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The preparation and characterization of a lithium borate glass prepared by the gel technique

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The preparation of an amorphous lithium borate gel by the metal organic procedure is described. In addition, a preliminary evaluation of the behaviour of the gel upon heating is given. In particular the crystallization tendency of the gel is studied with the aid of DTA and X-ray diffraction, and the structural changes in the gel are monitored with the aid of IR spectroscopy. The glass produced from the lithium borate gel is compared to both the gel precursor material and a glass of similar composition prepared by conventional techniques. Specifically, the relevant water contents, crystallization behaviour, and structural features are contrasted.

1. Introduction

Recently, there has been a growing interest in the use of the metal organic precursor method of producing glass. This interest has arisen not only due to the potential commercial value of this process [1], but also as a result of the new scientific information which may be gained regarding glass formation and structure via the detailed study of this procedure.

The metal organic (gel) route to glass formation has been utilized primarily for the formation of silica based glasses. Silicon alkoxides hydrolyse relatively slowly and incompletely even in the presence of excess water [2]. This feature allows polymerization to proceed without the undesired complication of oxide or hydroxide precipitation from solution. As indicated by Yoldas [2], other metal alkoxides generally hydrolyse rapidly, which consequently produces difficulties in the use of the gel method for the formation of non-silicate glasses. Although non-silicate glasses have been prepared by the gel technique [3, 4], they have been few in number.

In the present work we report on the preparation and characterization of a lithium borate gel and glass. Apparently, this is the first time gel formation in this compositional system has been accomplished, and is also only the second time a borate composition has been made by this procedure [3]. The preparation of borate glasses via the gel technique is of particular interest since, unlike silicates, borate glasses have complex structural features due to the possibility of having 3 and 4 coordinated borons in the glass. Hence, it is of importance to ascertain if the structure of borate glasses may be modified by employing gel methods.

2. Experimental details

2.1. Preparation of gel

The raw materials used in the preparation of the gel were tri-n-butylborate (Alfa Products), lithium methoxide (Alfa Products), acetone free absolute methyl alcohol (Mallinckrodt) and doubly distilled deionized water. Lithium methoxide (11.286 g) was dissolved in methanol (112.8 ml) by stirring in

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a closed flask at room temperature. Distilled water (10.7 ml) was added to this solution. Use of larger amounts of water caused precipitates to form when the boron alkoxides were added. The tri-n-butylborate (187.2 ml) was added slowly (approximately 10 ml min^{-1}) at room temperature. The solution was continuously stirred. Initially the solution turned somewhat cloudy, but it cleared when the remainder of the tri-n-butylborate was added. The final sol appeared as a transparent, colourless, low viscosity solution. The sol was stirred for 15 min, and then was prepared for gellation.

The sol was placed in a glass beaker, and was covered with cellophane which had fine holes (~ 0.5 mm diameter) punched in it. The partially sealed beaker was placed in a closed chamber and held at 50° C. While the sample was in the chamber, water and methanol were added (ratio of 50 to 1) to promote gellation. A gel was obtained in 2 to 5 days. After gellation occurred, the cellophane was removed in order to aid the drying of the gel. The sample remained in the chamber, which was held at 50° C, for 10 to 14 days. Subsequent to this time period the sample was removed from the chamber. It was now an opaque white powder.

Upon completion of this preliminary low temperature drying procedure the sample was fired. First, a heat treatment at 100° C was performed in an oxygen atmosphere to drive off the volatiles. Next, the sample was heated at 200° C in a high humidity atmosphere in order to hydrolyse any unreacted OR–groups. The latter procedure insured that further high temperature heating of the gel would not produce blackening. Finally, the gel was maintained at 200° C for an additional 12 h in dry oxygen to fully dehydrate the gel.

2.2. Glass preparation

The batch glass was prepared employing Li_2CO_3 and B_2O_3. The chemicals were weighed and then transferred to a glass jar which was placed on rollers for 1 h. The batch was melted in a platinum crucible for 2 h at 1100° C. The melt was stirred twice. The glass melt was allowed to cool for several seconds in the crucible, and then the crucible was placed in a muffle furnace which was held at 390° C. The glass was annealed for 15 min at this temperature, and then the furnace was turned off. The glass was removed from the furnace the day after melting.

