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Super Structural Units In Borate Glasses and Crystals

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Abstract

Borate glasses are known for their medium range structure with super structural units containing varying amounts of BO_3 and BO_4 The structure of sodium borate glasses in the system $xNa_2O(1-x)B_2O_3$ has been investigated for x values ranging from 0.05 to 0.33 with the aim of producing quantitative information on the fraction of these units from Raman spectroscopy.

Sodium Borate glasses were made and x-ray diffraction procedures carried out to compare with previous diffraction records to test the phase of the samples. Differential Thermal Analysis was carried out to obtain the crystallisation and glass transition temperatures for each sample.

Using NMR spectroscopy, N4 values were calculated and then compared to those obtained using various methods of calibration of the peak fitted Raman data. A linear relationship was seen between N4 values and the molar ratio of sodium which was also proportional to the intensity of the boroxol ring. Quantitative information could be found about the fraction of various super structural units from the medium range Raman frequencies.

1 Introduction

Borate glasses have generated a lot of interest in the past few years due to their difference in structure when compared to other glasses. Most glasses contain short range order, and crystals have long range order. Borate glasses however appear to have medium range order. This is thought to be due to the formation of super structural units within the glass.

The structure of oxide glasses is commonly explained by the Zachariasen's Random Network Theory. Zachariasen's theory was based on the fact that oxide glasses had similar mechanical properties to those of the crystals with the same composition. This lead to the prediction that the atoms in crystals and glasses were linked together by the same forces.

The Random Network Theory suggests that glasses are made of small structural units. These structural units are randomly linked to each other in a 3-dimensional model. Four rules were suggested by Zachariasen in order for the formation of the random network from an oxide of the form A_mO_n.

1. No oxygen atoms may be linked to no more then two cations$^{(4)}$
2. The cation coordination number is small (i.e. 3 or 4)
3. Oxygen polyhedra do share corners but not edges or faces
4. For 3D Networks at least three corners are shared

The structural units are connected together by oxygen ions which are called Bridging oxygens (BO). When A-O-A bonds are broken, non-bridging oxygens (NBOs) are created. NBO ions are only connected to the glass network at one end and partially have a negative charge. The decrease in connectivity means a larger flexibility of the structure is obtained.

Network formers are oxides capable of glass formation. Network modifiers do not participate in the forming of the network structure. Network modifiers can increase the oxygen coordination of cation A, break A-O-A bonds and create non bridging oxygen atoms, or a combination of both. Many materials are a combination of both network formers and modifiers and the role in which they play in the glasses characteristics depends both the quantity of the material present and the effect that other materials in the glass play.

Borate glass super structural units are thought to be composed of units of either BO_3 or BO_4 either in isolation or as a combination. BO_3 being boron coordinated with 3 oxygen atoms and BO_4 being boron combined with 4 oxygen atoms. The super structural units consist of boroxol, tetraborate, pentaborate groups etc.

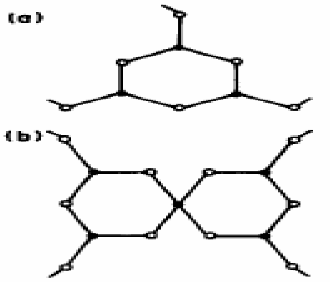

Fig 1.1 Super structural units present in borate glasses (a) Boroxol group (b) Pentaborate group (5)

By adding a modifying oxide to silicate glasses, the number of NBOs increases linearly with the alkali ions added. In the case of borate glasses, adding a modifying oxide to B_2O_3 results mainly in the conversion of B_3 to B_4, as opposed to the formation of NBOs as expected from other glasses. By adding different quantities of a modifying oxide, the glass can show different properties. $xM_2O(1\text{-}x)B_2O_3$ where M is an alkali metal and x is the concentration of the alkali.

Krogh-Moe predicted the important role of super structural units in the borate glasses. These super structural units are specifically arranged combinations of BO_3 and BO_4 units which contain no internal degrees of freedom due to torsion angles and variable bonds. These super structural units are also known to be found in the crystalline polymorphs of those glasses.

Different methods can be used for measuring these super structural units within glasses. Nuclear Magnetic Resonance (NMR) can give quantitative information on the amount of B_3 and B_4 present within the glass. What NMR cannot show is how these B_3 and B_4 units are connected to make the super structural units. Ramen Spectroscopy on the other hand can be used to show the presence of these super structural units in the borate glasses with sharp features in the spectrum seen at 808 and 770cm-1 for the boroxol and triborate rings for example.

NMR can be used to calculate the amounts of 3 and 4 fold coordinated boron. Borate glasses have a large amount of ^{11}B which has a spin quantum number of 3/2. This non-zero spin means that once the ^{11}B is placed into a magnetic field, it can either lineup in the same direction, or can line up in the opposite direction. These spin alignments have different energies. A nucleus with spin in the same direction as the field will have a lower energy then a nucleus with a spin in the opposite direction. When radio-frequency radiation is present, the nucleus will absorb the radiation, and can either flip to the state aligned with the magnetic field, or can flip to the high energy direction. The nucleus can then reemit the radiation back to the lower energy state. The local environment around the nucleus will slightly perturb the local magnetic field exerted on that nucleus and affects its exact transition energy. It is this transition energy (Zeeman transition frequency) that gives information on the amounts of 3 and 4 fold coordinated boron. Using this method the N4 fraction can be measured. The N4 fraction is the amount of 4-coordinated boron divided by the total boron content.

