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Raman spectroscopic investigation of sodium borosilicate glass structure

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Raman spectra of sodium borosilicate glasses with a wide range of Na_2O/B_2O_3 ratios were systematically measured. Variations of the spectra with glass composition were studied to interpret the implied distribution of Na^+ ions between silicate and borate units. When Na_2O/B_2O_3 is less than 1, all Na^+ ions are associated with borate units as indicated by the absence of the $1100\,cm^{-1}$ band of Si–O$^-$ non-bridging bond stretching. For the $(1-x)Na_2O \cdot SiO_2 \cdot xB_2O_3$ glass with $x \leq 0.4$ the peak-height ratio of the $950\,cm^{-1}$ band to the $1080\,cm^{-1}$ band was used to analyse semiquantitatively the distribution of the Na^+ ions between silicate and borate units. Sodium ions are divided between silicate and borate units approximately in proportion to the amount of SiO_2 and B_2O_3 present in these glasses. Some of the high sodium content glasses were crystallized and their spectra were compared with the bulk glass spectra. The distribution of Na^+ ions in the glass was quite different from their distribution after crystallization. Spectra of high silica glasses that had been heat-treated for phase separation indicated exclusion of borate units from the silica network and the formation of borate groups. For high boron content glasses, no change was observed on heat treatment. Raman bands due to borate groups seem to be little affected by their environments.

1. Introduction

Raman spectroscopy has proved to be a technique of great utility for the determination of the types of structural units in insulator glasses and giving some clues to their topologic and geometric arrangements [1–9]. This paper continues a series of Raman investigations with a discussion of the spectra and structure of the sodium borosilicate glasses, particularly those with compositions in the high sodium region. The silicate structural unit is the silicon–oxygen tetrahedron which contains a varying number of non-bridging oxygens depending on the alkali content of the glass. The borate structural units are more complex and less well defined. It is possible for the boron to change co-ordination from three to four and to change the linkages of borate units to accommodate changing alkali concentrations. Questions of interest include the geometry of the silicate and borate structural units, how these two types of glass formers are connected in the glass structure and how the modifier alkali cation is distributed between them.

The most systematic investigation of the structure of alkali borosilicate glass is probably the nuclear magnetic resonance (NMR) study of Yun and Bray [10, 11]. They formulated an experimental relation of the fractions of four- and three-fold co-ordinated borons with the glass composition. A structure model was then proposed and the theoretical formulae were derived from the model. However, the model is still crude and the theoretical formulae are not applicable to glasses in the region of high Na_2O/B_2O_3 ratio (>2).

A Raman spectroscopic study of borosilicate glass was reported by Konijnendijk and Stevels [7, 8]. The Raman bands at frequencies between 600 and $950\,cm^{-1}$ were tentatively assigned to

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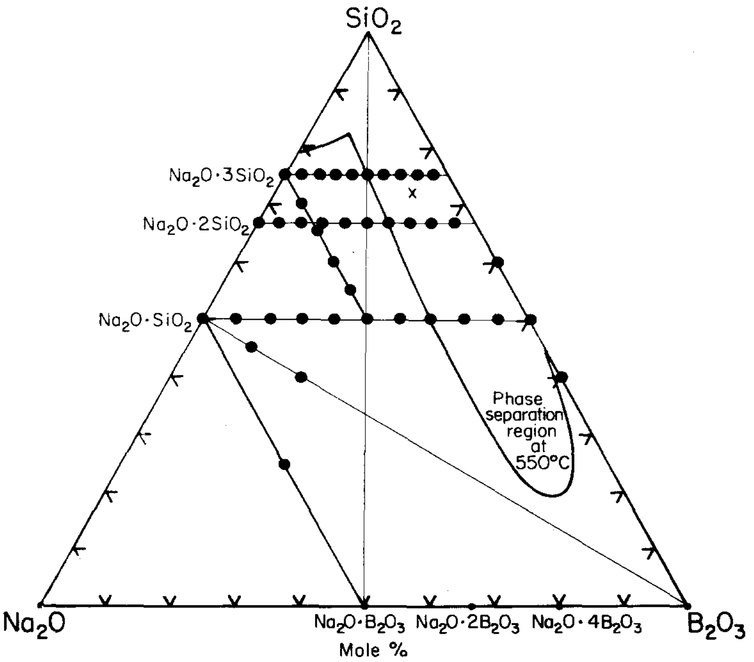

Figure 1 Nominal compositions of glass studied.

different types of borate groups by comparison with the spectra of crystalline borates. The glasses were mainly in the composition range with a Na_2O/B_2O_3 ratio less than 1.

Another subject of interest is the metastable phase separation of glass. An NMR study indicated no change in the fraction of the four-co-ordinated boron by phase separation [12]. Change of the composition of separated phases with different heat-treatment temperatures has been demonstrated by HF etch rate and HCl leaching rate measurements [13, 14]. The Raman spectrum of the $0.15Na_2O \cdot 0.535B_2O_3 \cdot 0.35SiO_2$ glass was reported to be identical to the spectrum of visibly phase-separated glass [7].

In the present study glass spectra with a wide range of Na_2O/B_2O_3 ratios were systematically measured and the variations of the spectra with glass compositions were analysed. Some of the glass spectra were also compared with the spectra of crystallized glass. Some effects of heat-treatment in the metastable phase separation region were re-examined.

2. Experimental procedure

Glasses were prepared from reagent grade Na_2CO_3, H_3BO_3, and SiO_2 (about 200 mesh silica floated powder). All chemicals were obtained from Fisher Scientific Company. About 50 g batches were well mixed by a pestle and mortar and melted in platinum crucibles in a SiC globar furnace at temperatures between 1000 and 1400° C depending on the batch composition. For the B_2O_3–SiO_2 binary glasses, H_3BO_3 was dissolved in colloidal silica solution (DuPont Ludox AS 40) and excess water was evaporated before melting. Glass rods of 1 to 2 mm diameter were drawn from the melt. The $Na_2O \cdot 0.5SiO_2 \cdot 0.5B_2O_3$ melt was quenched between graphite blocks. The nominal compositions of the glasses studied are shown in Fig. 1.

