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STRUCTURE OF BORATE GLASSES BY RAMAN SPECTROSCOPY

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INTRODUCTION

A large body of literature on the Raman spectra of glasses has now been accumulated. Vibrational spectra of borate glasses have been used to elucidate the structural units present in these glasses as exemplified by the work of Stevels, Konijnendijk, and Brill. Measurements are given in the present paper span for lithium, sodium, and potassium borate glasses. However, we will emphasize the linkages of the structural units and have something to say about phase separation in these glasses.

The spectrum of B_2O_3 glass itself is rather remarkable, and has attracted some attention apart from the binary and ternary glasses [1-3]. It contains a single strong band at 808 cm^{-1} which is very narrow for a vibrational mode of a glass. However, the remainder of the spectrum is very weak and smeared out. This band is considered strong evidence for boroxal rings in B_2O_3 glass [4].

Our interest in the Raman spectra of the alkali borates dates back to 1971 when some spectra of sodium and potassium borate glasses were reported [5]. Comprehensive investigations of alkali borate and borosilicate glasses by Konijnendijk and Stevels [6,7] provide strong evidence for the gradual replacement of the boroxal ring by other structural units as the alkali concentration is increased.

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EXPERIMENTAL

All glasses were prepared from reagent grade alkali carbonate and H_3BO_3 . Mixtures of appropriate composition were milled together and then heated in ten gram lots in platinum crucibles. The mixes were first fired in air at 950°C for two hours and then heated at 950°C ($\text{K}_2\text{O}-\text{B}_2\text{O}_3$ glasses), 1000°C ($\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ glasses) and 1000°C ($\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glasses) for an additional hour to achieve uniform melting. After this heating procedure, rods approximately 2 mm in diameter were drawn from the melt and rapidly quenched in a cool air stream. Other quenching procedures used in connection with phase separation studies will be described later.

To determine if the glass had crystallized upon cooling, pieces of the bulk glass were powdered and x-ray diffraction patterns were determined. Although the more alkali-rich borate glasses crystallize readily, all Raman data reported here were determined on rods for which there was neither optical nor x-ray evidence for crystalline phases.

As an additional control on composition, a selected group of the sodium borate glasses were chemically analyzed for B_2O_3 and Na_2O . In general the glasses were within one mole percent of the starting composition indicating little change in composition during the melting procedures.

Raman spectra were measured in a 90° scattering configuration from untreated bulk rods. The spectrometer was a Spex Ramalog with an argon ion laser source and cooled RCA 31034 photomultiplier. Best results were obtained from the 488 nm (blue) line using power levels of a few hundred milliwatts.

Griscom [8] lists some of the advantages of Raman spectroscopy as a tool for the investigation of glass structures. We would add another. Raman scattering from bulk rods produces a spectrum in which the line shapes are characteristic of the true spectrum. There is no distortion. This is in marked contrast to infrared spectra measured by conventional techniques of vacuum cold-pressing powdered glass into alkali halide pellets. In this case there are substantial distortions and additional broadening effects on the spectra. We will show that the Raman line shape, particularly the line width, is as important a measurement as the band frequency.

RAMAN SPECTRA OF THE ALKALI BORATE GLASSES

Spectra of the sodium and potassium borates have been published [6,7] and are not repeated here. Spectra of the lithium borate glasses (Fig. 1) illustrate the main features. For purposes of

Fig. 1. Raman spectra for $XLi_2O \cdot (1-X)B_2O_3$ glasses.

description and discussion the spectra can be divided into three regions: (i) the high frequency region from 900 to 1500 cm^{-1} where several broad relatively weak bands occur; (ii) the region from 200 to 900 cm^{-1} which is dominated by a pair of sharp intense bands at 806 and 776 cm^{-1} . These bands have also dominated most previous discussion of the alkali borate spectra; (iii) the region below 200 cm^{-1} .

The spectra for Region (i) are shown in Fig. 2. This is the region of the spectrum which for most structures is dominated by bands due to the symmetric stretching modes of the metal-oxygen bonds that make up the structural units. The borate glasses, however, are weak scatterers in this region. Much of the observed scattering may be due to the weakly allowed asymmetric stretching

Fig. 2. Raman spectra of lithium borate glasses in Region (i). All measurements were made on pulled rods and intensities are roughly ($\pm 20\%$) comparable.

modes. There is a broad and weak scattering continuum that extends from 1200 to 1600 cm^{-1} . At low alkali content the distribution is weighted towards the 1550 cm^{-1} broad maximum. The continuum changes relatively little until the alkali content reaches 0.25 mole percent where it shifts abruptly to 1450 cm^{-1} . The broad maximum first decreases and then increases in intensity and occurs at higher frequency for the $X = 0.4$ glass, the most alkali-rich composition examined.