^{11}B has a half-integer spin above 1. Nuclei with half-integer spin above 1 are called quadrupole nuclei due to their electric quadrupole moment which interacts with the electric field gradient (EFG) surrounding it as well as internal and external magnetic fields.

Magic Angle Spinning (MAS) NMR is a NMR technique where the sample is spun at angle of 54.7 degrees. MAS collapses the broad lines seen from an NMR spectrum into a central line close to the isotropic value with rotational sidebands spaced at intervals equal to the spinning frequency.

Raman spectroscopy involves exposing a sample to light. Most of the light is elastically scattered resulting in no change to the energy (frequency) of the light. A small proportion of the light experiences what is known as the Raman Effect. This is when the scattered lights' frequency is lower then that of the light exposed to the sample.

A technique called Differential Thermal Analysis (DTA) can be used to find the temperatures of phase transitions in a substance. It consists of two thermocouples connected to a voltmeter, one for a reference material and one for the sample. The temperature of the system is then increased, but as a substance begins to change phases a voltage is detected. This is because heat input will increase the temperature of the inert substance but be incorporated into the latent heat of the material changing phase. DTA can therefore be used to find the crystallisation temperature.

2 Experimental Details

2.1 Crystal and Glass Preparation

The glasses made were of the form $xNa_2(1-x)B_2O_3$. With reference to the conventional glass-forming regions (1) and the ICDS Crystallography database (2) crystals/glasses were chosen to be made with the following values for x; 0.2, 0.25, 0.33, 0.67. A ceramic was also made from x=0.5

The compounds used to make the crystals were Na_2CO_3 and B_2O_3. For each glass sample made the correct mass of each substance was weighed to that needed for the chosen value of x to make 30g for the total mixture. 0.1 mol% of iron oxide was also added to each mixture. These mixtures were mixed thoroughly for several hours on rollers before individually being placed in platinum crucibles and heating within a furnace with a temperature starting at room temperature and increasing at a rate of 10oC/min up to 1000oC. The crucibles could then be taken out and poured to make glasses on cooling at room temperature.

To make crystals from the glass, thermal analysis was performed on each of the glass samples which all used quartz as the reference material. Thermal events were recorded between 30°C and 900°C with the temperature increasing at a rate of 10°C/min. The results were also recorded from cooling at the same rate. The differential was then plotted against temperature and T_x could be measured from the endothermic and exothermic events (onset method). The value of T_x were accurate to +/- 3 degrees.

Crystals were made from the powders created from the grinding up of the glass with the same value for x. The powders were once again placed into a platinum crucible and into a furnace and heated at 10oC/min temperature up to the T_x found previously.

The attempt to make a glass from the x=0.5 mixture produced a ceramic which was brown in colour. It was also noticed that the glasses had a brown tint to them. This could have been due to the small amount of Iron oxide or possibly due to the platinum crucible. Difficulties were had with the x=0.67 glass sample which was very water sensitive. This created problems when trying to make the glass into a powder for x-ray diffraction analysis. This problem was sorted out by making it into a powder using a pestle and mortar in a argon chamber. The x-ray diffraction powder holders' rim was then covered in superglue. The powder was then placed into the holder and a thin clear piece of plastic places over the top held in place by the glue. This prevented moisture getting to the sample whilst in the machine.

2.2. X-ray diffraction

X-ray diffraction was performed on both the glass and crystal samples. The crystal sample results were then compared to known spectra to check for other potential phases being present. This involved comparing the position and intensity of known with known crystal structures likely to be present. These included all known crystals containing sodium, oxygen and boron.

2.3. NMR measurements

Results were taken by ^{11}B MAS (Magic Angle Spinning) NMR on both the Sodium Borate glasses and crystals with field strength of 14.1T (192.04MHz). The samples were used in powder form and packed into 4mm rotors. The samples spinning rate was set at 15 kHz. A 0.7μs pulse length was used (time of bombardment) with a 1s pulse delay between scans (relaxation time) with 1000 scans recorded.

A Fourier transformation was performed on the data recorded to produce a spectrum in the frequency domain. A peak fitting program was then used to correct the base line for the spectra. The spectra was fitted with two ½ Gaussian, ½ Lorentzian curves for the anti-symmetric and symmetric BO_4 and two quadrapole mass ½ curves for the anti-symmetric and symmetric BO_3. To take account of the spinning side bands which occur from the symmetric three coordinated boron sites, the symmetric three-coordinated boron peak had to be multiplied by 1.04. This results in a slight lowering of the N4 values.

2.4. Raman measurements

Raman spectra were recorded for each glass sample at room temperature on a back scatter set up. A laser with a power of 10mW was used with a magnification of X50. Flat glass samples were used to achieve better results. Raman measurements were also carried out using powdered glass samples for a comparison of the level of background noise with little difference noticed. 30 acquisitions of data were recorded over frequencies 100cm^{-1} to 2000cm^{-1}. Recording the higher frequencies allowed for an easier calculation of the background present