Raman spectra were measured on a Spex model 1401 double-grating spectrometer at a scattering angle of 90°. The excitation source was the 514.5 nm (19435.6 cm^{-1}) green line of a Spectra-Physics model 164 Ar-ion laser. The detailed measurement procedures and the scattering geometry are described elsewhere [5]. Both parallel (xx) and crossed (xy) polarized spectra were measured on the glass rods. Raman spectra of crystallized glasses were measured in an unpolarized mode. All the spectra were recorded with a spectral slit-width of 3 cm^{-1}.

3. Results

3.1. Spectra of bulk glass

Parallel polarized (xx) spectra of three series of glasses, $(1-x)Na_2O \cdot SiO_2 \cdot xB_2O_3$, $(1-x)Na_2O \cdot 2SiO_2 \cdot xB_2O_3$ and $(1-x)Na_2O \cdot 3SiO_2 \cdot xB_2O_3$ are shown in Fig. 2a to c. By addition of B_2O_3 to sodium silicate glasses new bands appear at 1460 to 1470 cm^{-1} and 620 to 635 cm^{-1}. The former band, probably due to the stretching mode of

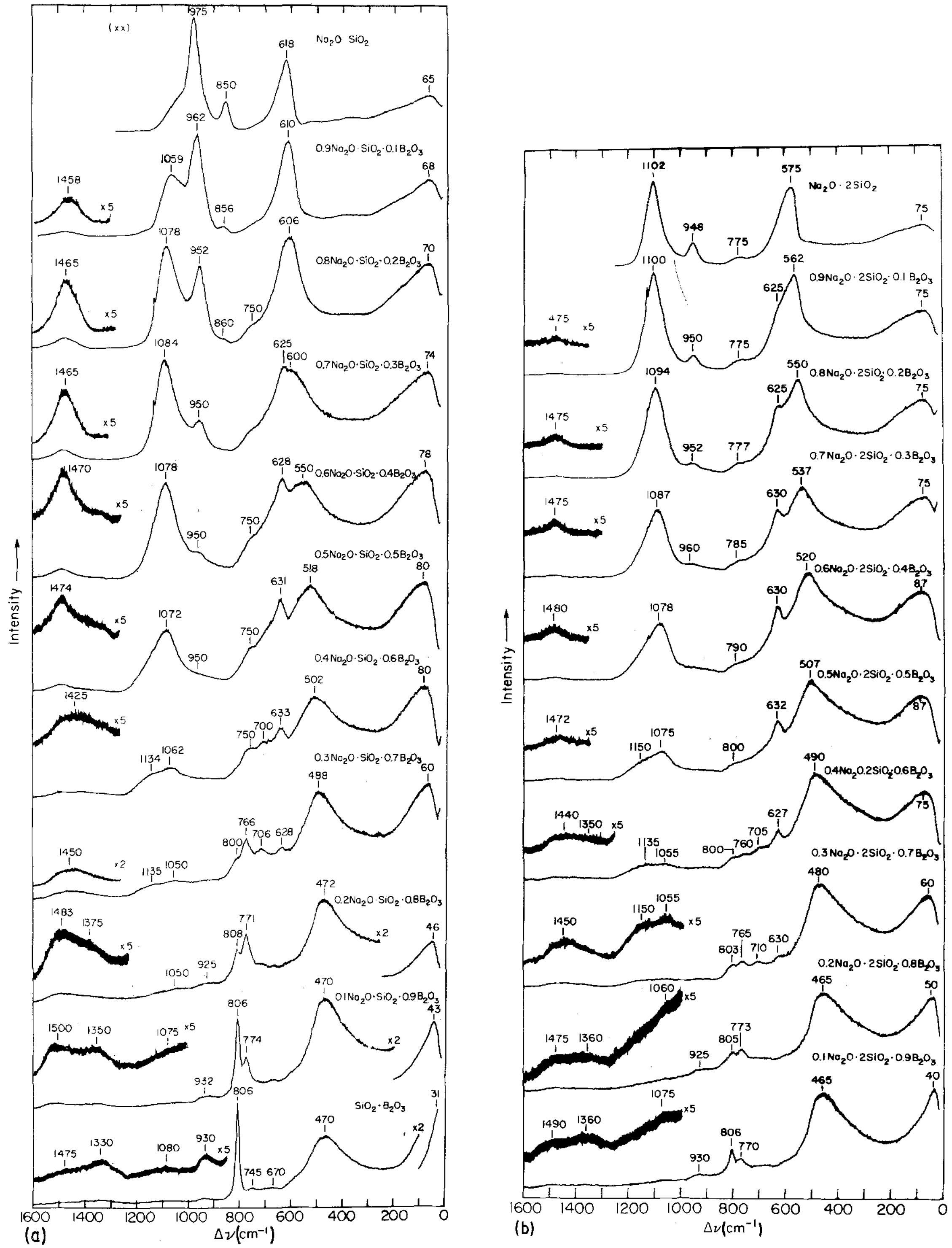

Figure 2 (a) Parallel polarized (xx) spectra of $(1-x)Na_2O \cdot SiO_2 \cdot xB_2O_3$ glasses, (b) parallel polarized (xx) spectra of $(1-x)Na_2O \cdot 2SiO_2 \cdot xB_2O_3$ glasses and (c) parallel polarized (xx) spectra of $(1-x)Na_2O \cdot 3SiO_2 \cdot xB_2O_3$ glasses.