The gel glass was prepared in a similar manner utilizing the gel precursor material. Gel glasses of two different compositions were prepared. These glasses were analysed using atomic absorption. Multiple analyses of these glasses indicated that one gel glass contained 14.2 wt % Li_2O (or 27.83 mol %) and the other 17.9 wt % Li_2O (33.7 mol %). A batch glass of composition 14.2 wt % Li_2O was also prepared.

3. Thermal treatment of gels

Heat treatment of the gel will facilitate the removal of residual organic groups and water, and assist the process of pore collapse. A detailed knowledge of these processes is important for monolith formation. Also, the determination of the crystallization tendency of the gel is essential since crystallization of the gel at low temperatures could negate monolith formation. Thus, information provided regarding the crystallization tendency of and water removal from the lithium borate gel will have important implications for the latter process.

3.1. Crystallization behaviour

Preliminary information concerning the crystallization behaviour of the lithium borate gel and glass was obtained using DTA and X-ray diffraction (XRD) analysis.

Fig. 1 shows a DTA curve obtained from the 33.7 mol % Li_2O gel precursor. The heating rate used was 20° C min^{-1}. An exotherm is observed at approximately 550° C and an endotherm appears at about 920° C. The endotherm may be associated with the melting of crystalline material since the liquidus temperature of this composition is known to be approximately 917° C. The exotherm at 550° C signifies that the gel crystallizes at this temperature.

In order to study the crystallization process in a bit more detail, gel precursor samples of the above composition were dried thoroughly at 200° C and then heated for 0.5 h at temperatures of 250, 350, 450 and 550° C. A ground gel glass was heated at 550° C for 0.5 h. The samples were analysed subsequently with the aid of powder X-ray diffraction. The results of this measurement for the glass are shown in Table I, where the *d*-spacings and corresponding integrated intensities associated with the strongest reflections are presented. It was surmised that the glass crystallized nearly completely, and that the sole crystalline phase produced was $Li_2O \cdot 2B_2O_3$. The gel

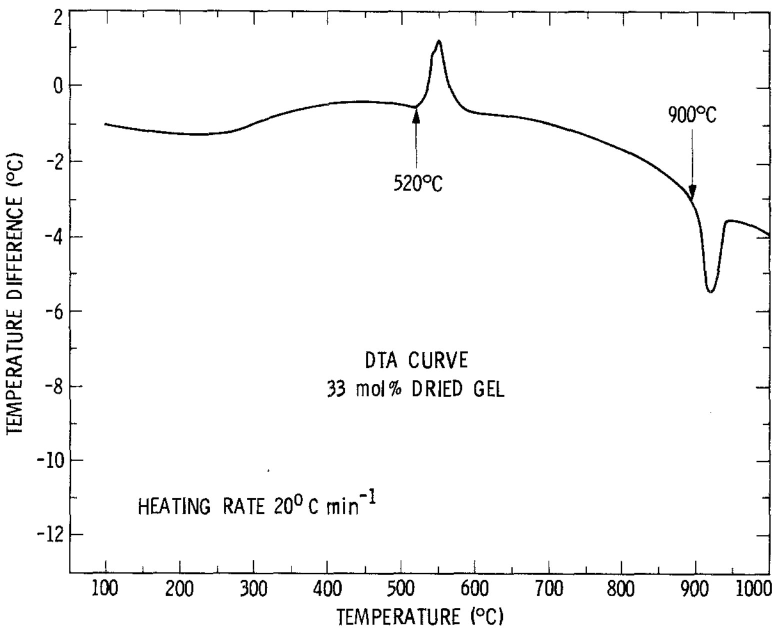

Figure 1 Differential thermal analysis curve from 33 mol% LiO_2 gel. Heating rate used was 20° C min^{-1}.

glass was prepared by melting the 33.7 mol% Li_2O precursor gel as described in the preceding section. The XRD results obtained for the gel precursor, which was heated at 550° C, were virtually identical to those found for the glass. The sample was nearly fully crystallized and $Li_2O \cdot 2B_2O_3$ was the only phase which formed. The gel samples which were heated at 450° C or lower were found to remain amorphous.