3 Results

3.1 Diffraction

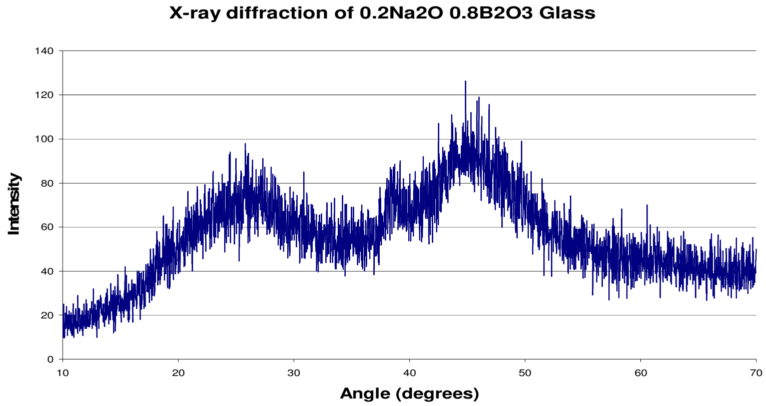

Fig 3.1.1 X-ray diffraction of x=0.2 sodium borate glass

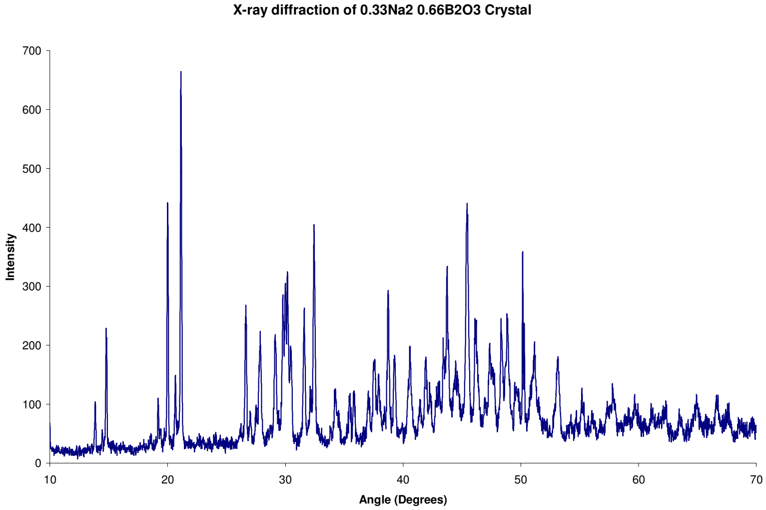

Fig 3.1.2 X-ray diffraction of x=0.33 sodium borate crystal

From the comparison of the X-ray diffraction spectra to those from the database its was concluded that two phases were present in the X=0.33 crystal.. The X=0.33 was matched by both $Na_2O.3B_2O_3$ and $Na_2O.4B_2O_3$ crystals when they were overlapped. This crystal was remade.

Characteristic spectra were achieved for all the glasses. Fig 3.1.1 shows typical glass spectra. Fig 3.1.2 shows the spectra for a sodium borate glass. It has well defined peaks which could easily be used for comparison to known glasses.

3.2 Differential Thermal Analysis

A typical heating and cooling curve from the differential thermal analysis of sodium borate glass is show in figure 3.2.1. The crystallisation temperatures are shown in fig 3.2. The temperatures in the table were used to produce the crystals. For x=0.5 a crystal was not produced but ceramic.

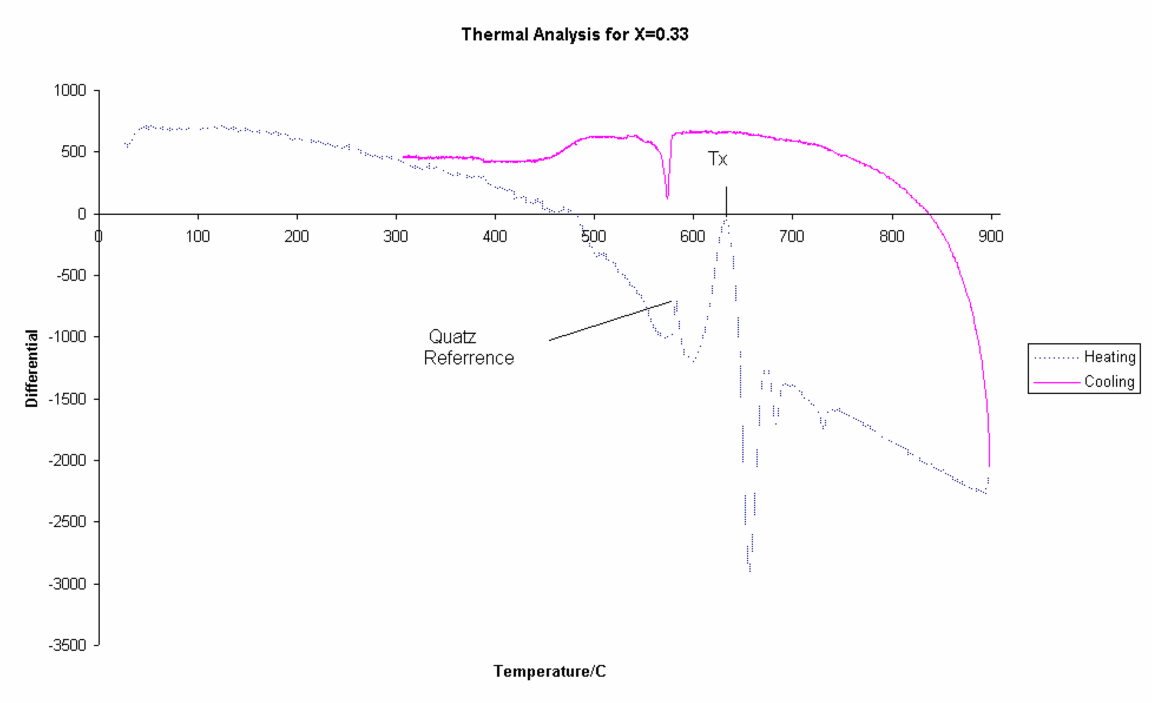

Fig 3.2.1 DTA of x=0.33 sodium borate glass

Fraction of Sodium (X-Value)	Tx Crystallisation Temperatures (oC) +/- 5oC
0.20	635
0.25	642
0.33	632