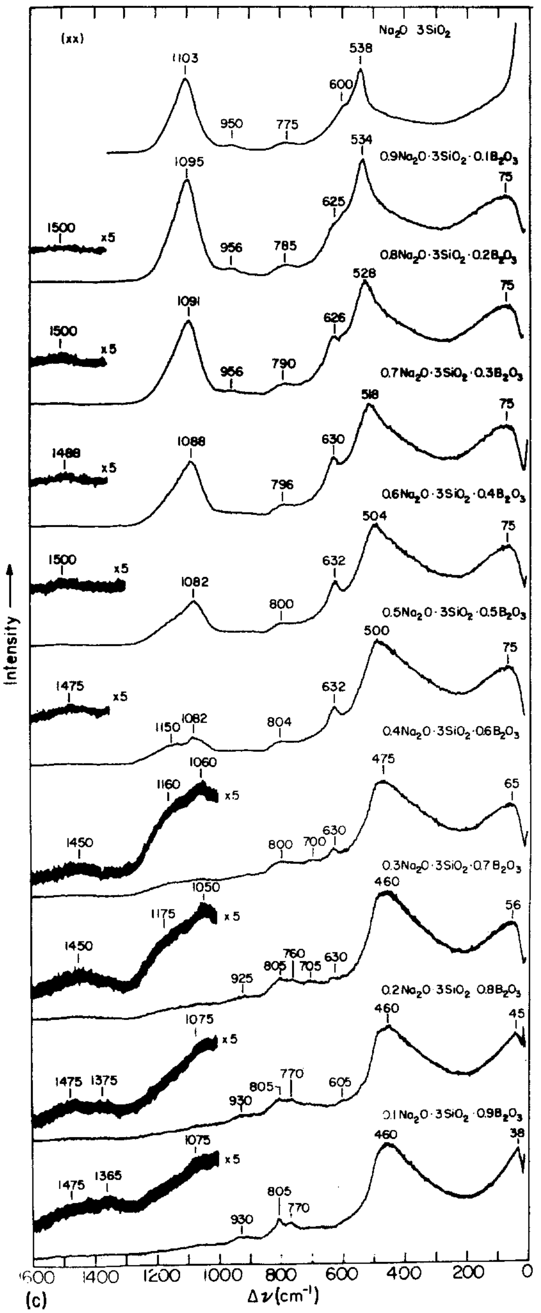

Figure 2 (Continued)

B–O bonds* is more intense for the glasses with a smaller SiO_2 content. The intensity of the band at 620 to 635 cm^{-1} seems to increase with an increase of x until x is about 0.5 and decreases at $x > 0.5$. This band was assigned to a vibration of the metaborate ring by Konijnendijk [7]. In the spectra of the $(1-x)Na_2O \cdot SiO_2 \cdot xB_2O_3$ glass, two bands at 950 to 975 cm^{-1} and at 1050 to 1080 cm^{-1} exhibit a relative intensity change at $x < 0.5$, similar to that observed in the binary alkali silicate glasses between the metasilicate and trisilicate compositions [2]. The band at 950 to 975 cm^{-1} is due mainly to the symmetric stretching mode of the non-bridging bonds of SiO_3 chain units and the band at 1050 to 1100 cm^{-1} is due to stretching of the non-bridging bond of $SiO_{5/2}$ sheet units [2, 4]. In the spectra of the $(1-x)Na_2O \cdot 2SiO_2 \cdot xB_2O_3$ and $(1-x)Na_2O \cdot 3SiO_2 \cdot xB_2O_3$ series, the intensity of the 1080 to 1100 cm^{-1} band decreases as x increases, which suggests a decrease in the number of $SiO_{5/2}$ units. The band is still observable at $x = 0.5$.

In Fig. 3a the frequency of the 1050 to 1100 cm^{-1} band is plotted against the B_2O_3/Na_2O ratio. For all four series of glasses the frequency decreases at approximately the same rate with increase of x, except in the $0.1 \leq x < 0.3$ region of the $(1-x)Na_2O \cdot SiO_2 \cdot xB_2O_3$ series. The increase of the frequency in the $0.1 \leq x < 0.3$ region of the $(1-x)Na_2O \cdot SiO_2 \cdot xB_2O_3$ glass is probably associated with the relative increase of the number of $SiO_{5/2}$ units to the number of SiO_3 units, which is also observed with binary alkali silicate glasses between the metasilicate and disilicate compositions [2]. When the frequency is plotted against the B_2O_3/SiO_2 ratio in Fig. 3b, the curves are spread out in contrast to the sodium aluminosilicate glasses. With aluminosilicate glasses, the frequency falls on a smooth curve only when plotted against the Al_2O_3/SiO_2 ratio [15].

In the composition region of $Na_2O/B_2O_3 < 1$, a broad band at 550 to 450 cm^{-1} becomes a dominant feature of the spectra. This band is probably due to bending or rocking of Si–O–Si bonds [4, 16] as well as mixed Si–O–B bonds of the three-dimensional network. The vibrations of different bonds may be coupled to give one broad band. The frequency of the band is higher for the glass series of the lower SiO_2 content. Another significant feature in this composition range is the appearance of two bands at 765 to 775 and 805 to 810 cm^{-1}. Their relative intensities change with Na_2O/B_2O_3 ratio in a similar manner to the binary alkali borate glasses. The band at 805 to 810 cm^{-1} has been attributed to symmetric vibration of the boroxy ring [6] and the band at

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*These descriptions of the vibrations are very crude. The actual vibrations may not be localized to the particular bond but are to some extent coupled to the vibrations of other bonds.

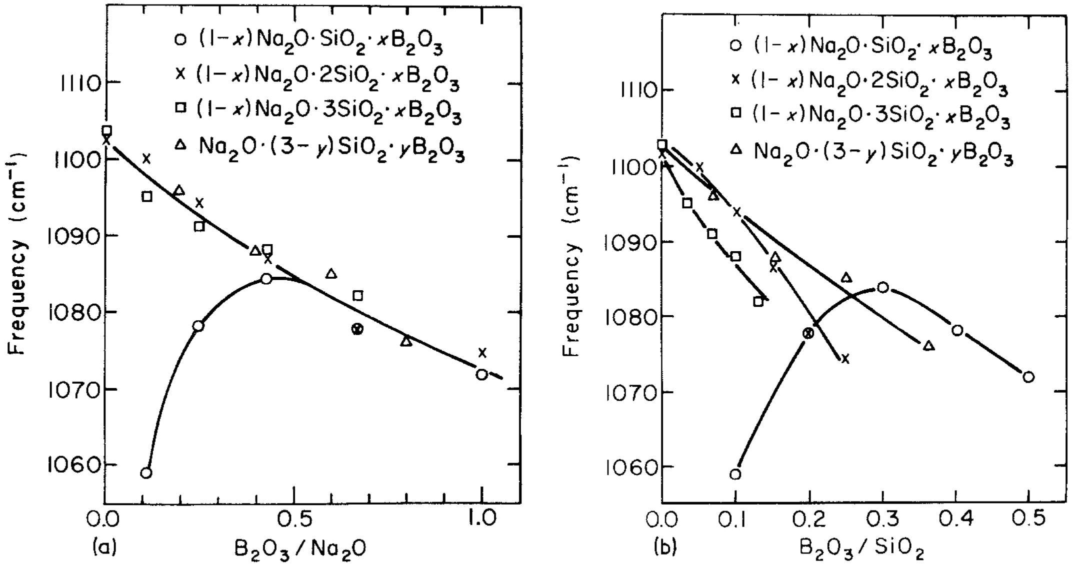

Figure 3 (a) Frequency of the 1050 to 1100 cm^{-1} band as a function of the Na_2O/B_2O_3 ratio and (b) frequency of the 1050 to 1100 cm^{-1} band as a function of the B_2O_3/SiO_2 ratio.

