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Lithium borate gel films prepared from aqueous solution

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Transparent, durable films of lithium diborate gel can easily be prepared on a variety of substrates from supersaturated aqueous solutions of lithium hydroxide monohydrate and boric acid by spin-coating. The gel to dried gel to glass to crystalline lithium tetraborate ($Li_2B_4O_7$) transformation has been studied by infrared spectroscopy of thin films cast on potassium bromide windows. Examination by scanning electron microscopy disclosed that distinctly different crystal morphology was associated with a difference in the transformation rate observed between gel and dried gel films. Films of 250 nm to 30 μm in thickness have been produced. *© 1998 Kluwer Academic Publishers*

1. Introduction

Modern work in borate sol–gels has focused on hydrolysis of alkoxides in an alcohol solvent, typically utilizing alkali–metal methoxides dissolved in methanol to which tributoxyborane (tri-*n*-butyl borate) is added. Gel derived powders and glasses [1–3], and fibres [4] have been produced. It has generally been assumed, aside from the complication of a change from threefold to fourfold coordination in boron atoms associated with the alkali metal, that gelation in borates occurs by the same hydrolysis and auto-condensation mechanism observed in the silicates leading to a polymerized gel network characterized by covalent bonding [5].

It is not, however, necessary to employ alkoxides in alcohol. As early as 1858 Ordway [6], though not specifically mentioning borates, noted that the basic salts of the sesquioxyds (M_2O_3 compounds) were generally capable of producing “tough, shining, transparent” non-crystalline “masses” by “spontaneous evaporation”. Further, in 1955 Reburn and Gale [7] reported observing the formation by separation from a supersaturated aqueous solution of boric acid and lithium hydroxide of a “gelatinous material of an indefinite degree of hydration” with “a mole ratio of B_2O_3 to Li_2O of 2” during their phase-equilibrium study of the system lithium oxide–boric oxide–water.

The aim of this paper is to demonstrate by infrared (i.r.) spectroscopy that lithium diborate gel films can be produced from aqueous solutions and to show that their characteristics are consistent with previously reported results on alkoxide gels. An i.r. transparent substrate was chosen in order to observe water content and also allow sensitive detection of crystallization. Thick, fully crystallized films were also prepared on soda-lime–silicate glass and silicon wafers to allow characterization by X-ray diffraction.

2. Experimental procedure

2.1. Solution preparation

The room temperature equilibrium solubility of lithium diborate ($Li_2O \cdot 2B_2O_3$ or $LiB_2O_{3.5}$), also known as lithium tetraborate ($Li_2B_4O_7$), in water is only about 3 wt%. Nevertheless, highly supersaturated aqueous solutions of up to 25 wt% lithium diborate are easily obtainable [7]. The procedure requires first preparing an aqueous solution of lithium hydroxide monohydrate and then adding boric acid. For instance, an approximately 10 wt% solution was obtained by adding 200 ml of water to 11 g of lithium hydroxide monohydrate (Fluka puriss. p.a., $> 99\%$), stirring over low heat (solution temperature less than 50 °C) for 30 min giving a clear, transparent solution with pH $\cong$ 14, then adding 32.5 g of boric acid (Fluka puriss. p.a., ACS, $> 99.5\%$), and continuing to stir for another 30 min giving a clear, transparent solution of pH $\cong$ 10. The result is a solution of the basic (i.e. hydrolysed) salt which is reasonably stable at room temperature.

2.2. Film preparation

The thin films are prepared from the above solution by spin-coating in the normal fashion. For instance, a pipette was employed to flood the surface of the potassium bromide (KBr) disc acting as a substrate with the 10 wt% solution and the substrate was then immediately spun at 1500 r.p.m. for 30 s producing a thin gel film. While both the concentration of the solution and the spinning speed affect the thickness of the resulting gel film, the single greatest factor affecting film thickness is the relative humidity. The relative humidity should be controlled and be within about 25–35% to obtain films thin enough (about 250 nm) to give a good i.r. absorption spectrum. Thicker films are obtained by lowering the relative humidity or by multiple deposition coating. Once cast, the films appear stable to atmospheric moisture; even exposure to 100% relative humidity at 50 °C for 1 week did not significantly alter the i.r. absorption spectra of the gel films nor was any crystallization of hydrates or other species observed. Films of good uniformity and extent are easily obtainable on hydrophilic surfaces including properly treated silicon wafers.