It is not too surprising to find that the 33.7 mol % Li_2O gel and gel glass crystallize in the manner described above since their composition is nearly identical to that of the $Li_2O \cdot 2B_2O_3$ crystalline material.

TABLE I XRD results for gel glasses containing 27.8 and 33.3 % lithia

Reference			27 % Li_2O		33 % Li_2O	
Phase	*d*	I/I_0	*d*	I_i	*d*	I_i
1–2	4.080	100	4.114	28	4.060	88
1–2	3.918	18	3.953	8	3.902	8
1–3	3.769	100	3.788	9		
			3.60	5		
1–2	3.485	40	3.506	14	3.467	24
1–3	3.263	100	3.285	20		
1–3	2.982	100	3.001	12		
			2.913	4		
1–3	2.823	80	2.839	6		
1–2	2.665	40	2.677	12	2.658	31
1–2	2.589	55	2.602	16	2.583	34
1–3	2.444	100	2.457	8		
1–2	2.243	14	2.251	7	2.238	8
1–2	2.086	10	2.096	7	2.082	8

1–2 = $Li_2O \cdot 2B_2O_3$, ASTM 18-717 [22].
1–3 = $Li_2O \cdot 3B_2O_3$, ASTM 32-549 [23].

However, one may anticipate that the "off-composition" glasses could produce a more interesting and varied crystallization behaviour. For example, it has been observed that ordinary glasses in the Na_2O–SiO_2 system produce a rich variety of meta-stable and stable species when non-stoichiometric compositions are heated [5]. Furthermore, ordinary glasses and gels and gel glasses in this composition family have been observed to crystallize in different manners [6]. Hence, we compared the crystallization behaviour of an ordinary and gel glass which contained a lower lithia content.

Samples of ordinary and gel glass of composition 27.8 Li_2O–72.2 B_2O_3 were ground and heated at 600° C for 0.5 h. The samples were then analysed with the aid of X-ray diffraction. The results for the gel glass are also shown in Table I. Both samples exhibited nearly identical crystallization behaviour, producing $Li_2O \cdot 2B_2O_3$ and $Li_2O \cdot 3B_2O_3$. The ratio of $Li_2O \cdot 2B_2O_3$ to $Li_2O \cdot 3B_2O_3$ crystals in each sample was approximately 2.5 : 1, and these samples contained about half of the amount of $Li_2O \cdot 2B_2O_3$ found in the 33.7 mol% composition. Hence, this preliminary study revealed no differences in the crystallization tendencies of gel, gel glass, and ordinary glass.

3.2. Water content

IR spectra of gels and glasses in the 4000 to

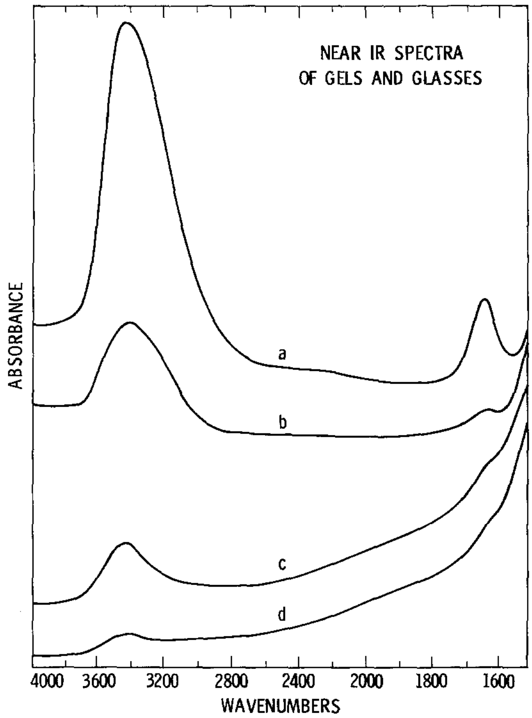

Figure 2 Near IR spectra using KBr pellet technique. (a) Dried gel, (b) dried gel after 30 min at 350° C, (c) ordinary glass, (d) gel glass.

