

NEUTRON SPECTROSCOPIC STUDIES OF CAESIUM BORATE CRYSTALS AND GLASSES

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The properties of alkali borate glasses are determined by the extent and detail of any molecule-like short-range order which persists in the amorphous structures. Although there is considerable evidence that these structures can contain significant proportions of superstructural units, quantitative evidence is difficult to obtain experimentally. Spectroscopic data are invaluable for testing models of glass structure and the inelastic neutron scattering technique can be used to supplement information gained from optical measurements. Since the observed spectra are free from the matrix element and selection rule effects that are unavoidable for optical spectra, quantitative interpretation should be easier. The use of inelastic neutron scattering techniques for investigating the role of superstructural units in $\text{Cs}_2\text{O-B}_2\text{O}_3$ glass structures is discussed. Data have been measured for the vitreous forms of caesium enneaborate and pentaborate along with polycrystalline caesium enneaborate, pentaborate and triborate. The known crystal structures allow any associated superstructural unit modes in the neutron-weighted vibrational density of states (VDOS) of the glass forms to be identified. The widths of the features in the VDOS give additional information on the dispersive nature of the modes and hence the molecular character. To assist in the identification of larger structural units, new Raman measurements have been completed for a range of five glasses and four crystalline compositions in the same system. It is concluded that boroxol units are only formed in vitreous samples containing alkali up to the tetraborate composition. A glass with the enneaborate composition contains both boroxol and triborate units, while glasses of pentaborate composition appear to contain pentaborate and possibly triborate groups.

Introduction

The use of spectroscopic techniques to investigate the superstructural unit concentrations in the borate glasses began with the detailed study of the Raman spectra of vitreous B_2O_3 , where there is an extremely sharp line at 100meV (803cm^{-1}) [1,2], due to the breathing mode of a B_3O_6 boroxol ring, where O represents a bridging oxygen atom. Earlier structural work on borate glasses [3,4,5] had provoked controversy when Hägg[6] challenged Zachariasen's continuous random network hypothesis and proposed groupings in glasses larger than the basic

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structural units. Krogh-Moe[7] and Bray and co-workers[8,9] both confirmed the existence of these larger structural groupings in borate glasses.

Raman spectroscopy [10] has proved valuable in identifying these larger groupings by comparisons with results for crystalline systems where peak assignments can be made reliably using the results of crystal structure determinations. Whilst there have been many crystal structure studies of complex synthetic borates and borate minerals, there is a surprising lack of structural data for the simple *anhydrous binary borates* required for the interpretation of both neutron and NMR data for the corresponding glasses. For example, in the case of the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ system, a full crystal structure determination has only been performed for 7 out of a total of 22 polymorphs listed in the Gmelin Handbook.[11]. It is important to note that the crystalline borate networks necessary for the interpretation of data for related glasses should ideally be formed by a *single superstructural unit species*, with no independent BO_3 triangles or BO_4 tetrahedra. Table 1 [12] lists such crystalline compounds or, for superstructural units where no known crystalline compound exists, one or more compounds containing the given superstructural unit, together with a list of the other units present. In Table 1, compounds of the form $m\text{Cs}_2\text{O}\cdot n\text{B}_2\text{O}_3$ are denoted by the abbreviation $m\text{Cs}\cdot n\text{B}$, NBO indicates a non-bridging oxygen atom. Greek letters are used for polymorphs that are stable at different temperatures and Roman numerals for those formed at different pressures.