765 to 775 cm^{-1} to vibrations of six-membered borate rings with one or two $[BO_4]$ units [6]. The band shape in the 1300 to 1500 cm^{-1} range is also very similar to the band shape of the binary borate glass spectra [7–9]. These spectral features of borate groups are more intense for the glass series of the lower SiO_2 content.

The low frequency band at 30 to 85 cm^{-1} shifts to higher frequencies and becomes broader as the Na_2O/B_2O_3 ratio increases just as observed for binary alkali borate glasses. The frequency shift was interpreted as due to a change of mass of a vibrating fragment by Bril [6]. The frequency shift shows a maximum at $x = 0.5$ or a plateau at $x \leqq 0.5$. Many physical properties show a maximum or minimum at $M_2O/B_2O_3 = 1$ (where M is a modifier action) [17, 18] of borosilicate glass.

3.2. Comparison of the glass and crystal spectra

In Fig. 4a to c the bulk glass spectra are compared with the spectra of the glasses crystallized at subsolidus temperatures. The $0.8Na_2O \cdot SiO_2 \cdot 0.2B_2O_3$ glass crystallized to Na_2SiO_3, β-$Na_2Si_2O_5$ and metaborate $Na_3B_3O_6$ at 640° C, for the composition is in the compatibility triangle of these compounds. The 1080 and 950 cm^{-1} bands correspond to the symmetric stretching of the non-bridging bonds of β-$Na_2Si_2O_5$ and Na_2SiO_3, respectively. Crystalline sodium metaborate exhibits bands at 480, 620, 690 and 780 cm^{-1} and a group of bands at 1500 to 1600 cm^{-1} (the shaded bands in Fig. 4a to c). The frequency range of the group of bands of crystalline metaborate between 1500 and 1600 cm^{-1} is about 100 cm^{-1} higher than the corresponding bands in the glass spectrum.

The composition of the $0.8Na_2O \cdot 0.8SiO_2 \cdot 0.4B_2O_3$ glass is on the join between the metaborate and disilicate compositions and the glass crystallized to metaborate $Na_2B_3O_6$ and α-$Na_2Si_2O_5$ (metastable) at 650° C. Although the intensity ratio of the 950 cm^{-1} band to the 1080 cm^{-1} band is as high as in the $0.8Na_2O \cdot SiO_2 \cdot 0.2B_2O_3$ glass spectrum, metasilicate did not crystallize. This indicates that more Na^+ ions are associated with silicate to create more SiO_3 chain units in the glass than expected from the distribution of Na^+ ions between disilicate and metaborate crystals.

The $Na_2O \cdot 0.5SiO_2 \cdot 0.5B_2O_3$ glass crystallized to Na_2SiO_3 and $Na_3B_3O_6$, for the composition is on the join between the metasilicate and metaborate compositions. The 960 cm^{-1} band and a part of the 635 cm^{-1} band or the 550 cm^{-1} band in the glass spectrum are due to SiO_3 chain units and the 860 cm^{-1} may be due to isolated SiO_4 tetrahedra. As for the rest of the bands, which are probably due to borate groups, present knowledge is not sufficient to make any definite assignments.

3.3. Spectra of heat-treated glasses

In Fig. 5 the spectrum of a glass with 7 wt% Na_2O, 70 wt% SiO_2, and 23 wt% B_2O_3 (the com-