Table 3.22: Crystallisation temperatures

Fraction of Sodium (X-value)	Tg Glass Transition Temperature (oC)+/- 5oC
0.05	318
0.10	379
0.15	421
0.20	472
0.25	491
0.33	546

Table 3.22 Glass transition temperatures

3.3 Nuclear Magnetic Resonance

The NMR results show two peaks with one peak due to the BO_3 and the other from BO_4. A diagram of a peak fit is show in fig 3.2. Each peak is composed of an anti-symmetric peak and a symmetric peak. The BO_3 peak was fitted with two quadruple mass ½ peaks and the BO_4 with 2 ½ Lorentzian ½ Gaussian peaks. To take account of the spinning side bands which occur from the symmetric three coordinated boron sites, the symmetric three-coordinated boron peak had to be multiplied by 1.04. This results in a slight lowering of the N4 values.

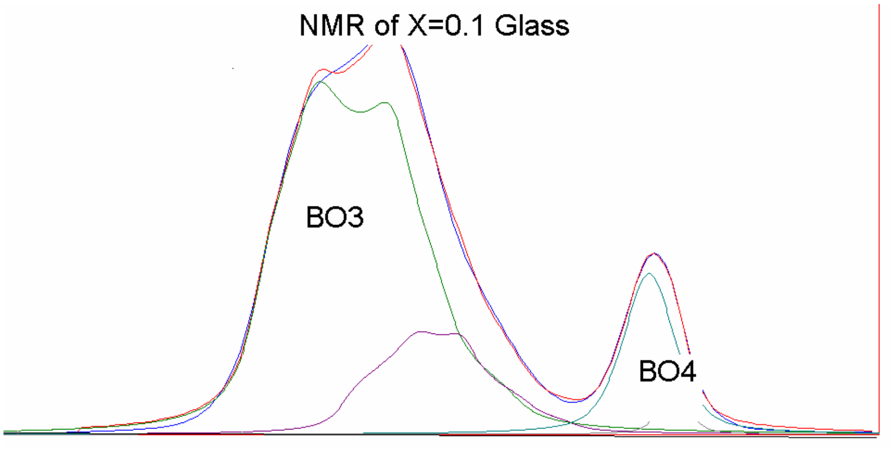

Fig 3.2 Diagram of peak fit for NMR spectra of x=0.1 Sodium borate glass

The N4 values were calculated using both the measured BO_3 symmetric peak and the corrected symmetric peak. Equation 3.3 was used to calculate the N4 value. The integrated areas under the peaks were used for this.

$$N4 = \frac{B4}{B3 + B4} \qquad (3.3)$$

Fraction of sodium (X-Value)	Uncorrected N4 Value	Corrected N4 Value
0.05	0.078	0.076
0.10	0.150	0.145
0.15	0.224	0.217
0.20	0.296	0.288
0.25	0.377	0.368
0.33	0.463	0.454

Table 3.31: N4 values obtained from NMR of sodium borate glasses

Fraction of Sodium (X-Value)	Uncorrected N4 Value	Corrected N4 Value
0.2	0.273	0.264
0.25	0.332	0.321
0.33	0.461	0.449

Table 3.32: N4 values obtained from NMR of sodium borate crystals

3.4 Raman

3.4.1 Background

The raw data from the Raman of the glass samples needed a baseline to be calculated to remove the background caused by Raleigh scattering. A smooth second order polynomial was used to attempt this. Obvious changes need to be applied to the polynomial for each set of data due to the differences in the scaling of the intensity. Once these changes are made the baseline calculated for a particular sodium borate spectra should be able to be used for the other spectra. To create the baseline, several known/suspected points of background on the spectra data could be used and a best fit second order polynomial used to join the points.

Raman data was recorded at frequencies higher then those needed to show the breathing modes of each species. This extra data could then be used as a guideline for background. This is the region above 1700cm^{-1}. Fig 3.41 shows this. Three points at equal intervals were used between 1700 – 2000cm^{-1} and the lowest value point of the trough around the 350cm^{-1} region. The point at the 350cm^{-1} trough may not necessarily be background, but with no known function for background this point was a likely point for the baseline to go through. .

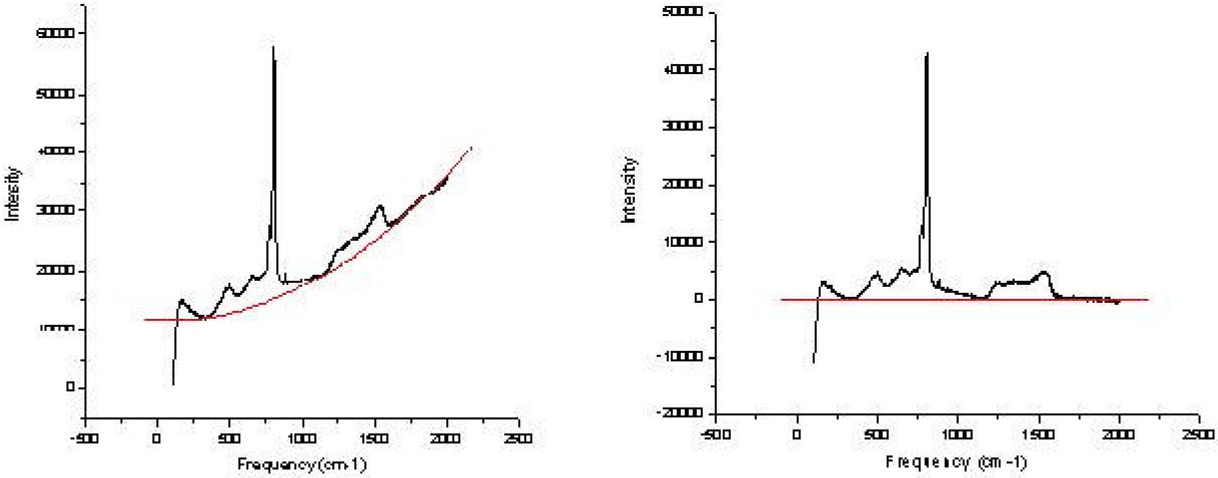

Fig 3.4.1: Graph of X=0.1 Sodium Borate Raman spectra with and without background