Unfortunately, Raman spectroscopy cannot be employed to determine the absolute numbers of superstructural units in borate glasses, because of unknown (and large) matrix element effects. This is not the case for the neutron inelastic scattering technique, which was used [13,14] to derive an effective VDOS for vitreous B_2O_3 . The relative size of the symmetric breathing mode of a B_3O_6 boroxol ring showed that the fraction of the boron atoms in such rings (f) is indeed very close to that given by neutron diffraction experiments, 0.80 ± 0.05 [15]. A similar study of the VDOS of a glass of composition $\text{Rb}_2\text{O}\cdot 0.33\text{B}_2\text{O}_3$ [14] agreed with Raman data [16] that boroxol rings are not present in the structure of this glass. However, a sharp peak observed at 610cm^{-1} (75.6meV) in the Raman spectrum attributed to the stretching mode of a $\text{B}_3\text{O}_3\text{O}_3^{3-}$ cyclic metaborate ion was not visible in the neutron data.

More recently, spectroscopic measurements using the neutron inelastic scattering method have begun [17, 18, 19] for the caesium borate glass system, which has the advantage that crystalline polymorphs contain known fractions of a variety of superstructural units that may also appear in the equivalent glasses. Data were presented for the neutron-weighted VDOS for samples of polycrystalline caesium pentaborate ($\text{Cs}_2\text{O}\cdot 5\text{B}_2\text{O}_3$), which contains only pentaborate groups (so f is equal to zero), for polycrystalline caesium triborate ($\text{Cs}_2\text{O}\cdot 3\text{B}_2\text{O}_3$; only triborate groups) and vitreous caesium enneaborate ($v\text{-Cs}_2\text{O}\cdot 9\text{B}_2\text{O}_3$.) The boroxol ring breathing mode was also observed in vitreous caesium enneaborate (at 99.9 meV) and, as expected, in the VDOS of polycrystalline caesium enneaborate. The triborate ring breathing mode was also identified from Raman data, and characterised in the neutron weighted VDOS for polycrystalline caesium enneaborate and polycrystalline caesium triborate. The sharpness of the split peak and its position (at 95.5 meV and 98.6 meV) in the polycrystalline caesium pentaborate effective VDOS, enabled its association with vibrational modes of the pentaborate double ring unit [7].

This paper reports and discusses a neutron scattering measurement of the VDOS for a vitreous sample with the caesium pentaborate composition, together with Raman measurements for a range of glasses and crystals in the same system.

2. Inelastic neutron scattering technique

The inelastic neutron scattering technique [20] can have an energy transfer resolution comparable to that available optically. A dynamical structure factor, $S(\mathbf{Q},E)$, may be measured with the optimum resolution in scattering vector and energy transfer for a variety of different types of excitation. \mathbf{Q} is the magnitude of the scattering vector and E is the energy transfer ($E = E_0 - E'$, where E_0 and E' are the initial and final neutron energies). Statistical accuracy remains a significant problem for detailed studies due to the limited source intensities available at present.

For borate glasses local atomic configurations in the short-range order result in localised vibrations (e.g. the breathing modes of superstructural units) revealed as sharp features in the effective vibrational density of states (VDOS).

The dynamical structure factor, $S(Q, E)$, may be derived from the measured quantity in an inelastic neutron scattering experiment which is the double differential scattering cross-section [21]. If the scattering function is averaged over a wide range of the scattering vector Q to eliminate coherent scattering effects, an effective neutron weighted VDOS, $G(E)$, can be derived from the one phonon creation self scattering function in the incoherent approximation as described in [21]. A more complete description of the theory is given in [19].

3. Experimental details and results

3.1. Sample Preparation

All of the samples for this series of neutron measurements were prepared using boric acid enriched to 99.27% ^{11}B to minimise neutron absorption due to the B^{10} isotope. A vitreous caesium pentaborate sample was prepared in Cedar Rapids. Boric acid was converted to B_2O_3 , crushed, mixed with high purity Cs_2CO_3 , and then heated (at 1100°C) in a platinum crucible under N_2 before pouring onto a stainless steel plate (still under N_2). The preparation conditions for the samples of polycrystalline caesium enneaborate, caesium pentaborate and caesium triborate compounds from glasses of the correct composition have been described in [17] and [18]. The phase purity of the crystalline samples was investigated by X-ray diffraction and by DTA determination of the melting point.