Region (ii) is of considerable interest. Most of the glass compositions examined exhibit two bands in this region (Fig. 3). One near 805 cm^{-1} is very sharp (as glass spectra go) and varies in intensity with alkali content. As the alkali percentage increases the 805 band decreases in intensity and at approximately 25 mole percent alkali it disappears. The second band at 775 cm^{-1} is already visible at 9% alkali and increases in intensity with

Fig. 3. Variations in the relative intensities of the $805\text{--}775\text{ cm}^{-1}$ bands for a series of sodium borate glasses.

increasing alkali content. It also is a sharp band in the low alkali region. The two bands are of comparable intensity at 16 mole percent alkali--the location of the so-called boron anomaly. The 775 cm^{-1} band continues to increase in intensity up to approximately 35 mole percent alkali where it reaches a maximum value. In the range of 25 to 40 mole percent alkali the 775 cm^{-1} band is the only feature in this region of the spectrum. It becomes noticeably broader but remains more or less constant in intensity across this composition range.

The frequency dependence of these two bands is shown in Fig. 4. The high frequency band decreases in frequency very slightly with increasing alkali content. Extrapolating to zero alkali the position of the band agrees exactly with the frequency of B_2O_3 glass

Fig. 4. Variation of band frequency with alkali content for a series of sodium borate glasses.

observed at 808 cm^{-1} . The band at 778 cm^{-1} remains constant in frequency to within experimental error between 9 and 25 mole percent alkali. Between 25 and 35 mole percent alkali the frequency continuously decreases.

The band width of these two sharp peaks also varies with alkali concentration. These widths were obtained by a careful graphical deconvolution of the overlapping bands. The results are shown in Fig. 5 and will be discussed later.

Spectra for Region (iii) are shown in Fig. 6. There is a well defined broad band in this region that is easily resolved from the descending Rayleigh tail. The peak shifts linearly towards higher frequencies as the alkali content of the glass increases. The linear trend in frequency extrapolates to the 24 cm^{-1} value found by Stolen [9] for B_2O_3 glasses. Similar bands have been observed

Fig. 5. Variation of full width at half height for a series of lithium borate glasses. The widths were obtained from carefully deconvoluted bands.

Fig. 6. Raman spectra of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glasses in low frequency region.

for pure B_2O_3 , SiO_2 and GeO_2 glasses [9]. It was shown (for a discussion see [10]) that the band is due to a temperature-weighted density of states arising from low-lying optic modes as well as the higher-lying acoustic modes. The shift in band position to higher frequency may be due to the less open structure of the glass with increasing alkali concentration.

PHASE SEPARATION

Alkali borate glasses are known to phase separate on prolonged heating and it is of interest to investigate the effect of phase separation on the Raman spectra. Shaw and Uhlmann [11] using electron microscopic techniques mapped the metastable solvi in the alkali borate systems by first phase separating the glasses at low temperatures and then clearing them by reheating at temperatures above the solvi. Shaw and Uhlmann's solvi for lithium and potassium borate glasses are shown in Fig. 7. Glasses with 0.1 mole fraction Li_2O or K_2O were heat treated at the temperatures shown by the circles in Fig. 7. Three heat treatments were used. First glasses were quenched from the melt at $1000^\circ C$ by squeezing drops of the liquid between aluminum blocks. Secondly, rods were pulled from the melt in the same manner as the rods used for all other Raman spectra. Thirdly, pulled rods were heat treated at $540^\circ C$ for 10 hours (potassium borate glass) and $600^\circ C$ for three hours (lithium borate glass). The main Raman band is shown in Fig. 8 for the potassium borate glass. The lithium borate glass gave an identical result. It can be seen that the line shapes are identical to within experimental error regardless of heat treatment.

The 808 cm^{-1} band and the 775 cm^{-1} band have been interpreted as measures of two quite distinct kinds of ring structures in the borate glass. Phase separation into a boron oxide-rich region and an alkali-rich region would require the formation of different sorts of rings in each of the phase separated glasses which might be expected to produce distinctly different Raman spectra.