1500 cm^{-1} spectral region are shown in Fig. 2. These spectra were obtained using the KBr pellet method. All spectra exhibit an absorption band at about 3400 cm^{-1} and an additional weaker absorption at or in the vicinity of 1640 cm^{-1}. From a comparison of Figs. 2a and b it is apparent that the intensity of both bands decreases as the gel is heated. In the spectra of the ordinary (Fig. 2c) and gel (Fig. 2d) glasses, these bands are observed to be further reduced in intensity.

These bands have been observed in the IR spectra of silica gel [7], and have been assigned to stretching and deformation modes for hydroxyl groups and molecular water [8].

Thus, inspection of Fig. 2 reveals that both gel and ordinary glasses contain less water than the gel precursor. However, it is observed that the gel glass contains less water than the ordinary glass. This somewhat surprising result may be attributed to the fact that the B_2O_3 which was used for the preparation of the ordinary glass was partially hydrated, and that no special provisions were made to remove water during the melting procedure. On the other hand, the gel was dried thoroughly at 200° C. Thus, if equilibrium between the melt and partial pressure of water above the melt was not reached, then one might expect the gel glass to have a lower water content. If equilibrium conditions were attained, then the water content of the glasses would just reflect the atmospheric conditions during the various melting periods.

4. IR analysis of gel and gel glass

Evidence has been presented which indicates that the structure of gels may differ from the structure of the corresponding gel glasses [9]. Since such structural differences appear in silicate compositions, one may anticipate a much broader and richer selection of variations between gel and glass structure in borate compositions since there are a number of basic structural units which may be incorporated in the construction of a borate glass.

An array of experimental methods must be employed to clearly establish the structure of borate glass. The use of IR analysis alone does not provide complete and unambiguous information regarding glass structure. However, IR spectroscopy has proven to be a useful tool for obtaining knowledge of the structural development of the gel upon heating. Below, the IR spectra of lithium borate gels and glass obtained using the KBr pellet technique are presented and discussed.

Fig. 3 shows the IR spectra, in the 1600 cm^{-1} (6.25 μm) to 400 cm^{-1} (16.67 μm) region, obtained from the 33.7 mol % Li_2O gels which were subjected to the following heating schedules: (a) unheated; (b) 30 min at 250° C; (c) 30 min at 350° C; and (d) 30 min at 450° C. In general, all four spectra appear quite similar. The dominant absorptions at 1350 cm^{-1} (7.41 μm) and 1030 cm^{-1} (9.71 μm) exhibit the same relative intensities in each spectrum, and only very small shifts in the absorption peaks of the latter bands are noted. As the heating temperature is increased, the former absorption band peak shifts to shorter wavelengths, while the latter moves to longer wavelengths. In either case, an inspection of Fig. 3 reveals that the shift is no more than 10 cm^{-1}. The minor peaks which occur at longer wavelengths, 750 cm^{-1} (13.33 μm), and 690 cm^{-1} (14.49 μm), appear roughly the same in all four spectra, with the exception of the 560 cm^{-1} absorption which seems to decrease in intensity upon heating. The only obvious difference in these spectra is the disappearance of the shoulder at 880 cm^{-1} (11.36 μm) as the samples are heated to higher temperatures.