2.3. Film treatment

One group of the resulting films was pretreated by placing them in an oven at 280 °C for 15 min. This treatment produced the dried gel films. A Perkin-Elmer 1725X Fourier transform-infrared spectrometer (FTIR) was employed to obtain the i.r. absorption spectra of the fresh and of the dried gel films prior to and at 15 min intervals during heat treatment at 500 °C. The procedure involved placing the KBr discs, film up, on an aluminium foil boat, putting the boat into the tube furnace and, after 15 min had elapsed, removing the boat. The samples were allowed to cool for about 5 min prior to having the spectra taken in room air, employing background subtraction. The KBr discs were positioned in the spectrometer sample holder such that the centres were offset, and thereby the spectra represent a sampling of a radial band beginning about one-third of the way out from the centre and ending one-third of the way in from the edge. Finely powdered crystalline lithium tetraborate (Fluka puriss. p.a., ACS, > 99%) was placed between two KBr windows to obtain a reference spectrum for the crystallites. Additionally, a reference spectrum for the conventional melt glass was obtained by dipping a platinum loop into a melt of the Fluka lithium tetraborate at 1100 °C and slowly withdrawing it so that the glass film formed was thin enough to show optical interference colours.

A Hitachi S4500 field-emission scanning electron microscope (FSEM) was employed to examine the films after heat treatment. Sections of the KBr discs were broken off by fracture and these fragments were coated by vacuum-sputtering with a gold/palladium alloy. The films were viewed both in plan view and in cross-section.

The lithium borates are exceptionally transparent to X-rays because of the combined effects of low atomic mass and low crystalline density; hence, films of the thinness necessary to obtain good i.r. spectra are not suitable for X-ray diffraction. Multiple deposition coating with each film layer being dried for 15 min at 280 °C was employed to provide thick films for X-ray diffraction on a Scintag, Inc. XDS 2000.

3. Results

3.1. Infrared spectroscopy

Characteristic i.r. spectra, smoothed, normalized, and shown as absorption peaks, of the fresh gel films, the dried gel films, and a conventional melt glass thin film are shown in Fig. 1 over the range 500–4000 cm^{-1} and in Fig. 2 over the "fingerprint" region of 500–1700 cm^{-1}. There was no evident change in the spectra of the dried gel films upon subsequent heat treatment at 500 °C prior to crystallization. The fresh gel films (i.e. containing the water of gelation) crystallized very rapidly upon being heated to 500 °C, while the dried gel films by contrast required about four more 15 min treatments before showing visible i.r. crystallization peaks. An overlay of as-taken spectra is shown in Fig. 3 comparing crystalline lithium tetraborate powder to the crystallized dried and fresh gel films.

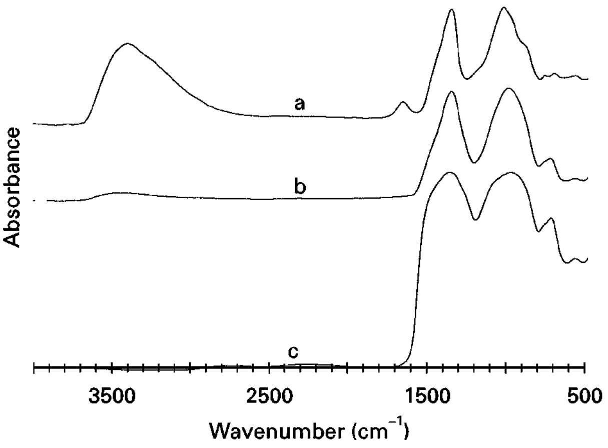

Figure 1 Infrared spectra showing relative water content for (a) fresh gel film, (b) gel film dried for 15 min at 280 °C, and (c) 1100 °C melt glass thin film.