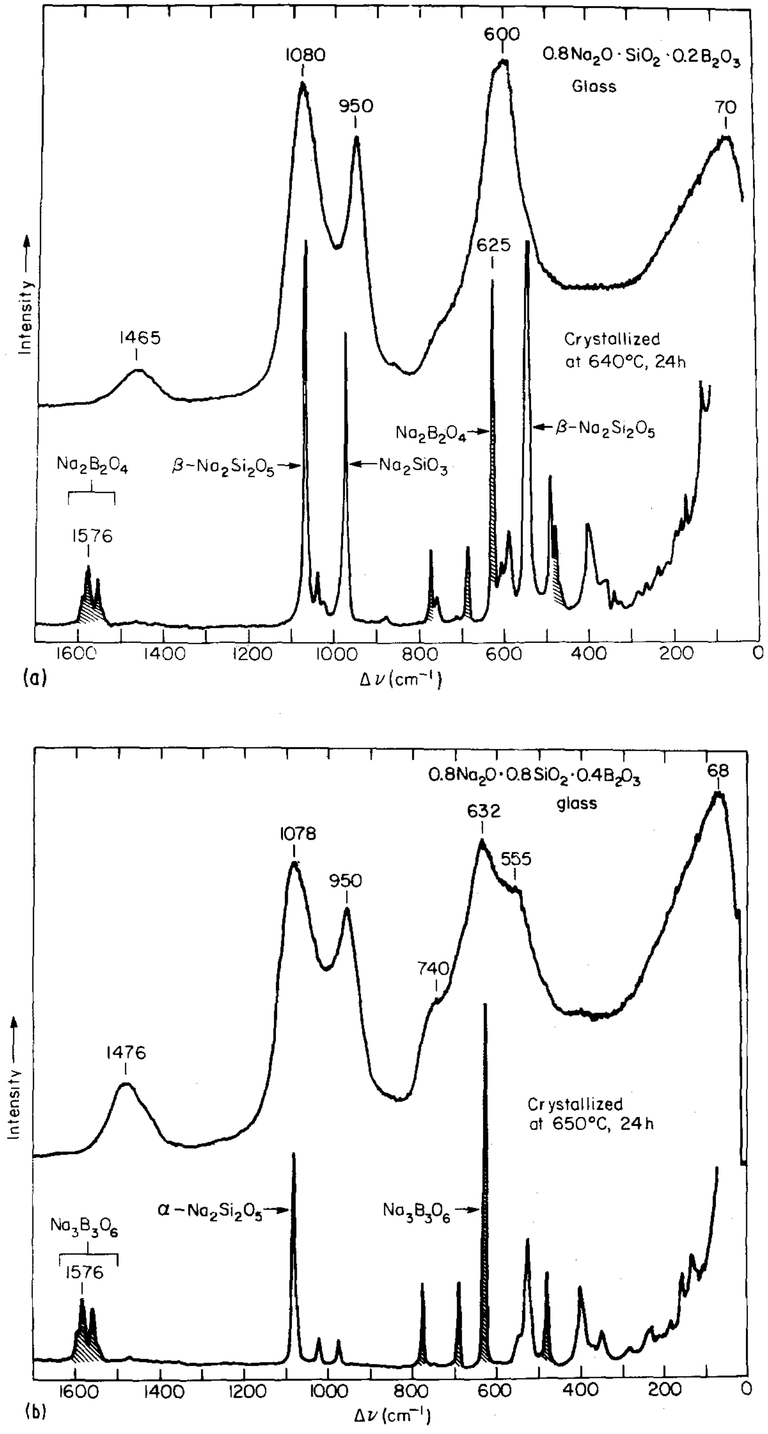

Figure 4 Comparison of the bulk $0.8Na_2O \cdot SiO_2 \cdot 0.2B_2O_3$ glass spectra and the crystallized glass spectra, (b) comparison of the bulk $0.8Na_2O \cdot 0.8SiO_2 \cdot 0.4B_2O_3$ glass spectra and the crystallized glass spectra and (c) comparison of the bulk $Na_2O \cdot 0.5SiO_2 \cdot 0.5B_2O_3$ glass spectra and the crystallized glass spectra.

position of the glass is indicated by x in Fig. 1), after heat-treatment at 600° C for 1 h, is compared with the spectrum of the glass as-drawn. Metastable phase separation of this glass has been extensively studied [13, 14]. After the heat-treatment the intensity of the $774\,cm^{-1}$ band increases relative to the $810\,cm^{-1}$ band, and the $470\,cm^{-1}$ band shifts to $450\,cm^{-1}$ developing a shoulder at 480 to $490\,cm^{-1}$. Identical effects were observed by heat-treatment at 550° C for 24 h. The effects of heat-treatment become less as the SiO_2 and Na_2O concentrations increase and no effects were detected for the $0.2Na_2O \cdot 2SiO_2 \cdot 0.8B_2O_3$, $0.1Na_2O \cdot SiO_2 \cdot 0.9B_2O_3$ and $0.2Na_2O \cdot SiO_2 \cdot$

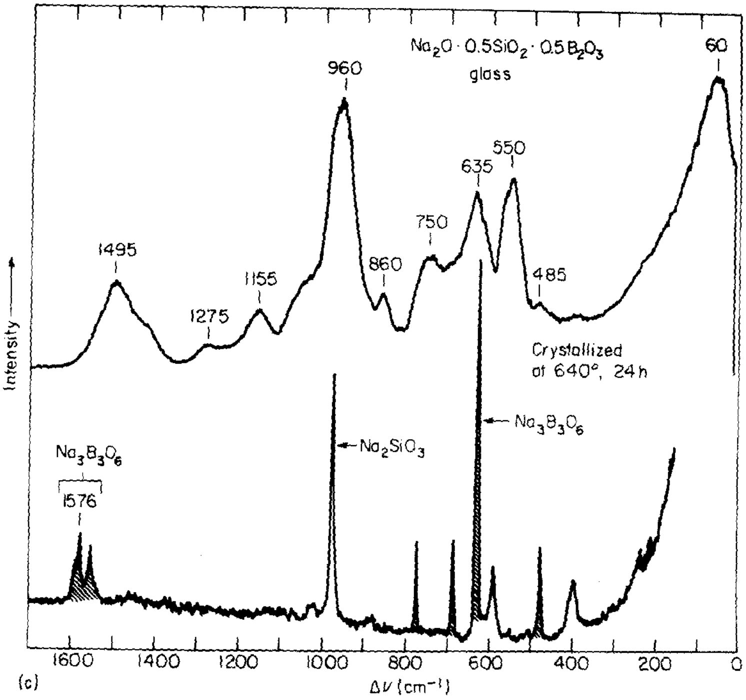

Figure 4 (Continued)

$0.8B_2O_3$ glasses after heating at 550° C for 24 h, although they are in the phase separation region at 550° C.

The effects of heat-treatment were different for the SiO_2–B_2O_3 binary glasses. An increase of the relative intensity of the $810\,cm^{-1}$ band to the $470\,cm^{-1}$ band was observed after heat-treatment depending on temperature, composition, and the thermal history of the glass. The onset of the intensity change occurred at much lower temperatures for phase-separated glasses [19]. A detailed investigation of these effects will be reported elsewhere [20].

4. Discussion

4.1. The $Na_2O/B_2O_3 \geqq 1$ region

For the $(1-x)Na_2O \cdot SiO_2 \cdot xB_2O_3$ series of glasses, the variation of the relative intensities

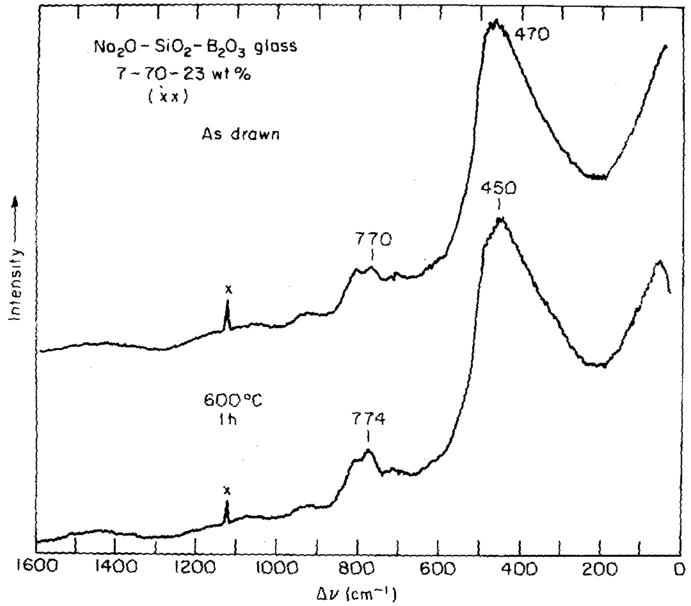

Figure 5 Comparison of the spectra of glass of 7 wt% Na_2O, 23 wt% B_2O_3, 70 wt% SiO_2 as-drawn and heat-treated for phase separation.