3.2. Inelastic Neutron Scattering

The phased rotor inelastic scattering spectrometer MARI [22] uses the time of flight method at the ISIS UK pulsed neutron source. Measurements were performed at two incident neutron energies, 250 meV to investigate the full VDOS and 135 meV to obtain the best energy transfer resolution in the region of sharp superstructural breathing modes. In each case, the scattering was recorded as a function of the scattered neutron time of flight in 922 detectors located at scattering angles between 3° and 135° at an evacuated path length of 4.0m from the sample. A powdered sample of vitreous caesium pentaborate weighing 53g was held at 15K in a thin walled aluminium alloy container in a closed circuit refrigerator. The neutron weighted VDOS ($G(E)$) for this sample (Fig. 1 and Fig. 2) was obtained from data corrected for instrumental background and container scattering by then integrating the 135 meV scattering function between Q values of 4\AA^{-1} and 12\AA^{-1} and the 250 meV data between 7\AA^{-1} and 15\AA^{-1} as discussed in section 2. The spectrometer resolution at 100 meV (800 cm^{-1}) energy transfer for the 135 meV data was 1.6 meV (12 cm^{-1}).

3.3. Raman Spectroscopy

Raman spectra were obtained at Warwick University with a Renishaw Invia Raman spectrometer equipped with a 20mW Argon Laser operating at 514nm. The measurements reported here were acquired at room temperature with 10mW incident laser power and a x50 objective. The spectrometer resolution was approximately 2 cm^{-1} . Measurements for five glass compositions in the caesium borate system are shown in Fig. 3. Raman spectra for the same polycrystalline samples whose VDOS was reported in [19] were also recorded (Fig. 4). Peak positions obtained by Gaussian fitting techniques are given Table 2 for the glass samples and in Table 3 for the polycrystalline samples.

4. Discussion

As the alkali (Cs_2O) content is increased, the fraction of four-fold co-ordinated boron atoms, x_4 , increases linearly up to a $\text{Cs}_2\text{O}/\text{B}_2\text{O}_3$ ratio, R , of about 0.4 and is equal to R . The pentaborate group requires the least alkali content to form followed by the triborate unit. As these groups increase in concentration, the fraction of boroxol rings should decrease. To attempt to detect the formation of these superstructural units all the VDOS and Raman spectra were fitted using a Gaussian line shape to extract frequencies, intensities and line widths wherever this was

possible. By comparison to the result for vitreous B_2O_3 , signatures of 3-fold boron coordination in all the measured VDOS (Fig.1, 2, 5 and 6) for the other crystals and glasses are provided by broad features at 661 and 730 cm^{-1} with a further unresolved feature at about 1335 cm^{-1} . These features correspond to peaks 4, 5 and 6 in the numbering scheme used by Galeener and Thorpe[1] for the Raman spectrum. The lower two modes arise from the symmetric stretch and out-of-plane deformation of BO_3 triangles while the highest at 1335 cm^{-1} has been found to be a signature of 3-fold co-ordinated boron[23].

4.1. Vitreous and Crystalline Caesium Pentaborate

The crystal structure of $Cs_2O.5B_2O_3$ [24] is based on zigzag boron oxygen layers built up from rigid pentaborate groups and the measured Raman spectrum (Fig. 4) is dominated by sharp modes at 589, 760, 786, 876, and 1476 cm^{-1} with FWHM values of 15.7, 17.4, 18.0, 13.7 and 18.9 cm^{-1} respectively (Table 3). The Raman spectrum for a glass of composition $Cs_2O.4B_2O_3$ (Fig. 3)(Table 2) is also dominated by an equally narrow mode at 767 cm^{-1} (FWHM 22.1) with a nearby small unresolved feature at 794 cm^{-1} (FWHM 15.3). The Raman results are inconclusive but suggest that the pentaborate group is present in this glass. There are no indications of a significant fraction of boroxol rings.