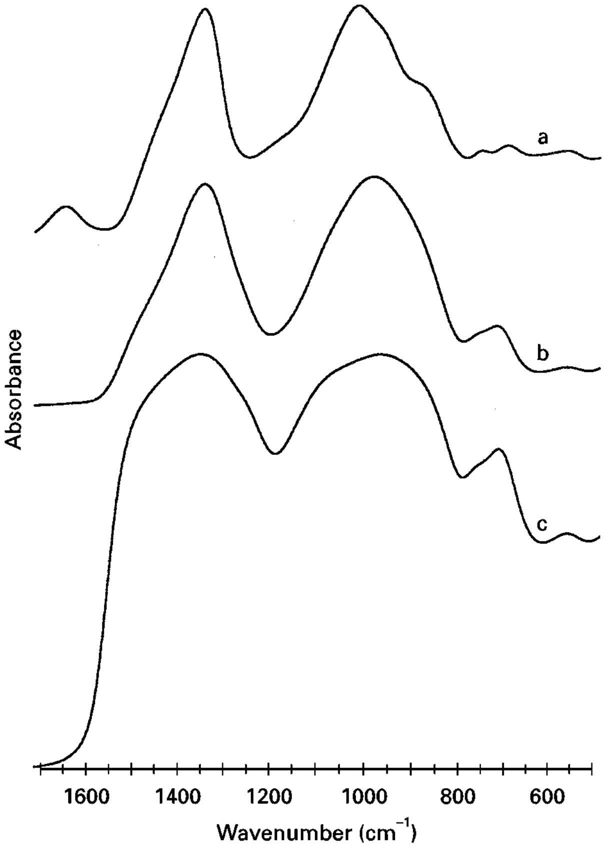

Figure 2 Infrared spectra showing "fingerprint" region for (a) fresh gel film, (b) gel film dried for 15 min at 280 °C, and (c) 1100 °C melt glass thin film.

3.2. Scanning electron microscopy

All of the films exhibited cracking with the width of the cracks apparently proportional to the total

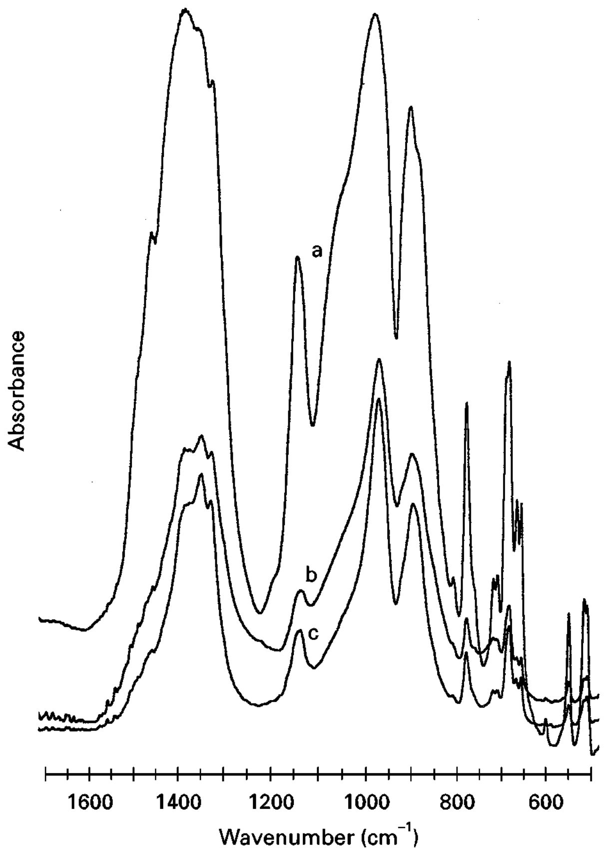

Figure 3 Infrared spectra showing crystallization. (a) Lithium tetraborate powder, (b) dried gel film after total of 90 min at 500 °C, and (c) fresh gel film after total of 30 min at 500 °C.