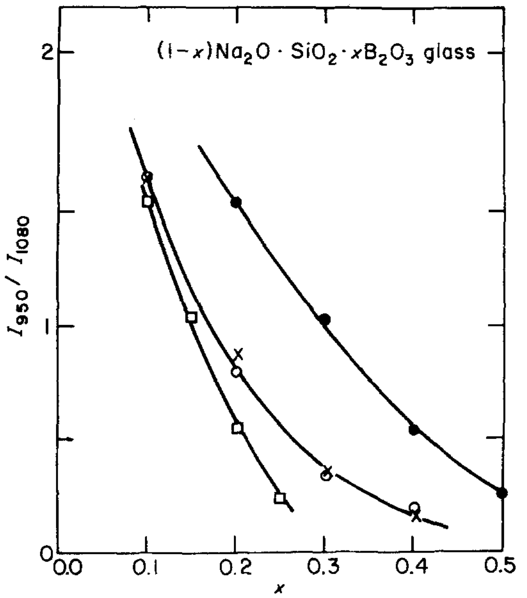

Figure 6 The peak-height ratio of the 950 cm^{-1} band to the 1080 cm^{-1} band of the $(1-x)Na_2O \cdot SiO_2 \cdot xB_2O_3$ glass as a function of x. Experimental: (○), by assuming model (1): (●), by assuming model (2): (□), by assuming a proportional distribution of Na^+ ions to the amount of SiO_2 and $B_2O_3(x)$.

of the 950 to 975 cm^{-1} band and 1060 to 1080 cm^{-1} band, with glass composition shown in Fig. 6, allows a semiquantitative analysis of the distribution of Na^+ ions between the silicate units and borate units. The ratio of the intensities of the two bands is a function of the number of non-bridging oxygens linked to the silicate units, which is equal to the number of Na^+ ions associated with silicate units.* In Fig. 7 Raman spectra of sodium silicate and silica glass are shown for comparison. In Fig. 8 the ratio of the peak height (I_{950}/I_{1100}) of the binary glass spectra is plotted against x, the mole ratio of SiO_2 to Na_2O. This curve can be used as a calibration for the determination of the amount of the Na^+ ions linked to silicate units in the borosilicate glasses.

If structural units such as $[BO_4]$ tetrahedra with non-bridging oxygens or $[BO_3]$ triangles with more than two non-bridging oxygens are ignored, the following two extreme cases of the Na^+ distribution can be considered:

(1) All Na^+ is associated with silicate units. The chemical formula of $(1-x)Na_2O \cdot SiO_2 \cdot xB_2O_3$

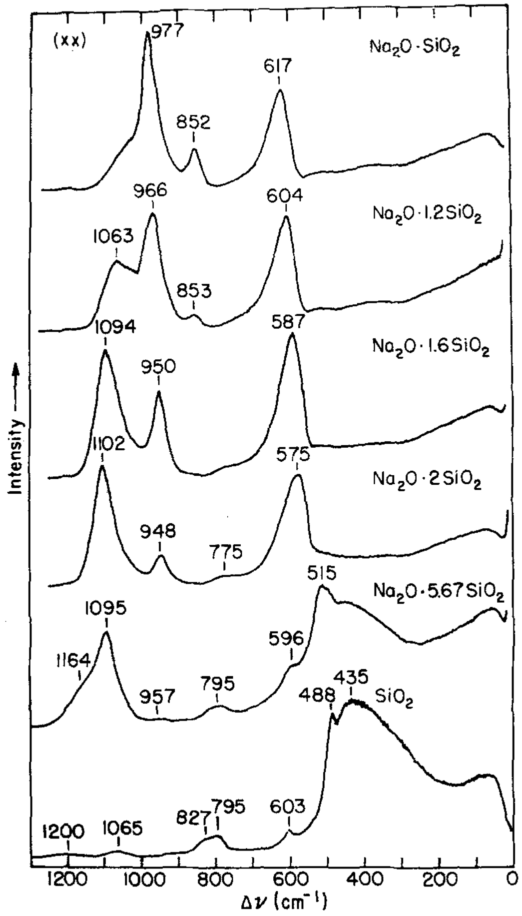

Figure 7 The parallel polarized (xx) spectra of sodium silicate glasses.

glass is expressed as,

$$(1-x)\left(Na_2O \cdot \frac{1}{1-x} SiO_2\right) + xB_2O_3. \quad (1)$$

In this model all borons are three-fold co-ordinated and have no non-bridging oxygens.

(2) Some of the Na^+ ions are used to form $[BO_3]$ triangles with one non-bridging oxygen or to form $[BO_4]$ tetrahedra without non-bridging oxygens and the rest of the Na^+ ions are associated with silicate units. The chemical formula of the glass is then expressed as,

$$(1-2x)\left(Na_2O \cdot \frac{1}{1-2x} SiO_2\right) + x(Na_2O \cdot B_2O_3). \quad (2)$$

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*A Na^+ ion may be co-ordinated not only by non-bridging oxygens of silicate units but also by non-bridging oxygens of borate units at the same time, but for the sake of simplicity each non-bridging oxygen is assumed to associate with one Na^+ ion.

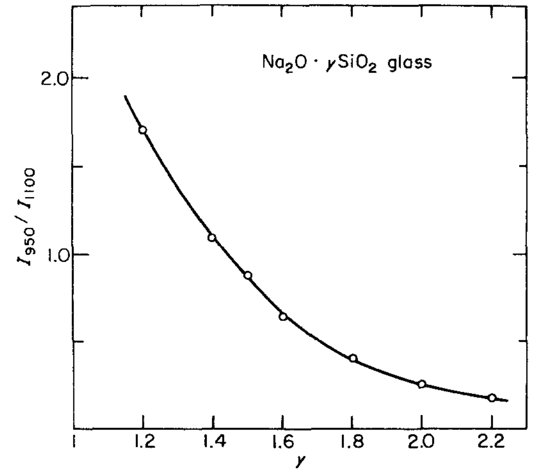

Figure 8 The peak-height ratio of the 950 cm^{-1} band to the 1100 cm^{-1} band of the $Na_2O \cdot ySiO_2$ glass as a function of y.