$G(E)$ derived from $S(Q, E)$ measured for the caesium pentaborate crystalline sample (Fig. 5 and Fig. 6) has a broad feature at 588 cm^{-1} , along with distinctive narrow peaks 769, 794 and 1205 cm^{-1} associated with the pentaborate grouping. The result of an identical experiment for a vitreous sample with the caesium pentaborate composition $Cs_2O.5B_2O_3$ (Fig. 1 and Fig. 2) show distinguishing weak peaks at 589, 764 and 796 cm^{-1} thus confirming the presence of pentaborate groups in the glass. As the key signature mode for the triborate group is at 764 cm^{-1} (see section 4.2 below) the presence of this grouping cannot be eliminated by these data. A strong feature in the Raman spectrum for the crystal at 1205 cm^{-1} was not present in the glass and is shown later to be indicative of the fraction of 4-fold coordinated boron atoms, x_4 . Again the data do not indicate any boroxol rings in the glass form.

4.2. Vitreous and Crystalline Caesium Triborate

Crystalline caesium triborate also contains one type of borate grouping, in this case the triborate group [25]. The measured Raman spectrum (Fig. 4)(Table 3) for this compound has strong narrow peaks at 753 and 1340 cm^{-1} (FWHM 15.9 and 20.8 cm^{-1}) with weaker narrow features at 653, 950 and 981 cm^{-1} (FWHM 14.6, 20 and 19 cm^{-1}). The results for a vitreous sample with the same composition (Fig. 3)(Table 2) also show a strong narrow feature at 764 cm^{-1} (FWHM 28.4 cm^{-1}), which has been assigned to a ring breathing mode of six atom borate rings in the triborate grouping [25].

The VDOS derived from neutron scattering measurements from the polycrystalline sample (Fig 5 and Fig. 6) should also indicate features which can provide indications of the presence of triborate groups. Strong features are found at 765, 730, 704 and 1353 cm^{-1} . The first and last of these peaks provide a signature of the group in both Raman and neutron spectra. A broad feature centred at about 600 cm^{-1} is also found in the VDOS of the pentaborate glass.

4.3. Vitreous and Crystalline Caesium Enneaborate

The crystal structure of all phases of caesium enneaborate ($Cs_2O.9B_2O_3$) consists of two separate interpenetrating boron oxygen networks [26]. Each network is made up of planar boroxol groups (B_3O_6) and triborate groups, (B_3O_7). The number of boron atoms associated with each group is in the ratio 2:1 respectively and thus f is equal to 0.67.

The Raman spectrum (Fig. 4; Table 3) for a polycrystalline sample has features at 669 and 800 cm^{-1} (FWHM 15.7 and 22.8 cm^{-1}), which characterise the boroxol groups in the structure [2]. Peaks at 656 and 745 cm^{-1} (FWHM 15.6 and 14.5) identify the triborate groups, as found for the caesium triborate crystal in section 4.2. For the glass with the enneaborate composition, the Raman spectrum (Fig. 3; Table 2) exhibits a peak at 803 cm^{-1} (FWHM 18.2 cm^{-1}) arising from the symmetric stretching mode of the boroxol ring which is the most intense peak. A second

broad peak at 662 cm^{-1} may contain components from the 669 and 656 cm^{-1} excitations of boroxol and triborate groups, respectively, as observed for the crystal form. The strong peak at 771 cm^{-1} also provides evidence of the presence of the triborate group in this glass but may prevent observation of pentaborate modes at 769 and 794 cm^{-1} .