DISCUSSION

Before embarking on a detailed analysis of Raman spectra in relation to glass structure, it is perhaps worthwhile to review briefly some of the experimental tools that have been used to investigate glass structures. Many more details are given by Griscom [8]. Each of these tools allows one to "see" in some indirect way the structure of the glass, but their "field of view" is substantially different.

Certain tools, notably NMR, EPR, Mössbauer and optical spectroscopy focus on specific target atoms in the glass. The geometry

Fig. 7. Metastable solvi for alkali borate glasses from [10]. Circles show temperature-composition of heat treated glasses.

of the nearest neighbor anion coordination polyhedron of the target atoms can be determined with some certainty. The existence of BO_4 tetrahedra and BO_3 triangles as the basic structural building blocks of borate glasses rests on a fairly substantial foundation.

Larger structures in glasses become more equivocal. Infrared spectroscopy should be sensitive to short range order structures and should reveal all primary bonds including those that link the triangles and tetrahedra into larger structural units. Unfortunately, there are few reliable infrared spectra of borate glasses.

Fig. 8. Raman spectra of potassium borate glass after the heat treatment shown.

Common practice is to grind the glasses to powders, vacuum cold press these into alkali halide pellets, and measure the spectra on the resulting pellets. It is known (for example Ref. 12) that IR spectra of powders have distorted line shapes and shifted peak frequencies. Although the general features of covalent structures such as the borate glasses are likely to be approximately correct, arguments based on small details of band frequency and band shape are not reliable. More measurements using either thin films for direct transmission measurements or measurements by specular reflectance spectroscopy followed by Kramers-Kronig analysis to transform the reflectance spectra into absorption spectra would be helpful.

Raman scattering measurements from bulk glasses give accurate spectral line shapes so that comparisons and analyses of the spectra can be made with some confidence. However, the scale of the structures which will have some influence on the line shapes are less certain. Based on empirical experience with crystalline

materials, it appears that Raman spectra are sensitive to structures on a size scale of 2 to 3 nm. Structural detail within volumes of glass of these dimensions can be quite complex and when the Raman spectrum consists of only a few broad bands, there is considerable indeterminacy in the structural interpretation.

Concepts of Glass Structure

Borate glass structures are complex, and there is the possibility of at least four hierarchies of structural organization: (i) the triangles and tetrahedra that act as the basic structural units; (ii) possible closed ring molecular-like structures that make up the building blocks of the Krogh-Moe model [8]; (iii) organizations on a larger scale which might be described as clusters, thermal fluctuations in composition, or incipient nuclei for phase separation, and (iv) distinct phase-separated regions.

These latter two require comment because the term phase-separation is somewhat confused in the glass literature. A two-phase glass must consist of two non-crystalline regions separated by a distinct boundary or interface. The individual phases must have a uniform Gibbs free energy within the bulk, but a discontinuity in the Gibbs free energy across the interface. Phase-separated regions, therefore, are larger structures than the first three and would appear to most of the measuring tools as additive mixtures of two different materials. Clustered glasses are not phase-separated in the phase rule sense but merely consist of regions of differing composition, without any distinct phase boundary between the regions. One could imagine the scale of these regions being rather small, perhaps on the order of 2 to 10 nm, a size range very difficult to observe by any of the available tools.

Interpretation of the Raman Spectra

Returning now to the specific problem of relating observed Raman spectra to borate glass structure, we begin by pointing out three salient features of the spectra: (i) the exceptionally sharp bands at 775 and 808 cm^{-1} that have attracted so much attention; (ii) the absence of any intense or well defined feature in the high-frequency region, and (iii) the overall lack of spectral detail in the low alkali glasses and the gradual transition to more detailed spectra as the alkali content increases. In the glasses of highest alkali content (Fig. 1) all bands are of comparable intensity and width and only these alkali borate glass spectra are comparable to spectra observed in alkali silicate and more complex ternary silicate and even borosilicate glasses [13-17].

The Raman and infrared spectra of borate glasses are generally interpreted as arising from a few well defined ring structures in the glass. This interpretation seems to be most firm for B_2O_3 and alkali borates with low alkali content in which the existence of boroxal rings can be inferred with some confidence.