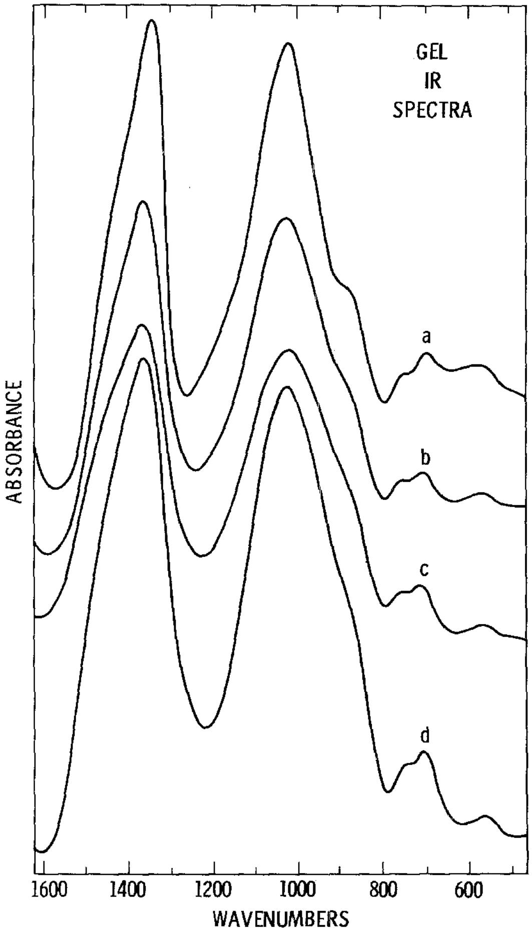

Figure 3 IR spectra of gel precursor. (a) Dried gel, (b) dried gel after 30 min at 250° C, (c) dried gel after 30 min at 350° C, (d) dried gel after 30 min at 450° C.

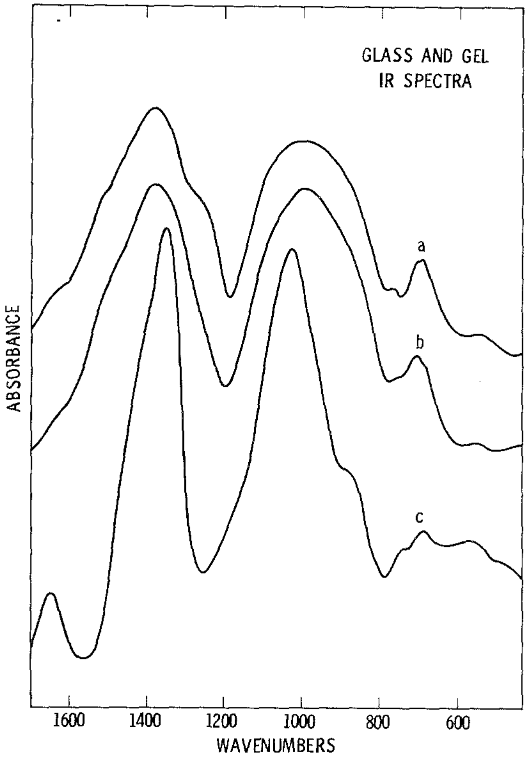

Figure 4 IR spectra of gel and glass. (a) Ordinary glass, (b) gel glass, (c) dried gel.

The IR spectra obtained from the gel derived glass, the ordinary glass, and the gel (which was dried at a temperature of 200° C) are shown in Fig. 4. The traces (Figs. 4a and b) are very similar, and correspond to the spectra obtained from the ordinary and gel derived glasses respectively. However, two minor differences exist in the latter spectra. The ordinary glass spectrum exhibits a shoulder at 1250 cm^{-1} (8 μm) which is not clearly discernible in the gel derived glass. Also, the absorption band at 1000 cm^{-1} (10 μm) has a flatter maximum in the spectrum of the ordinary glass. On the other hand, the differences between the glass and gel spectra are more pronounced. The dominant absorption bands are much narrower in the latter spectrum, and their peak positions are shifted with respect to the glass spectra. The positions of the maxima of the major bands occur at 1350 cm^{-1} (7.41 μm) and 1030 cm^{-1} (9.71 μm) in the gel, while in the glass they occur at 1380 cm^{-1} (7.25 μm) and 1000 cm^{-1} (10 μm). Also, a shoulder which appears at 880 cm^{-1} (11.36 μm) in the gel spectrum is absent in the glass spectra. In addition, the structure of the minor absorptions in the long wavelength part of the gel and glass spectra differ. In the gel spectrum weak absorptions occur at 750 cm^{-1} (13.33 μm) and 690 cm^{-1} (14.49 μm), while in the glass spectra a weak band with a double peak is centered about 700 cm^{-1} (14.28 μm) and a very weak absorption may be present at 770 cm^{-1} (12.99 μm).