The data around 900-1200cm^{-1} in Fig 3.4.1 showing a straight line looks as if it is background. To include this in the baseline using a second order polynomial would then cause the baseline to go above much of the data. Keeping the second order polynomial as it is leaves the curve shown on the right in fig 3.4.1. To include this area in the baseline a higher order polynomial would need to be used. To do this, known background points between 600 and 1700cm^{-1} would need to be found which is not possible in any of the samples. It is assumed that this area is not background, but a region that is hard to fit with peaks. If a perfect black body radiator was used for Raman then an accurate measure of the background function could be found and subtracted but this was not possible.

3.4.2 Band Characteristics

From the Raman spectra of the X=0.05 powdered glass sample, several distinctive peaks can be seen. The most obvious peak at 806cm^{-1}(E) which is also shown in figure 3.4.2.1 and was assigned to the boroxyl ring which is characteristic of low alkali level borates. The peak then reduces in relative intensity until it is no longer noticeable at X=0.25. At X=0.05 this peak has a noticeable shoulder to the lower frequency side at ~770cm^{-1} (D). This becomes the most distinct peak at X=0.2. It becomes clear at X=0.15 that another peak is developing at ~735cm^{-1} (C) which develops into the shoulder of the peak D at increased sodium contents.

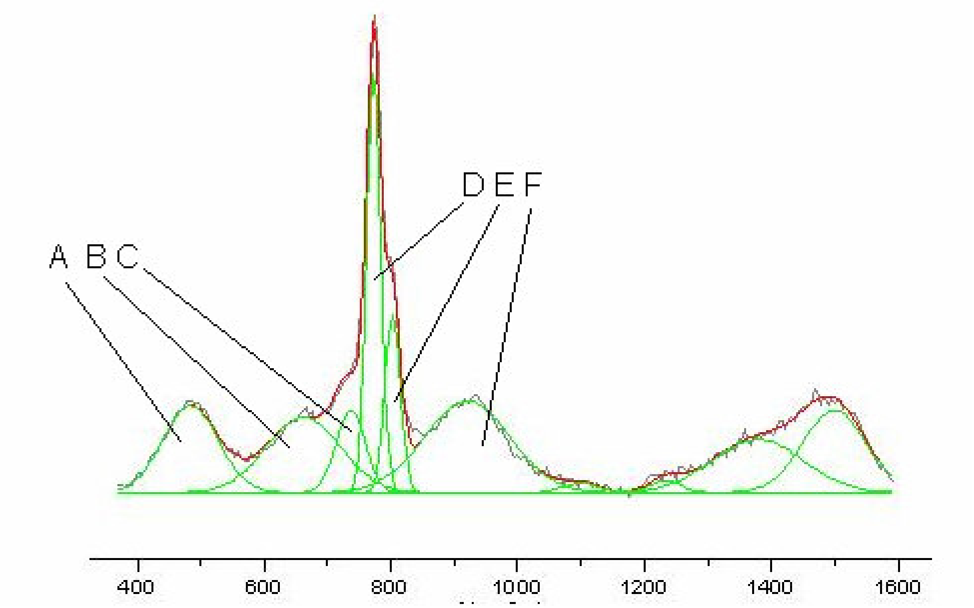

Fig 3.4.2.1. Diagram of a peak fit for X=0.2 Sodium borate glass

Species Type	Frequency cm-1	Peak Position of Individual X-Value					
		0.05	**0.1**	**0.15**	**0.2**	**0.25**	**0.33**
A	460-570	481	489	492	484	493	437
							503
B	630-690	658	653	672	662	651	680
C	~750	728	730	730	736	737	738
D	~775	795	773	773	773	772	767
E	~806	806	806	804	803		
F	895-920	878	883	900			871
G	~950				920	934	977
H	~1115		1067	1055	1100	1103	1112
I	~1210	1252	1237	1227	1233	1243	
J	1300-1600	1342	1348	1396	1378	1406	1394
		1514	1529	1519	1499	1500	1492

Table 3.4.2: Table of the peak positions for Sodium Borate Raman

At the higher and lower frequencies the peaks become less distinctive. The peaks have large FWHMs (Full Width Half Maximums) making peak fitting a less accurate procedure. Between 1200-1600cm^{-1} a collection of peaks merge. This section was fitted using 3 peaks. The peak at ~1250cm^{-1} (I) was assigned to pyroborate whilst the remaining two were assigned to B-O- bonds attached to large borate structures[9] (J, K). The peaks noticeable at ~1115cm^{-1} in the samples with an X value above 0.1 and at ~950cm^{-1} in samples with an X value above 0.2 were assigned to Interconnected and Loose Diborate groups respectively. At ~650cm the peak was assigned to Metaborates. Figure 3.4.2.2. shows how the Raman spectrum changes with the value of X.