duration of the 500 °C treatment. A sharp interface between the films and the KBr substrate was always evident, even for a film which had undergone a total of 90 min at 500 °C and which showed thickening to double the usual film thickness at the crack edges suggesting that the films were not strongly adhering. The films were typically about 250 nm thick. The fresh and dried gel films exhibited dramatically different crystallite morphology. The fresh gel films crystallized internally to form spherical aggregates of about 80 nm diameter. The spherulites appeared to have formed randomly within a cross-section of the fresh gel film treated for a total of 30 min at 500 °C, and to be of roughly uniform size. By contrast, a dried film formed under identical conditions required five 15 min treatments before it exhibited the same degree of crystallization by i.r. and the crystals formed appeared to have square sides. The tops of the crystallites appeared to be randomly scattered and just beginning to grow through the surface of the film; a cross-sectional view was not obtained. The size appeared roughly uniform with sides about 60 nm. In both cases, crystallization was easily detected by infrared absorption while the crystals were still quite small and scattered.

3.3. X-ray diffraction

A film of about 30 μm thickness was prepared on a soda-lime–silicate glass slide by sequentially spin-coating eight films and drying each coat for 15 min at 280 °C. Heat-treating the resulting thick film for 1 h at 500 °C produced complete crystallization. When viewed by optical microscopy in cross-section, the crystals were densely packed, transparent, of irregular height with prismatic termination, and appeared primarily columnar and orthogonal to the surface. The X-ray results for thick films on soda-lime–silicate glass show lithium tetraborate as the major crystallization product (Fig. 4), but also show an absence of pronounced orientation. Fig. 5 shows the X-ray powder diffraction pattern for a bulk sample of the aqueous gel dried at 280 °C and heat-treated for 1 h at 500 °C; the only observed crystallization product was lithium tetraborate.

4. Discussion

The i.r. spectra shown in Figs 1 and 2 correspond very well with those obtained for gel-derived powders by previous workers [2, 4] using alkoxide precursors in alcohol. The fresh gel characteristic water and OH absorbances at about 3400 and 1640 cm^{-1} observed both here and in previous alkoxide gel work appear to represent the gelation medium. That is, the alkoxide-derived materials formerly described as "dried" gel since the alcohol had been completely removed appear to have been the aqueous gel in a powdered form.

There is a fully dried state obtainable by heating the water-containing gel thin films at temperatures exceeding 280 °C. The i.r. spectrum of this dried, amorphous material exhibits characteristics intermediate between those of the gel and those of the conventional melt glass. That is, the primary absorption peaks exhibit both the slight shifts in the point of maximum absorbance and an increase in peak width, as observed in the melt glass. Both groups also reported that the gel powders were amorphous and that the only observed crystalline product of the diborate gels upon heat treatment was lithium tetraborate. This was corroborated in the present case by X-ray diffraction, as shown in Fig. 5 for the bulk gel dried material. Further, as shown in Fig. 3, the absorbance peaks of both the spherical and rectilinear crystallites in the glassy matrix correspond well both to each other and to the reference spectrum of powdered lithium tetraborate pressed by hand onto the surface of a KBr window. Neither group reported on crystallite morphology, but spherulitic crystallites have been previously reported for lithium tetraborate crystals obtained by hydrothermal synthesis [8]. In addition, preliminary work with thicker gel films on both soda-lime–silicate glass slides and silicon wafers where the crystallites within the transparent film were observable by optical microscope gives identical results and provides the additional information that the spheroidal crystallites, when viewed under crossed polarizers, exhibit the "Maltese cross" pattern typical of polycrystalline spherulites.