Note that the chemical formula of $[BO_3]$ triangle with non-bridging oxygen and $[BO_4]$ tetrahedron without non-bridging oxygen cannot be distinguished and are both expressed as $Na_2O \cdot B_2O_3$. For each model the peak-height ratio I_{950}/I_{1080} was determined from the curve in Fig. 8 as a function of the mole ratio of SiO_2 to Na_2O of the average chemical formula for the silicate units. The calculated curves for the two models are plotted in Fig. 6. The experimental curve lies between the two calculated curves, which suggests that the actual distribution of Na$^+$ ions is somewhere between the two extreme models.

If it is assumed that the actual distribution of Na$^+$ ions results from both mechanisms, then the chemical formula of the glass can be expressed as,

$$(1-x-fx)\left(Na_2O \cdot \frac{1}{1-x-fx}SiO_2\right) + x(1-f)B_2O_3 + fx(Na_2O \cdot B_2O_3),$$

where f and $(1-f)$ are the fractions from Model 2 and Model 1, respectively. The fraction f is then determined by finding the SiO_2/Na_2O ratio $[1/(1-x-fx)]$ of the silicate units from the measured I_{950}/I_{1080} value and the curve in Fig. 8. The calculated f is plotted against x in Fig. 9. The fraction f decreases as x increases indicating that at small x more boron tends to form either $[BO_3]$ with one non-bridging oxygen or $[BO_4]$ with no non-bridging oxygen, while as x increases the fraction of $[BO_3]$ with no non-bridging oxygen increases. It is not possible here to determine which borate units exist and what kind of borate groups are formed in these glasses. The bands at about 630 and 1475 cm^{-1} may be due to some borate group(s) but it is too premature to make any definite assignments.

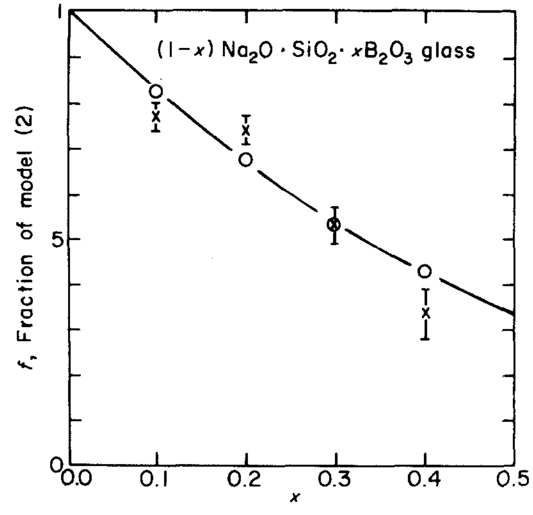

Figure 9 The fraction contributed by model (2): (●), and calculated from $f = (1-x)/(1+x)$ (○), in the $(1-x)Na_2O \cdot SiO_2 \cdot xB_2O_3$ glasses as a function of x.

If the distribution of Na$^+$ ions between the silicate and the borate units is assumed to be in proportion to the amount of SiO_2 and B_2O_3, the chemical formula of the $(1-x)Na_2O \cdot SiO_2 \cdot xB_2O_3$ glass is written as shown in Table I. The I_{950}/I_{1080} ratio is determined from the SiO_2/Na_2O ratio of the silicate units of each glass and the curve in Fig. 8. The results, plotted in Fig. 6 show a fairly good agreement with the experimental values. The fraction of the contribution from Model 2 is now expressed as,

$$f = \frac{1-x}{1+x}, \tag{3}$$

TABLE I Distribution of Na_2O between silicate and borate units of $(1-x)Na_2O \cdot SiO_2 \cdot xB_2O_3$ glass when a proportional distribution of Na$^+$ between SiO_2 and B_2O_3 is assumed

x	Composition
0.1	$0.812(Na_2O \cdot 1.22SiO_2) + 0.082(Na_2O \cdot B_2O_3)$ $+ 0.018B_2O_3$
0.2	$0.667(Na_2O \cdot 1.5SiO_2) + 0.133(Na_2O \cdot B_2O_3)$ $+ 0.067B_2O_3$
0.3	$0.538(Na_2O \cdot 1.86SiO_2) + 0.162(Na_2O \cdot B_2O_3)$ $+ 0.138B_2O_3$
0.4	$0.428(Na_2O \cdot 2.34SiO_2) + 0.171(Na_2O \cdot B_2O_3)$ $+ 0.229B_2O_3$
0.5	$0.333(Na_2O \cdot 3SiO_2) + 0.167(Na_2O \cdot B_2O_3)$ $+ 0.333B_2O_3$

and is plotted in Fig. 9. The values are close to those determined before. It implies that the distribution of Na^+ ions between the silicate units and the borate units is approximately proportional to the amount of SiO_2 and B_2O_3 present in these glasses of high Na_2O and low SiO_2 content.

Another example of the proportional distribution of Na^+ to the amount of SiO_2 and B_2O_3 is found in the $0.8Na_2O \cdot 0.8SiO_2 \cdot 0.4B_2O_3$ glass. The chemical formula of the glass can be expressed as $0.533(Na_2O \cdot 1.5SiO_2) + 0.267(Na_2O \cdot B_2O_3) + 0.133B_2O_3$. The I_{950}/I_{1080} ratio is 0.78, which is very close to 0.79 of the $0.8Na_2O \cdot SiO_2 \cdot 0.2B_2O_3$ glass and both glasses have SiO_2/Na_2O ratio = 1.5 for the average silicate unit. However, the composition $0.8Na_2O \cdot 0.8SiO_2 \cdot 0.4B_2O_3$ is on the join between disilicate and metaborate and the glass crystallized to α-$Na_2Si_2O_5$ and $Na_3B_3O_6$ (Fig. 4b) while the $0.8Na_2O \cdot SiO_2 \cdot 0.2B_2O_3$ glass crystallized to β-$Na_2Si_2O_5 + Na_2SiO_3 + Na_3B_3O_6$ (Fig. 4a). Thus, the mechanism governing the distribution of Na^+ ions in the glass is quite different from the one that operates during crystallization. If the same rule applied to the $Na_2O \cdot 0.5SiO_2 \cdot 0.5B_2O_3$ glass, Na^+ ions are found to be distributed equally between metasilicate and metaborate units both in the glass and during crystallization (Fig. 4c).