Peak fit of sodium borate glass Raman spectra

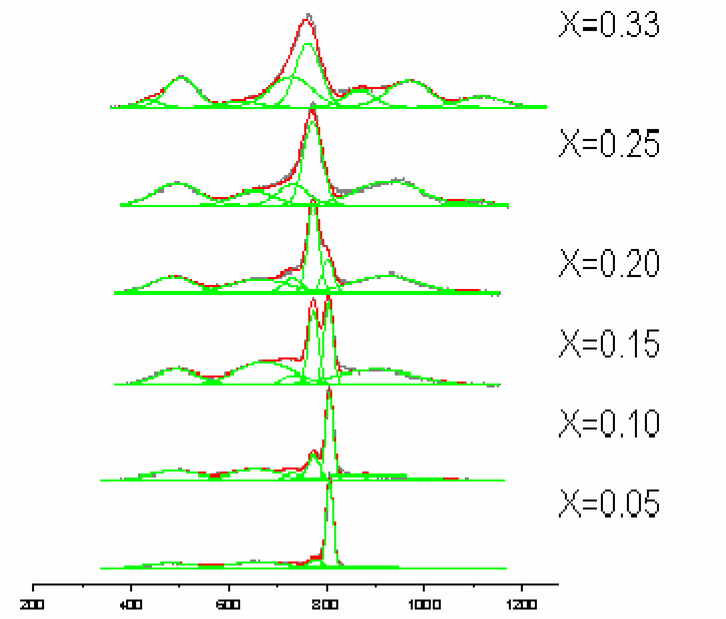

Fig 3.4.2.2 Raman peak fits for sodium borate glasses

4 Discussion

4.1 Raman Spectra Peak Assignment

The addition of an Alkali to borates is known to result in the conversion of B_3 to B_4 as opposed to the formation of non-bridging oxygen's hence increasing the N4 value of the sample. From the results recorded from the NMR it appears there is an approximately linear relationship between alkali modifier and N4 value. The reducing intensity of the peak assigned to the boroxyl ring implies that a proportion of the B_3 is being converted to B4 and is contributing to the number of super structural units with an N4 value above zero. It was also noted that the integrated area, I, of the peak representing the boroxyl ring was proportional to the N4 values for the samples which had this peak present.

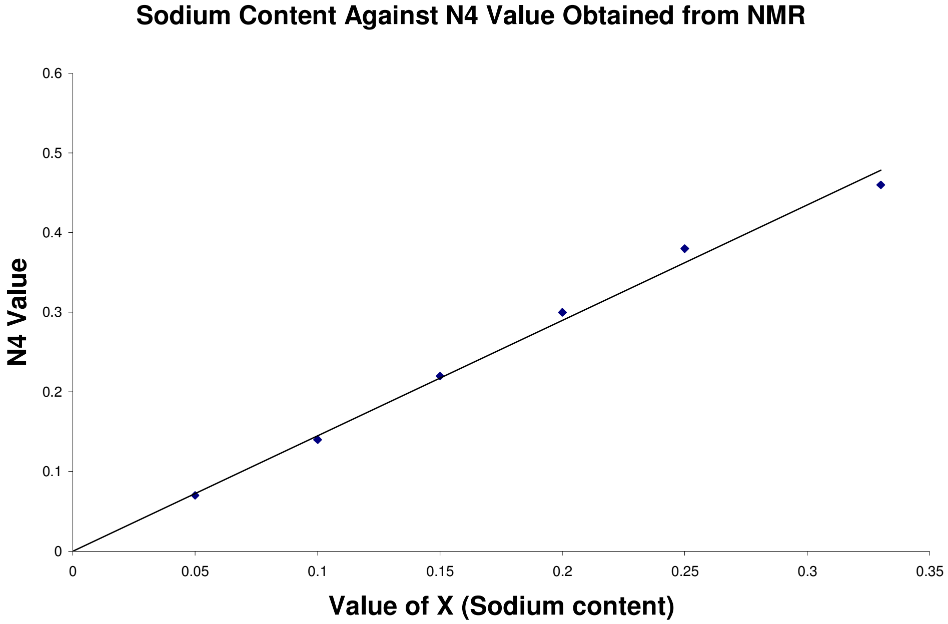

Fig 4.1.1 Relationship between N4 value and ratio of Sodium to Borate

The N4 value of a sample is calculated by

$$N4 = \frac{B4}{B3 + B4} \text{ ....Equation 1}$$

If the integrated area under each peak of the Raman spectra is proportional to the quantity of the super structural unit that it is attributed to then this formula would become

$$N4 = \frac{\sum_n I_n N4_n}{\sum_n I_n} \text{ ....Equation 2}$$

where I_n is the integrated area under peak n, and $N4_n$ is the N4 fraction value of peak n. The bottom line can be ignored if all the peaks are used and there summed total has been normalised so that it is unity (so each I_n represents a fraction of the total spectra. Whilst this should be a relatively easy calculation, the assignment of the peaks in Raman spectra for borates is a topic of much debate with many chosen assignments contradicting each other. The peaks at 750cm^{-1} and 770cm^{-1} are of the most concern. Konijnendijk[6] suggested that the boroxol ring is converted primarily to tetraborate (770cm^{-1}) below an alkali content of 20% and to diborate (750cm^{-1}) above 20%. Konijnendijk also assigned the 940cm^{-1}, 820cm^{-1}, and 630cm^{-1} to orthoborate, pyborate and metaborate respectively. Brill [7] assigned the 770cm^{-1} peak so the vibration of 6 membered rings with one BO_4 and the 750cm^{-1} peak to 6 membered rings with two BO_4.

```
       B ----- O
O <              > B
       B ----- O
```

Fig 4.1.2 Diagram of a 6 membered ring

If Brill's assignment is correct, then the bands at 770cm^{-1} and 750cm^{-1} cannot be given any one N4 value. The 770cm^{-1} would be tetraborate, pentaborate and triborate, and the 750cm^{-1} would be dipentaborate, diborate and ditriborate. Crystalline Na20-2B203 is made of triborate groups with one NBO and rings with 2 BO$_4$ tetrahedra in the form of dipentaborate groups[10] and has a dominant band at ~755cm^{-1}. Hence the 755cm^{-1} can be assigned to dipentaborate groups.