Nevertheless, it would be misleading to imply, even by omission, that it is simple to produce amorphous bulk gel or gel powder by the aqueous route; it is quite difficult. In fact, evaporation of the aqueous solution by heating gives a white powder of crystalline hydrate, $LiB_2O_3(OH)\cdot H_2O$, with very interesting properties

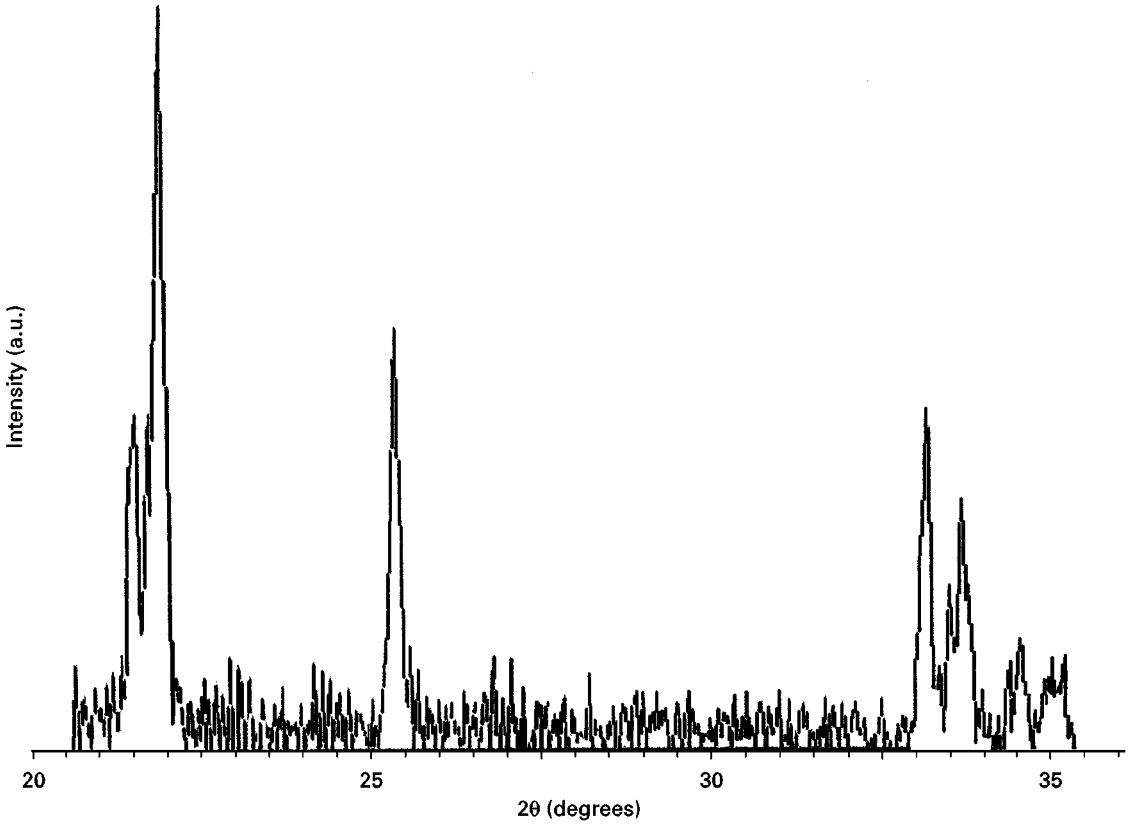

Figure 4 X-ray diffraction pattern for thick film on soda-lime–silicate glass slide.