Various problems exist in attempting to extract structural information from the IR spectra of alkali borates. The most fundamental difficulty in making structural assignments via any structure-sensitive experiment has been described thoroughly and elegantly by Griscom [10]. This problem relates to the uniqueness of the model used to make computations for comparisons with experimental results. In the present case the theoretical model which has best stood the test of experimental scrutiny appears to be the one proposed by Krogh-Moe [11, 12]. He has proposed that alkali borate glass compositions containing 33.3 mol% alkali or less should contain only four structural units linked together in various proportions. These four groups are the boroxol group, the pentaborate group, the triborate group, and the diborate group. The relative number of these groupings present in a glass of a given composition may be calculated by the lever rule. However, complications arise in any attempt to obtain a quantitative fit of the spectra via this model. First of all, it has been observed that the IR spectra of even the corresponding crystalline materials cannot be interpreted solely in terms of the basic structural units since new structural features in the spectra are introduced via the linkage of structural units [13]. This problem is greatly exacerbated in the case of glasses since the linkage of groupings occur in a wide variety of fashions. An additional difficulty relates to the identification of those absorption bands which are not a reflection of structural motion, but which may be attributed to hydroxyl motions. Krogh-Moe [13] has provided some clues to resolve this question via the spectra he has taken of undeuterated and partially deuterated $Na_2O \cdot 2B_2O_3$, $10H_2O$ crystalline samples. However, similar spectra have not been obtained from the corresponding partially deuterated diborate glasses.

In addition to the intrinsic problems discussed above, there may be errors introduced which are attributable to experimental methodology. For example, Borelli *et al.* [14] have studied the IR spectra of Na_2O–B_2O_3 glasses using thin films, the reflection method, and the KBr pellet technique. They observed that the KBr pellet technique produced inconsistent results for hygroscopic glasses. Also, although they found that film and reflectance techniques were in agreement, this agreement was only qualitative and not quantitative.

Recognizing all of the potential pitfalls, useful qualitative structural information may still be extracted from the IR spectra. Prior to presenting a discussion of each of the observed absorption bands, several general remarks will be made concerning the spectra. First, it should be noted that the spectra of the glasses shown in Figs. 4a and b are in quite good agreement with the IR spectrum of $Li_2O \cdot 2B_2O_3$ glass found by Krogh-Moe [15]. However, there are several minor discrepancies which should be observed. The shoulder present in the spectrum of the ordinary glass (Fig. 4a) at 1250 cm^{-1}, the very weak absorption at 770 cm^{-1} and the weak peak at 690 cm^{-1} present in the ordinary and gel glasses are absent in the Krogh-Moe spectrum. The positions of the maxima and the breadths of the major absorptions are in excellent agreement. Next, one should note that the major difference between the gel and the glass spectra is the increased breadth of the dominant absorptions in the glass spectra. This difference may be attributed to an increased degree of polymerization in the glass samples. Krogh-Moe [13] has made comparisons of the IR spectra of anhydrous and hydrated alkali borate compositions of identical borate content. The hydrated compounds were found to exist as isolated polynuclear anions, while the dehydrated forms exhibited linkage of structural groups. He found that the anhydrous spectra were similar to the hydrated, but exhibited broader absorption bands. In turn, the spectra of the corresponding glasses are broader and show less resolution than the anhydrous crystal spectrum. Thus, one may conclude that increased linkage is reflected in a broadening of the bands and a masking of spectral details.