In the effective VDOS for crystalline caesium enneaborate (Fig. 5 and Fig 6) a sharp feature at 803 cm^{-1} , as in the VDOS for vitreous B_2O_3 (Fig. 1), corresponds to the boroxol ring symmetric stretch mode in which two thirds of the boron atoms participate. It has a weighting similar to that at 808 cm^{-1} in the VDOS for vitreous B_2O_3 . Thus f for vitreous B_2O_3 cannot be significantly less than that found in this crystalline structure (0.67). A sharp feature observed at 761 cm^{-1} is associated with the peak at 771 cm^{-1} in the equivalent Raman spectrum and confirms the assignment as a stretching mode of the triborate unit. There is no indication of the other triborate signature mode at 1353 cm^{-1} although a complex feature is observed at 1306 cm^{-1} . The signature of the boroxol ring at 806 cm^{-1} is also observed for the sample of vitreous caesium enneaborate (Fig. 1 and Fig 2) with a similar weighting to the same mode in the VDOS for vitreous B_2O_3 . A complex small feature centred at 770 cm^{-1} is unfortunately not well defined statistically but does suggest that pentaborate and triborate groups may be present in the structure of this glass. In contrast, the Raman spectrum (Fig. 3; Table 2) would indicate that only triborate groups are present.

5. Conclusions

The experiments described above demonstrate that neutron scattering studies, with high-energy transfer resolution, can provide important extra information about the structure of borate glasses when used in conjunction with measured Raman spectra. Narrow lines arising from localised vibrational modes of boroxol, triborate and pentaborate units have been identified by studying the VDOS and Raman spectra of polycrystalline caesium borates containing structural units which may occur in the glass.

The size of the symmetric breathing mode features in the VDOS of the vitreous and crystalline samples provides evidence that the fraction of boron atoms in boroxol rings in vitreous B_2O_3 is close to that given by the diffraction and NMR experiments.

For the caesium borate system, boroxol units are only formed in vitreous samples containing alkali up to the tetraborate composition. A glass with the enneaborate composition contains both boroxol and triborate units, while a glass of pentaborate composition definitely contains pentaborate groups and possibly triborate units. It is not possible to deduce the fractions of these more complex superstructural units from the results presented here. These can only be determined by comparing the measured VDOS with those derived from dynamical calculations that are based on realistic model structures containing predicted populations of superstructural units.

6. Acknowledgements

Support both financial and technical from ISIS, RAL CLRC, EPSRC and the J. J. Thomson Physical Laboratory are gratefully acknowledged.

7. References

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Figure Captions

- Fig. 1 The neutron weighted VDOS, $G(E)$, for samples of vitreous B_2O_3 , $Cs_2O\ 9B_2O_3$ and $Cs_2O\ 5B_2O_3$, measured using neutrons with 135meV incident energy
- Fig. 2 The neutron weighted VDOS, $G(E)$, for samples of vitreous B_2O_3 , $Cs_2O\ 9B_2O_3$ and $Cs_2O\ 5B_2O_3$, measured using neutrons with 250meV incident energy
- Fig. 3 Raman spectra for five glasses in the caesium borate system
- Fig. 4 Raman spectra for 4 crystalline compositions in the caesium borate system
- Fig. 5 The neutron weighted VDOS, $G(E)$, for samples of polycrystalline $Cs_2O\ 9B_2O_3$, $Cs_2O\ 5B_2O_3$ and $Cs_2O\ 3B_2O_3$, obtained using neutrons with 135meV incident energy
- Fig. 6 The neutron weighted VDOS, $G(E)$, for samples of polycrystalline $Cs_2O\ 9B_2O_3$, $Cs_2O\ 5B_2O_3$ and $Cs_2O\ 3B_2O_3$, obtained using neutrons with 250meV incident energy.

