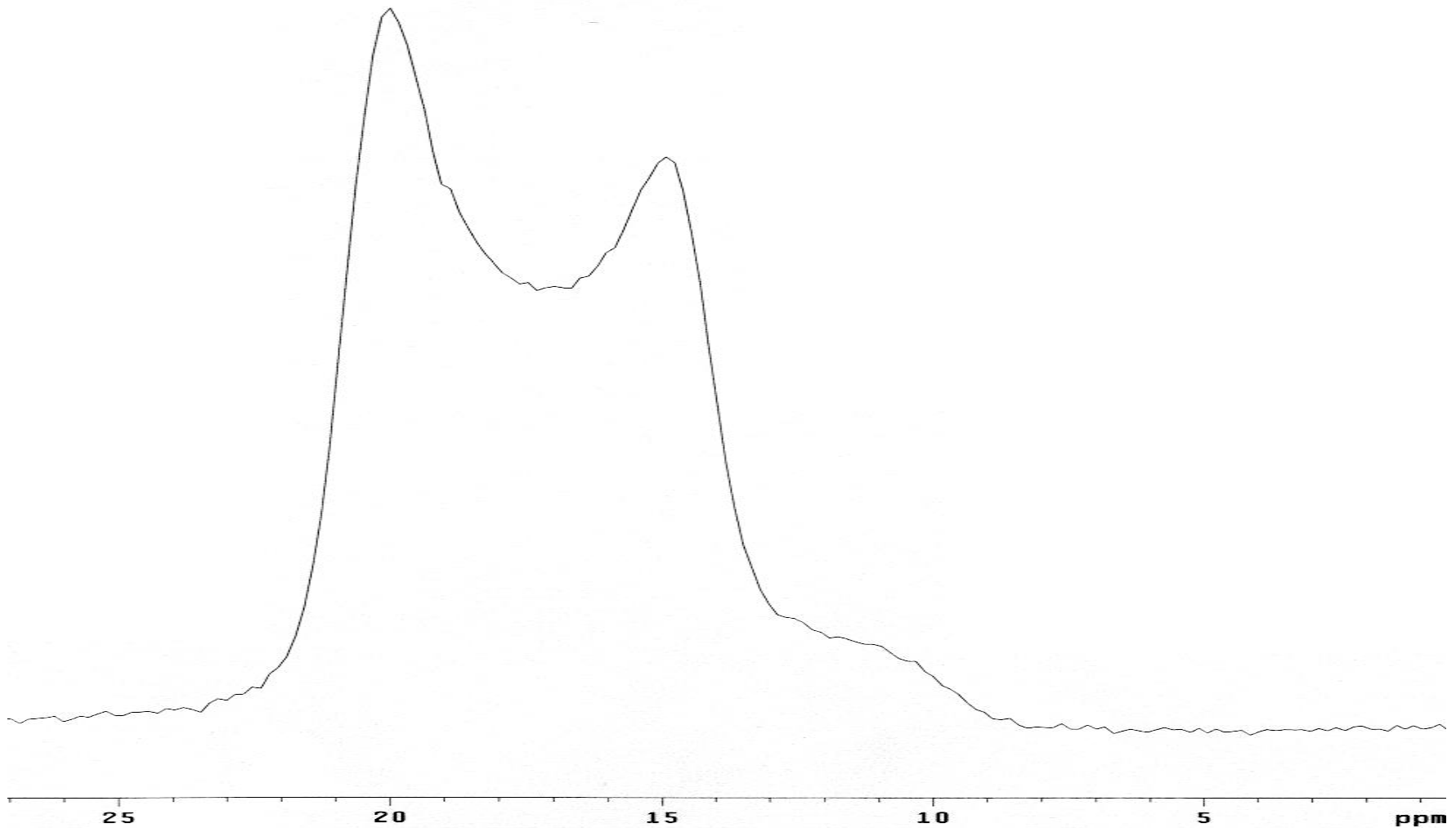
# NMR fit parameters for Solution-based Glasses

<b>System</b>	<b>R</b>	<b>Q<sub>cc</sub> (MHz)</b>	<b>η</b>	<b>Isotropic Chemical Shift (ppm)</b>	<b>N<sub>4</sub> (± 0.01)</b>	<b>Tetrahedral Boron Chemical Shift (ppm)</b>
<b>Potassium (glass)</b>	<b>3.0</b>	<b>2.53</b>	<b>0.57</b>	<b>21.0</b>	<b>0.035</b>	<b>1.9</b>
<b>Potassium (glass)</b>	<b>3.5</b>	<b>2.48</b>	<b>0.68</b>	<b>21.4</b>	<b>0.00</b>	<b>----</b>
<b>Potassium (precursor)</b>	<b>3.0</b>	<b>2.4</b>	<b>0.68</b>	<b>18.5</b>	<b>0.38</b>	<b>2.1</b>
<b>Sodium (glass)</b>	<b>2.5</b>	<b>2.57</b>	<b>0.62</b>	<b>21.2</b>	<b>0.02</b>	<b>1.9</b>