4.2 Calibration of Raman Spectrum with NMR N4 Values

The most noticeable changes in the Raman spectra with Na content for x-values between 0.05 and 0.33 are the 806cm^{-1}, 750cm^{-1} and 770cm^{-1} bands and there intensity. These bands show the important changes in borate structure with Na with reference to the numbers of 3 and 4-coordinated boron. As the sodium content increases, the 806cm^{-1} band reduces in intensity and the 770cm^{-1} band increases up to a sodium content of 25%. Above this content the 770cm^{-1} band reduces slightly. The 750cm^{-1} band increases steadily with the decrease in the 806cm^{-1} band and then increases to a greater extent with the decrease in the 770cm^{-1}.

Another key factor is deciding whether these bands alone will give a fair representation of the whole of the sample. This is especially important at higher percentage levels of Sodium where the boroxol ring is not present and the 750cm^{-1} and 770cm^{-1} bands are no longer the most distinct peaks. It should also be noted that at higher sodium contents, the N4 values no longer have a linear relationship with the ratio of sodium to borate.

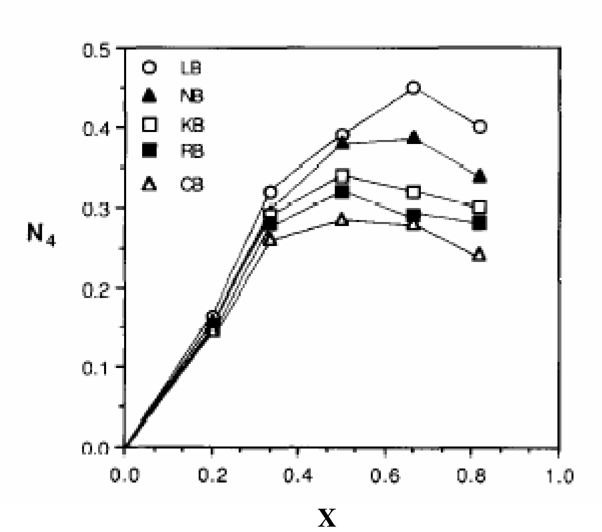

Fig 4.14: N4 value against ratio of alkali to borate (NB = sodium borate) [8]

For these reasons, the peaks that influence the N4 value largely are peaks C, D and E whilst at higher Sodium contents other peaks would need to be included.

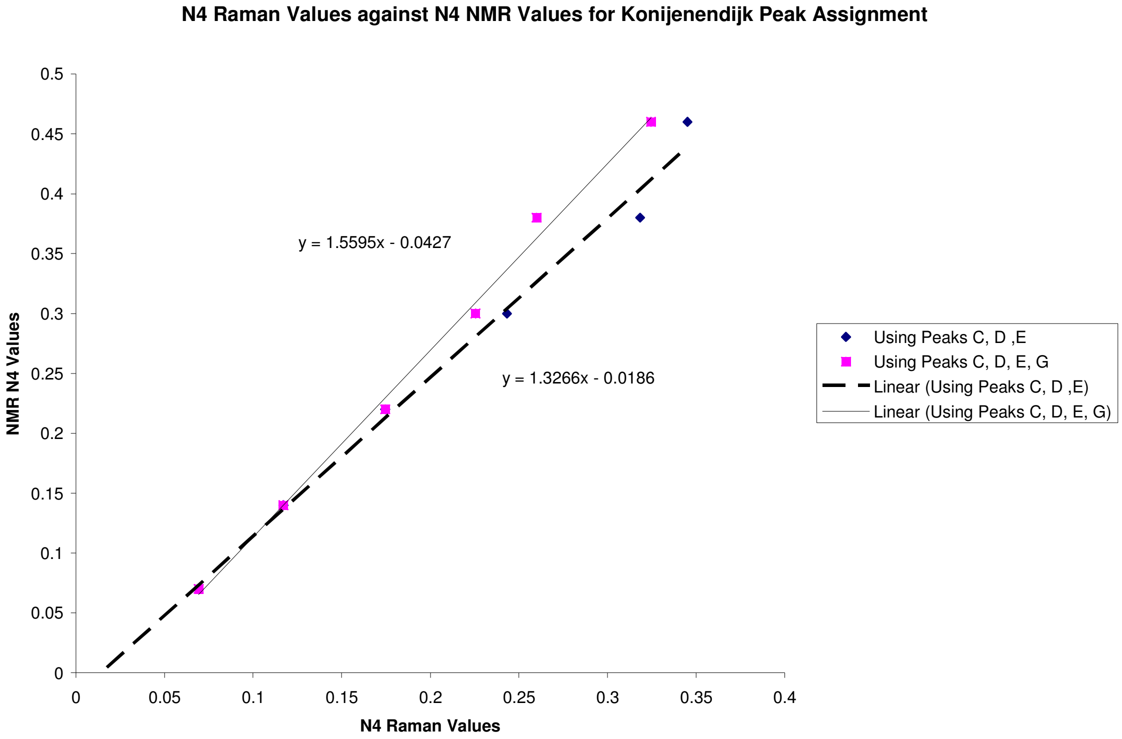

Fig 4.15 A comparison of N4 values from NMR and Raman Using Equation 2 with different Peaks combinations