Table 1 Borate Crystalline Compounds Containing Superstructural Units

Unit	Formula	Crystalline Compound(s)	
		Single Unit	Multiple Units
Structural Units			
BO ₃ Triangle	BØ ₃	B-I	-
BO ₄ Tetrahedron	BØ ₄ ⁻	γ-Li·B	-
BO ₃ Triangle with NBO	BØ ₂ O ⁻	Li·B, Ca·B	-
Superstructural Units			
Boraxol	B ₃ Ø ₆	-	Cs·9B (+ B ₃ Ø ₇ ⁻)
Pentaborate	B ₅ Ø ₁₀ ⁻	K·5B, Rb·5B, Cs·5B	-
Triborate	B ₃ Ø ₇ ⁻	Li·3B, Cs·3B	-
Di-pentaborate	B ₅ Ø ₁₁ ²⁻	-	Na·2B (+ B ₃ Ø ₆ O ²⁻), Ba·2B (+ B ₃ Ø ₈ ²⁻)
Diborate	B ₄ Ø ₉ ²⁻	Li·2B, Zn·2B, Mg·2B	-
Tri-pentaborate	B ₅ Ø ₁₂ ³⁻	-	2Ca·3B (+BØ ₄ ⁻)
Di-triborate	B ₃ Ø ₈ ²⁻	-	3Li·7B (+ B ₃ Ø ₇ ⁻ + BØ ₃), K·2B & Rb·2B (+ B ₄ Ø ₉ ²⁻ + BØ ₃), Ba·2B (+ B ₅ Ø ₁₁ ²⁻)
Triborate with NBO	B ₃ Ø ₆ O ²⁻	-	Na·2B (+ B ₅ Ø ₁₁ ²⁻)
Metaborate	B ₃ Ø ₉ ³⁻	Ca·B-IV, Sr·B-IV, Cu·B	-
Anions			
Cyclic Metaborate	B ₃ Ø ₃ O ₃ ³⁻	Na·B, K·B, α-Rb·B, Cs·B, Ba·B	-
Pyroborate (2 × BØO ₂ ²⁻)	B ₂ ØO ₄ ⁴⁻	2Na·B, 2Mg·B, 2Ca·B, 2Sr·B	-
Orthoborate	BO ₃ ³⁻	α-3Li·B, 3Na·B, 3Ag·B-I, 3Tl·B, 3Zn·B, 3Mg·B, 3Ca·B, 3Sr·B	-

Table 2 Peak positions (cm^{-1}) in Raman spectra for caesium borate glasses and vitreous boron oxide

$\text{Cs}_2\text{O} \cdot 2\text{B}_2\text{O}_3\text{-v}$ Raman	$\text{Cs}_2\text{O} \cdot 2.4\text{B}_2\text{O}_3\text{-v}$ Raman	$\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3\text{-v}$ Raman	$\text{Cs}_2\text{O} \cdot 4\text{B}_2\text{O}_3\text{-v}$ Raman	$\text{Cs}_2\text{O} \cdot 9\text{B}_2\text{O}_3\text{-v}$ Raman	$\text{B}_2\text{O}_3\text{-v}$ Raman
432	447	440	442		
465				467	
486	487	483	475		471
510	523	534	500	498	501
589					
606					601
635		625	627		
				662	665
710	714	704	696		
729	732	736	747	729	737
755	759	764	767	771	
			794	803	808
				883	

Table 3 Peak positions (cm^{-1}) in Raman spectra for crystal in the caesium borate system.

$\text{Cs}_2\text{O} \cdot 0.9\text{B}_2\text{O}_3$	$\text{Cs}_2\text{O} \cdot 0.5\text{B}_2\text{O}_3$	$\text{Cs}_2\text{O} \cdot 0.3\text{B}_2\text{O}_3$	$\text{Cs}_2\text{O} \cdot 0.2\text{B}_2\text{O}_3$
415		433	447
474			
497	480	480	
512	510		
531		529	531
	572	562	553
	589		573
			593
607			618
656		653	
669	672		
	690	698	688
707	709	720	723
745	724	753	
	760		750
	774		
801	786		801
			846
	861	855	865
876	876	874	
905	931		926
	949	950	949
975	977	981	977
992		1001	
1018	1016		1017
1030			1057
1077	1084	1072	
			1131
1182	1192	1171	
1286	1251	1233	1224
		1244	
1312	1299		1310
	1334	1340	1345
	1379	1391	1373
		1406	
1414		1417	
	1445	1445	1449
1481	1476	1462	
1561			