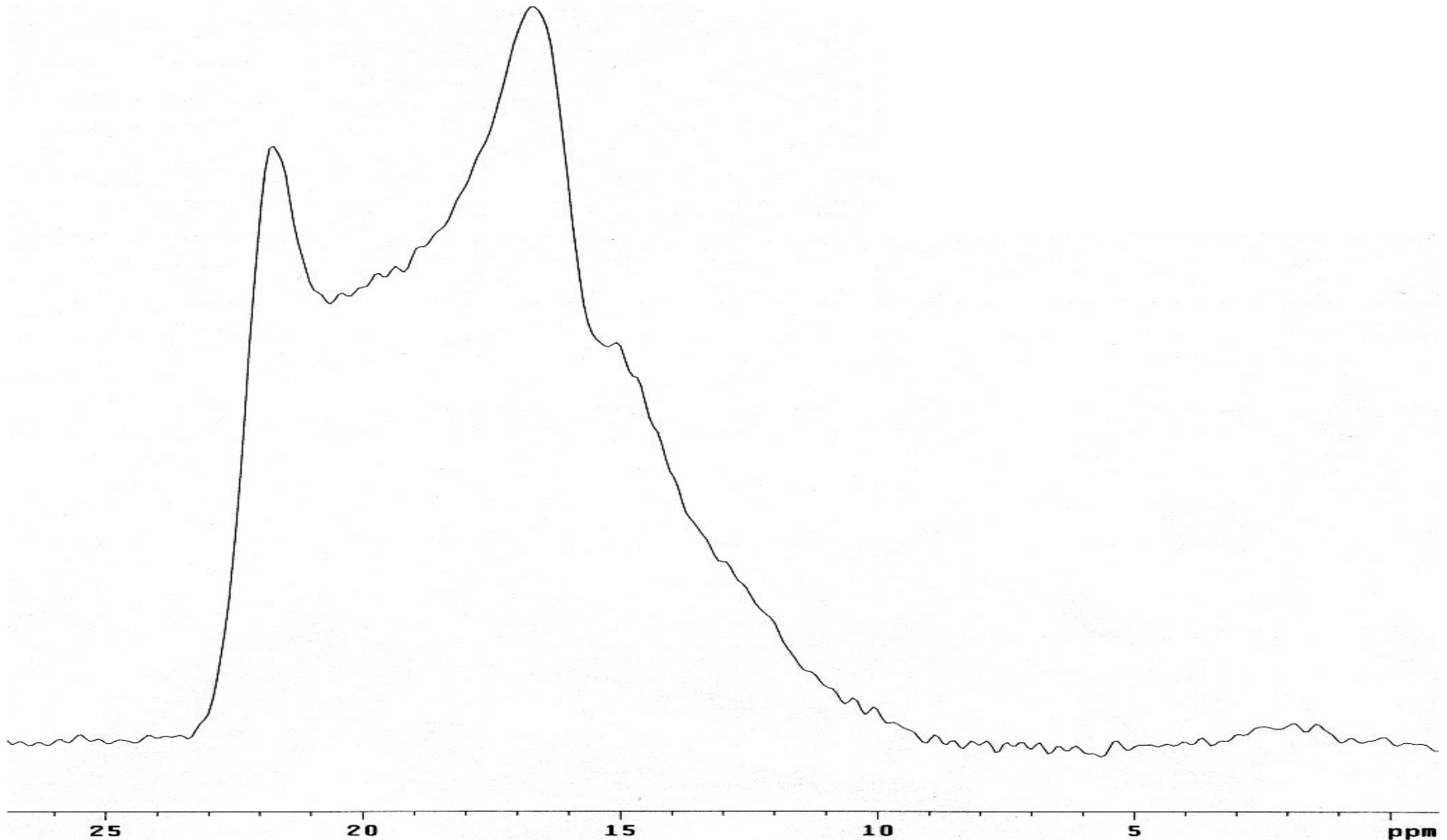
# NMR fit parameters for Oxide-based Glasses

<b>System</b>	<b>R</b>	<b>R<sub>eff</sub></b>	<b>Q<sub>cc</sub> (MHz)</b>	<b>Average <math>\eta</math></b>	<b>N<sub>4</sub> (<math>\pm 0.05</math>)</b>
<b>Rubidium (glass)</b>	<b>2.0</b>	<b>1.7</b>	<b>2.36</b>	<b>0.62</b>	<b>0.14</b>
<b>Rubidium (glass)</b>	<b>3.0</b>	<b>2.3</b>	<b>2.40</b>	<b>0.63</b>	<b>0.00</b>
<b>Rubidium (glass)</b>	<b>3.5</b>	<b>2.6</b>	<b>2.40</b>	<b>0.63</b>	<b>0.02</b>
<b>Rubidium (glass)</b>	<b>3.8</b>	<b>2.9</b>	<b>2.44</b>	<b>0.62</b>	<b>0.01</b>

# Lithium Borate Solution Method, R = 5.0



# Sodium Borate Solution Method Glass, R = 5.0



# Conclusions

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, and molar volumes and packing fractions were deduced from our measurements. The packing fractions of the alkali borates are split into two separate groups based on their bonding, one being an ionically dominated group ( K, Rb, Cs) and other being covalently dominated ( Li, Na). Our experimental data follow literature values.

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  $CO_2$  retention, their data can be compared to draw conclusions about glass structure.

# Acknowledgements

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