Fig 4.15 shows how N4 values from equation 2 vary with the N4 values from NMR when using Konijenedijk peak assignments. The trend line which uses peaks C, D and E produces a more linear relationship with the actual values straying less from the trend line. The intercept is also closer to zero and the gradient closer to being one. Hence to get more accurate results using peaks C, D and E with Konijendijk peak assignment and equation 2 a constant of 1.33 would need to be multiplied to it.

$$N4 = 1.33\frac{\sum_n I_n N4_n}{\sum_n I_n} - 0.02 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Equation 3}$$

Fig 4.16 shows how the N4 value from equation 2 vary with N4 values for NMR with Brills peak assignments.

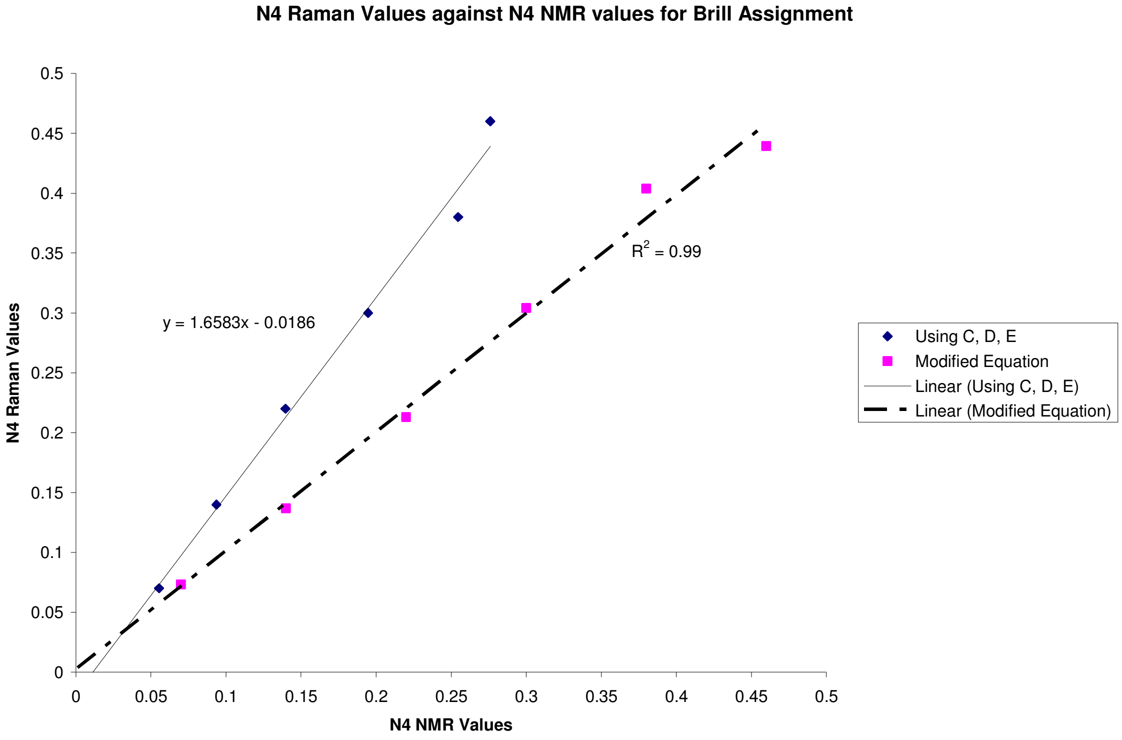

Fig 4.16: *A comparison of N4 values from NMR and Raman Using Equation 4 with Brill's assignments*

The modified equation 2 then becomes:

$$N4 = 1.66\frac{\sum_n I_n N4_n}{\sum_n I_n} - 0.02 \text{ ....Equation 4}$$

The R^2 correlation coefficient for this fit is 0.9900. Fig 4.16 also shows NMR N4 values against Brill's assignment of peaks with equation 4. There appears to be a good correlation between the two N4 values up to x=0.33, above which, the points stray further from the trend line. This is likely to be due to larger changes in one of the other bands which is becoming more important in the total N4 value. In terms of the glasses structure, this means that one of the super structural units is increase/decreasing at a greater rate with sodium content then before. Equation 4 would be likely to improve in accuracy at high values of x if a peak representing a super structure with an N4 value of 0 was included which reduced in intensity with an increase in the value of x such as metaborate. Metaborate was not included however as its change in intensity appeared erratic. This was likely to be due to a combination of a book baseline subtraction and poor peak fit at the ~650cm^{-1} frequency region.

5 Conclusion

A correlation can be seen between the N4 values obtained from Raman using Brills assignment of peaks using the peaks for the boroxol ring, pentaborate and dipentaborate. Using this equation with peaks at higher molar ratios of sodium would not hold though due to different super structural units being dominant in the spectra. At these higher ratios the N4 values no long have a linear relationship with the molar ratio of sodium.

To make a more useful calibration of Raman spectra with a quantitative N4 value a more accurate procedure for background subtraction and peak fitting would need to be carried out. This would become easier with a higher resolution Raman spectra. A larger number and range of x values for the sodium borate glasses would allow for clearer trends in peak shift, and intensity change to be calculated.

Peak assignment also appears to be an area of concern with many varying opinions upon which peaks in the Raman spectra belong to which structures.

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