In a theoretical study [18-19] Krogh-Moe provided strong evidence that such boroxal rings can give rise to a sharp Raman peak at 800 cm^{-1} even if they are joined in a random manner. Moreover, he showed that all other peaks in the spectra should be much broader than the 800 cm^{-1} band. Braver [14] has shown in a more general study how a similar behavior can arise in silicates. The results of this latter study suggest that for any network glass certain vibrational modes will be relatively insensitive to disorder. These modes will then stand out in the Raman spectra of the glass. The width and frequencies of these bands do respond to a small degree to the general glass structure, but the random nature of the glass is most dramatically apparent in the width of all the other peaks in the spectra.

The interpretation of the Raman spectra of a glass usually reduces to an interpretation of the behavior of the strong Raman peaks. The information obtainable is, generally, the peak frequency and peak width. These two parameters can in no way be used to uniquely deduce the structure of a glass, the random nature of which may require tens of parameters to describe. However, in combination with other physical and chemical evidence some qualitative information may be deduced. It is in this spirit that the Raman spectra are usually interpreted in terms of well defined ring structures [6,7,13-17].

Let us assume, then, that the Raman spectra of alkali borate glasses indicate that, as alkali is added to B_2O_3 , the boroxal rings giving rise to the 808 cm^{-1} peak are systematically replaced by some other type of structure (or structures) giving rise to the peak at 776 cm^{-1} . (We will speak here of two structures, although there are possibly more.) The question we would like to ask is the following: Are these different structures intimately joined together or do they occur in different phase-separated regions of the glass? (We will not enter here into a discussion of the nature of these structures, as this has been discussed exhaustively by the Dutch group.)

The experimental evidence bearing on this question consists of: the frequencies of the two peaks at about 805 and 775 cm^{-1} (Fig. 4), the widths of these peaks obtained by careful deconvolution of the spectra (Fig. 5), and the behavior of the spectra for different heat treatments (Fig. 8).

Consider first the peak frequencies. The fact that the peak

frequencies are relatively insensitive to concentration does not mean that the two types of structures giving rise to the peaks are in different phase-separated regions. As discussed above, the strong Raman peaks of some kinds of ring structures can be expected to be relatively insensitive to the way in which the rings are joined together. The constancy of peak frequencies is then taken to indicate that basically the structures are well defined for all compositions.

However, the fact that the peak width of the 805 cm^{-1} band increases monotonically with increasing alkali concentration (Fig. 5) does indicate that the environment of the boroxal rings does vary with changing alkali concentration. This in turn suggests that these rings are not in macroscopically phase-separated regions, but rather that the different structures present are linked to each other in some manner.

It does not seem likely, however, that the two different structures are linked together in a completely random manner, but rather that some sort of clustering of like structures occurs. The evidence for this is the behavior of the spectra upon heat treatment (Fig. 8). The fact that the spectra are independent of a heat treatment which, according to Shaw and Uhlmann, causes the glass to phase-separate means that the immediate environment of each type of structure is unchanged by the heat treatment.

Thus we may conclude that the two different ring structures that give rise to the two Raman peaks at 805 and 775 cm^{-1} are clustered in some manner.

We must emphasize that we are not talking about phase separation in the Gibbs phase rule sense. The spectral behavior observed can be accounted for by clusters of some unknown size scale which are strongly linked to each other to form a continuous network. Such glasses would be extremely disordered with a large variability in the B-O-B bridging bond angles. Although the proposed ring structures may be present, certainly there is great disorder in the way in which the rings are linked.

There is some evidence for compositional fluctuations in the thermodynamic behavior of borate liquids. An earlier study [20,21] probed the structure of alkali tetraborate liquids using Ni^{2+} as a probe. Thermodynamic modeling of the liquidus surface suggested that the liquid segregated into boron-rich regions and nickel (and perhaps also alkali) rich regions. Optical spectra of Ni^{2+} in alkali tetraborate glasses provided supporting evidence for the thermodynamic model.

CONCLUSION

Raman spectra of the alkali borate glasses have been presented with emphasis on the implications of detailed frequency shifts and line shapes. The results have been interpreted on a rather complicated three-level hierarchy of glass structures which include boron-oxygen polyhedra, topologically closed rings of polyhedra, and larger scale interconnected clusters of alkali-rich and alkali-poor structures. Both the model and the argument are deliberately vague. The borate glasses appear to be highly disordered materials with a size scale such that no presently available tool gives a really clear view of the structural detail.

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