The dominant band in both the glass and gel spectra is located in the 1380 cm^{-1} (7.25 μm)–1350 cm^{-1} (7.41 μm) region of the spectrum. The location and intensity of this absorption in $Li_2O \cdot 2B_2O_3$ glass closely resembles that found in anhydrous crystalline $Li_2O \cdot 2B_2O_3$ [15]. A very similar absorption band has also been found in the IR spectrum of $Na_2O \cdot 2B_2O_3$ glass [14]. Although it is difficult to make a definite identification of the origin of the band, utilizing the results of previous investigations a plausible hypothesis may be advanced. From the work of Krogh-Moe on deuterated $Na_2O \cdot 2B_2O_3 \cdot 10H_2O$ crystalline samples, one may conclude that this absorption is *not* associated with hydroxyl motions but with framework motion. Spectra of crystallized $4ZnO \cdot B_2O_3$ glass exhibit the highest frequency band at about 1000 cm^{-1}. Since it is known that all borons are 4-fold coordinated in this case, consequently the motion of a 4-fold coordinated boron cannot be responsible for the 1380 cm^{-1} (7.25 μm) band. Tohge and Mackenzie [16] find similar absorption bands in a $20Na_2O \cdot 80B_2O_3$ gel (centred at 1350 cm^{-1}) and glass (centred at 1360 cm^{-1}). They have assigned this band to a B–O stretch associated with a 3-fold coordinated boron unit "which are under the circumstances similar to those in B_3O_3 $(OH)_3$" and in which the units are polymerized to some extent (in the case of the gel). Wong and Angell [17], utilizing the data of Borrelli *et al.* [14], have illustrated the change in IR spectra of $Na_2O \cdot B_2O_3$ glass with increasing soda content. They point out that the 1350–1390 cm^{-1} band develops as the soda content of the glass increases. However, according to the Krogh-Moe theory the ratio of 4-fold to 3-fold coordinated borons increases continuously up to 33 mol% soda. Thus, although the motion giving rise to this band is not associated with a 4-fold coordinated boron, the boron is contained in a structural unit which contains at least one 4-fold coordinated boron. In light of these results, and the specifications of the Krogh-Moe theory, a reasonable conjecture is that this band is produced by a B–O stretch in which the boron is 3-fold coordinated, but is part of a diborate structural unit. In the case of the gel, these units are certainly not fully polymerized, and undoubtedly contain hydroxyl (and/or alkyl) groups. The slight shift and broadening of this band in the glass spectra may be accounted for by the removal of the latter groups and increased linkage of the structural groups in the glass structure.

The broad band in the 1200 cm^{-1} (8.5 μm) to 800 cm^{-1} (12.5 μm) region of the glass spectra is more complex. From an inspection of the spectra of anhydrous crystalline $Li_2O \cdot 2B_2O_3$ given by Krogh-Moe [15], one observes that the latter spectrum exhibits three separate maxima in this spectral region (centred at approximately 1135 cm^{-1}, 975 cm^{-1}, and 900 cm^{-1}). Thus, in all likelihood the broad band in the glass arises as a result of several independent modes whose frequency domains overlap. The series of $Na_2O \cdot B_2O_3$ spectra shown in [17] indicate that the strength of this absorption increases with increasing alkali content and that this band is not present in B_2O_3. Thus, this band is clearly associated in some manner with BO_4 groupings. From an inspection of the corresponding crystalline spectra, one observes that the peak at 1135 cm^{-1} does not shift with deuteration of the sample, and the band does not increase in intensity upon dehydration. Thus, the motion giving rise to this absorption is associated with framework members and can be interpreted in terms of an isolated group. On the other hand, the peak at 900 cm^{-1} appears to increase in intensity upon enhanced polymerization of the sample and thus may not be interpreted in terms of a simple, isolated structural unit. The hydrated $Na_2O \cdot 2B_2O_3$ crystalline spectra has a maximum at 945 cm^{-1} which is shifted in the deuterated sample. This feature indicates that a portion of the intensity of the 1030 cm^{-1} (9.71 μm) band in the gel may be due to hydroxyl motions. Due to the complexity of this band, additional understanding of its origin and alteration in shape and position in the gel and glass is not possible. However, clearly 4-fold coordinated borons are required for its appearance and, hydroxyl motions may contribute to some extent to its intensity. The differences between the absorption band in the gel and glass may be accounted for by water and alkyl group removal and increased structural linkage in the glass.