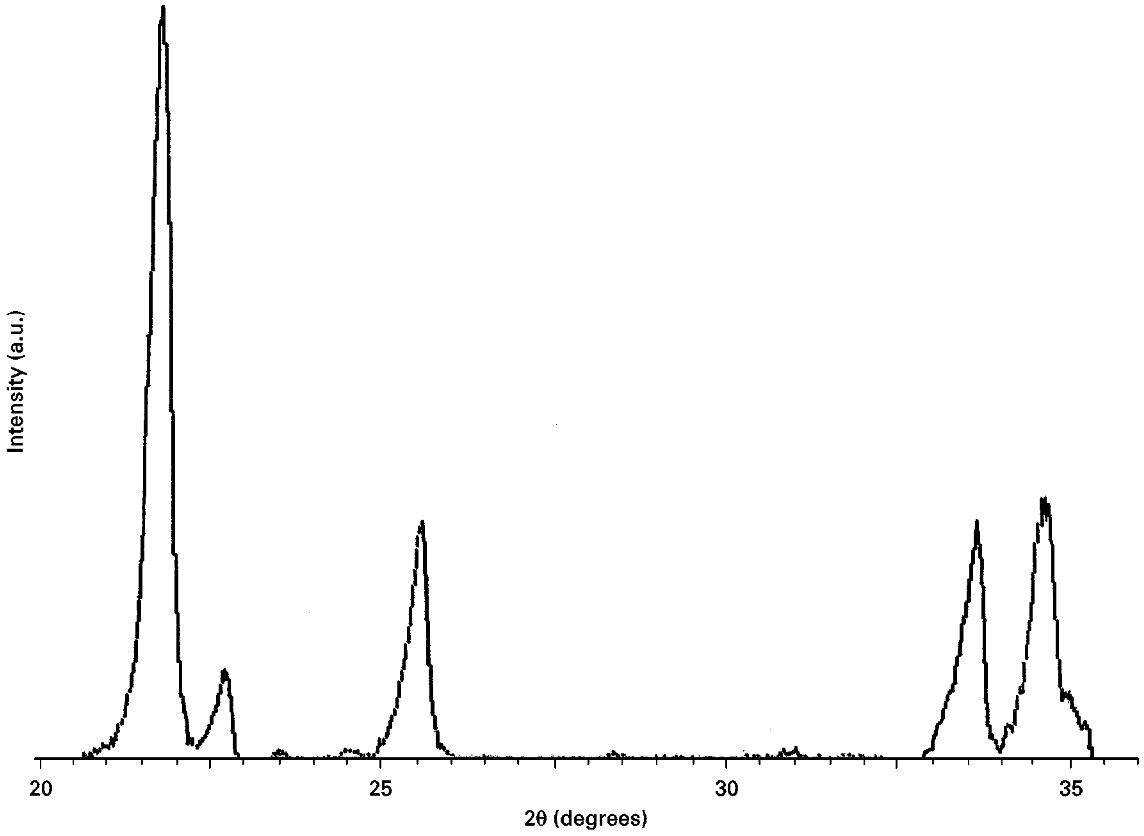

Figure 5 X-ray diffraction pattern for bulk gel powder dried at 280°C and heat-treated for 1 h at 500 °C.

[9]. It dehydrates at relatively low temperature forming an X-ray amorphous anhydrous intermediate which begins transforming to crystalline lithium tetraborate at temperatures 200 °C lower than observed in the glass and without any pronounced exothermic effect. This hydrate, also referred to as lithium tetraborate trihydrate [7], can also be produced by extended storage of the solution or by boiling and may

be of use in seeding films when low processing temperatures are required since a gradual transformation to lithium tetraborate occurs even below 300 °C. The trihydrate forms spontaneously when the aqueous gel is heated; apparently the surface of the bulk material dries rapidly trapping the remaining water and resulting in bloating at temperatures as low as 100 °C. Alternatively, large, transparent, crystals of an unidentified hydrate can be grown simply by placing the aqueous solution into a refrigerator. Thus, it is only near room temperature and by prolonged evaporation in a dry atmosphere that the amorphous bulk gel, and eventually the gel powder, is obtained.

By contrast, it is quite difficult to form durable, transparent thin films from the alkoxide/alcohol solutions. A single group [10] reported having so done by diluting the solution to 0.8 M boron concentration in methanol, adding relatively large quantities of water for the alkoxide route, and then adding hydrochloric acid. This procedure neglects the effect of transesterification [11]. The 1953 report by Schlesinger *et al.* [12] on a greatly improved method for extracting methyl borate (boric acid trimethyl ester) from methanol solutions by the addition of lithium chloride discusses the chemistry of the reaction in detail. The tri-*n*-butyl borate alkoxide precursor hydrolyses to boric acid, which in methanol converts to trimethyl borate, but trimethyl borate forms a highly volatile (boiling point 54.6 °C) azeotrope with methanol and thus can easily lead to the loss of essentially all boron by evaporation. Transparent, thin films are indeed produced, but at higher hydrochloric acid concentrations they are likely comprised primarily of residual, non-volatile salts.