The above analysis is semiquantitative, because of the uncertainty introduced by the use of the peak height instead of integrated intensity. Accurate determination of the base line and deconvolution of the two bands were difficult for accurate intensity measurements. Also the uncertainty of the I_{950}/I_{1080} values in Fig. 8 was ignored when the curve was used for the determination of the SiO_2/Na_2O ratio or the I_{950}/I_{1080} ratio of the borosilicate glasses.

For the $(1-x)Na_2O \cdot 2SiO_2 \cdot xB_2O_3$ and $(1-x)Na_2O \cdot 3SiO_2 \cdot xB_2O_3$ series, the intensity of the 1100 cm^{-1} band decreases as x increases. This is probably due to the decrease in the number of $SiO_{5/2}$ units. Available Na^+ ions to create SiO^- non-bridging bonds decrease because, in addition to the decrease of the Na_2O/SiO_2 ratio of the glass composition, some of the Na^+ ions are also associated with borate units. As the B_2O_3 concentration increases, more Na^+ ions associate with borate units and beyond $x = 0.5$ almost all the Na^+ ions are linked to borate units and there are few Si–O$^-$ non-bridging bonds. Quantitative analysis of the distribution of Na^+ ions could be performed if the intensities of the 1100 cm^{-1} band were compared between the different samples with a good accuracy. In the present study, however, such measurement was not possible.

The results of the distribution of Na^+ ions in the glasses of high Na_2O/B_2O_3 ratio cannot be compared with the structure model proposed by Yun and Bray [10, 11]. This is because their structure model is not applicable to the glasses in the composition region where $Na_2O/B_2O_3 > 2$ due to a condition imposed by the fact that the total fraction of four-fold co-ordinated boron and three-fold co-ordinated boron must not be greater than one. The three equations derived from their structure model are:

$$N_{3A} = \frac{1.25}{1+K}(R - R_{max}),$$

$$N_4 = N_{4max} - \frac{0.25}{1+K}(R - R_{max}) \qquad (4)$$

and

$$R_{max} = \tfrac{1}{16}K + 0.5,$$

where N_{3A} and N_4 are the fraction of three-fold co-ordinated boron with 2 or 3 non-bridging oxygens and the fraction of four-fold co-ordinated boron, respectively. R is the mole ratio Na_2O/B_2O_3, K is the mole ratio SiO_2/B_2O_3, and R_{max} is the R where N_4 reaches maximum. For these equations R and K must be within the limit of

$$R \leqq -\tfrac{1}{16}K^2 + \tfrac{1}{2}K + 1, \qquad (5)$$

in order to satisfy the condition,

$$N_4 + N_{3A} \leqq 1. \qquad (6)$$

4.2. $Na_2O/B_2O_3 < 1$ region

In this composition range almost all Na^+ ions are linked to borate units and few Si–O$^-$ non-bridging bonds are present, which is also the conclusion reached from the NMR studies [10–12]. For the high SiO_2 content glasses the broad band at 460 to 500 cm^{-1} is a predominant feature of the spectra as in the SiO_2 glass spectrum. The broad band at about 440 cm^{-1} of SiO_2 glass is probably mainly due to bending or rocking of Si–O–Si bonds [4, 16]. The change of the band shape and the band shift to higher frequencies are probably caused by the incorporation of $[BO_4]$ units, $[BO_3]$ units and possibly some borate groups into the silica network. The shift of the 470 cm^{-1} band to 450 cm^{-1}, development of a shoulder at 480 to 490 cm^{-1} and the increase of the 770 cm^{-1} band intensity observed after the phase separation heat-treatment of the glass of 7 wt% Na_2O, 23 wt% B_2O_3, 70 wt% SiO_2 are due to the ejection of some boron from the silica network. The ejected boron may form a borate group responsible for the increase of the 770 cm^{-1} band intensity.

As the SiO_2 concentration decreases the 450 to 500 cm^{-1} band becomes less intense and the bands at 750 to 810 cm^{-1} due to borate groups become dominant in the spectra. The spectral features of borate groups in the borosilicate glasses (750 to 810 cm^{-1} and 1300 to 1600 cm^{-1}) are almost identical to those in the alkali borate glass spectra. For the lower SiO_2 content glasses the similarities are more clear, and moreover, the spectral features do not change after the glasses have been given phase separation heat-treatments.

Two plausible explanations for the above observations are:

(1) The phase separation is already present on a very small scale even before the phase separation heat-treatment, as suggested by Konijnendijk [7]. The spectral features of borate groups are mainly from the boron-rich phase and are not effected by the presence of the SiO_2-rich phase. However, this explanation is not compatible with the temperature dependence of the compositions of separated phases [13, 14].

(2) An alternative explanation is that in the high B_2O_3 and low SiO_2 concentration region only the Na_2O/B_2O_3 ratio determines types of borate groups occurring either in homogeneous glass or in phase-separated glass since all Na^+ ions are associated with borate units. The spectral features of the borate groups are due to strongly isolated vibrations of the atoms in the groups which are independent of how the groups are connected to the rest of the structure. Kristiansen and Krogh-Moe [21] calculated the normal frequencies of the metaborate ring with atoms of different mass substituted for hydrogen, and found that the symmetric vibration of the ring at 817 cm^{-1} is independent of the mass of atom substituted for hydrogen. Thus, the second explanation seems more plausible but more theoretical calculations on normal vibrations of borate groups are necessary.

5. Conclusions

Detailed Raman spectra of $Na_2O–SiO_2–B_2O_3$ glasses taken at small composition intervals show features due to both silicate and borate structural units. The spectra of the silicate structural units change systematically with composition reflecting the changing numbers of non-bridging oxygens per silica tetrahedron. The borate structural units seem to be less sensitive to details of composition. The implication is that the borate units are more molecular and that their vibrations are more highly localized that those of the silicate units.

Glasses with Na_2O/B_2O_3 ratios greater than 1 have sodium ions distributed between silicate and borate structural units approximately in proportion to the concentration ratio of silicon to boron. This is inferred from the changing ratio of bridging to non-bridging oxygens in the silica tetrahedra.

The Na^+ ions in glasses with $Na_2O/B_2O_3 < 1$ appear to be associated entirely with the borate groups and not with the silicate part of the structure. The characteristic Raman bands due to $Si–O^-$ non-bridging oxygens do not appear in these glasses.

The spectra of heat-treated glasses are very similar to the as-drawn glasses even in the phase separation region. It is inferred that these glasses are already clustered on an atomic scale.

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