A very weak absorption which is present at 770 cm^{-1} (13 μm) in the spectra of the ordinary glass (and perhaps in the gel glass too) does not appear in the spectrum of $Li_2O \cdot 2B_2O_3$ glass obtained by Krogh-Moe. This absorption is absent in the spectrum of $Na_2O \cdot 2B_2O_3$ glass [14, 17]. The gel spectra show a weak absorption band at 750 cm^{-1} (13.33 μm) which could be related to the latter band which we have observed in the glass. However, we believe that this possibility is unlikely. Tohge and Mackenzie [16] also observed an absorption in the 745–750 cm^{-1} region in the spectrum of a $20Na_2O \cdot 80B_2O_3$ gel. However, this absorption decreased in intensity as the gel was heated to higher temperatures, and this absorption was not present in the IR spectra of the glass. On the other hand, anhydrous crystalline $Li_2O \cdot 2B_2O_3$ exhibts a weak to moderate absorption at about 775 cm^{-1}. Thus, it is believed that the glass samples devitrified to some extent during glass preparation and that the 770 cm^{-1} absorption is due to the presence of crystallites in the glass. Further evidence of the presence of crystallites is obtained by inspection of the band structure in the vicinity of 700 cm^{-1} (14.28 μm). The absorption at 700 cm^{-1} is present in B_2O_3, and thus is associated with 3-fold coordinated borons. This absorption has been assigned to a bending mode of BO_3 units [18]. In the glass spectra which we have obtained, however, weak absorption maxima occur at 700 cm^{-1} (14.28 μm) and at 690 cm^{-1} (14.5 μm). The anhydrous crystalline $Li_2O \cdot 2B_2O_3$ spectrum exhibits an absorption maximum in the 680–685 cm^{-1} region, providing further indications of the existence of crystallites in the glass samples.

As mentioned previously a shoulder at 880 cm^{-1} (11.36 μm) which occurs in the gel spectrum is absent in the glass spectra. Furthermore, from an inspection of Fig. 3, one observes that this shoulder disappears from the spectrum as the gel is heated. Similar absorptions have been noted in $Na_2O \cdot SiO_2$ gels [19] and $Na_2O \cdot B_2O_3$ [16] gels, and these have been attributed to Na_2CO_3 which forms via a reaction of the sample with the atmosphere. Thus, the shoulder occurring at $880\,cm^{-1}$ in the gel spectrum most likely may be attributed to Li_2CO_3.

Thus, our preliminary results on the $30Li_2O \cdot 70B_2O_3$ system indicate that the gel and glass structures appear to be quite similar, at least with respect to the fraction of 3-fold and 4-fold coordinated borons.

5. Summary

Amorphous lithium borate gels containing approximately 27 and 33 mol% Li_2O have been prepared by the metal organic procedure. The gels and the glasses produced from them by melting have been characterized with respect to water content, crystallization behaviour, and structure.

It was observed that if no special techniques are employed to remove water during melting, then the water content of the gel glasses can actually be less than that of the ordinary glass. Hence, one may speculate the water removal from the gel glass may not be a serious problem in this composition.

The limited information which was gathered concerning crystallization tendency of the gel, gel glass, and ordinary glass revealed no striking differences in behaviour. This result is in contrast to results obtained in other systems [16, 20, 21], and deserves further study.

The results of the IR analysis of the gel and glass indicate that no major structural differences exist between these materials. In particular the fractions of 3-fold and 4-fold coordinated borons appear to be roughly the same in each. Tohge and Mackenzie [16] have obtained similar results for the $20Na_2O \cdot 80B_2O_3$ system. Two cautionary remarks should be made, however, concerning these findings. First, IR spectra is only one in a vast array of techniques which may be used to obtain information regarding structure. IR spectra alone only provide limited information regarding structural details. Next, one should realize that the gel preparation technique may strongly influence the resulting gel structure. The gel preparation techniques used herein and in [16] were quite similar. It is possible that alkali borate gels with unique structures might be prepared by utilizing different preparation procedures. Additional research efforts are required in both of these areas.

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