The behaviour of borate gel powders and films is strongly influenced by the presence of alcohol. In solution or in a bulk sample of alkoxide-derived gel, the alkoxy groups tend to interchange with the hydroxyl groups. This inhibits the formation of the crystalline trihydrate. In a thin film, however, gradual hydrolysis of the residual alkoxy groups by atmospheric moisture after rapid evaporation of solvent alcohol tends to disrupt the film and produce discontinuous formations of powder.

Observation of the gelation conditions for the alkoxide precursor in alcohol route [2] at the specified concentration of boron is quite interesting. Gelation occurs rapidly when the solution is allowed to evaporate freely from a large surface area even when no water has been added. By contrast, when kept in a sealed container the solution does not gel, even over as long as period as 18 months, in spite of the specified amount of water being added. It has been generally assumed that gradual hydrolysis by atmospheric moisture is a prerequisite for gelation, but concentration of the solution by evaporation appears necessary.

Further, it is easily observed that a sample of the alkoxide-derived gel exposed to a high vapor pressure of methanol will swell and even return to the liquid state with an increase in volume. Alternatively, the gel can be produced within a freshly made alkoxide in methanol solution simply by diluting the solution with diethyl ether or other solvent of low relative permittivity. Gelatinous material rapidly forms, agglomerates, and settles to occupy what appears to be about the same volume as would have been obtained by evaporation. Conversely, however, if the diluted solution with the gelatinous material is further diluted by the addition of more methanol to increase the overall relative permittivity of the solution, the gel disappears.

These observations suggest that gelation in the borates does not occur by the same hydrolysis and autocondensation mechanism as in the silicates. Both the aqueous and the alkoxide routes to borate gels involve adding a weak Lewis acid to a strong base; in both cases the gels form after concentration by evaporation. Potentiometric measurements of boric acid–borate equilibria of aqueous solutions of up to 0.6 M boron concentration in 1.0 M KCl at variable hydroxide ion concentration strongly support the notion that polyborates of at least trimer form do occur [13], but it does not in fact appear necessary to postulate covalently bonded polymers as simple ionic clusters of the form $B_x(OH)^{-y}_{3x+y}$ can account for the data. Further, boric acid, $B(OH)_3$, does not spontaneously condense near room temperature; it must be heated to over 100 °C before it begins to lose water and condense to form covalently bonded metaboric acids. This behaviour is in marked contrast to that of silicic acid, $Si(OH)_4$, which at room temperature exists in monomer form in very low concentration and has a strong tendency to spontaneously polymerize to high molecular weight silicates.

In the absence of a strong tendency to condensation hydrolysis does not imply an irreversible reaction. Thus, boron alkoxides, while known for extremely rapid hydrolysis, do not hydrolyse completely in a neutral solvent [14] and in alcohol interchange hydroxyl and alkoxy substituents indefinitely in an equilibrium reaction which is shifted only by the removal of one of the reactants. Specifically, as the alcohol in an alkoxide borate gel evaporates the tetracoordinated mixed hydroxyl/alkoxy borates tend to form $Li^+B(OR)_n(OH)^-_{4-n}$ complexes where the R denotes an alkyl group. The electrostatic forces associated with these complexes may suffice to account for observed gelation behaviour near room temperature without any need to postulate condensation polymerization by elimination of water.

5. Conclusions

Films of lithium diborate gel can easily be produced from aqueous solution by spin-coating. The thickness of the film is determined primarily by the relative humidity which should be less than about 35%. Gel films which are sufficiently thin may be dried to an anhydrous, amorphous film by rapid heating to about 280 °C. Multiple dried film coats may be employed to produce thick films. Bulk gel crystallizes to a hydrate upon heating as do samples of powders; the rate at which the water can be removed appears to be determining. The amorphous films crystallize in the same temperature range as the melt glass, but the rate of transformation and the crystallite morphology depend upon the water content of the film.

Gelation near room temperature in borates may not proceed by a mechanism of hydrolysis and auto-condensation leading to a covalently bonded polymerized gel network, as observed in the silicates. Rather, electrostatic forces appear capable of forming gels which can be reversibly formed and dissolved repeatedly.

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