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Glass formation region and electrical conductivity in the system B_2O_3-Li_2O-Li_3PO_4

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Abstract. Glass formation region was determined for the B_2O_3-Li_2O-Li_3PO_4 system. Under the present experimental conditions, binary lithium borate glasses could be formed containing a maximum of 27 mol% Li_2O. However, this could be increased to 36 mol% in the ternary system. Electrical conductivity was measured at temperatures ranging from room temperature to 350°C. The temperature dependence of the electrical conductivity of these glasses follows Arrhenius equation. The conductivity increased with increasing alkali content. Maximum conductivity of the order of 10^{-4} ohm^{-1} cm^{-1} was obtained with the glass containing about 36 mol% Li_2O at 250°C. Activation energy for conduction also varied with total Li_2O content.

Keywords. Glass formation region; electrical conductivity; lithium borate glasses; Arrhenius equation.

1. Introduction

Solid lithium ion conductors are increasingly used as electrolytes for high density miniature batteries. Most of the materials so far developed for this purpose are either single crystals or poly-crystalline in nature. Recently, some glassy lithium ion conductors have also been studied with conductivity comparable to that of their crystalline counterparts. Smedly and Angel (1978); Boehm and Angel (1979) reported a number of glasses in the system Li_2O-LiF-Li_2SO_3-Li_2SO_4-B_2O_3 with total Li_nX (where X = O,F, SO_4,SO_3) content ranging from 43 to 84 mol%. A maximum conductivity of 2.26×10^{-3} ohm^{-1} cm^{-1} was obtained at 200°C for the glass containing about 70 mol% Li_nX. Takahashi and Yamamoto (1979) studied glasses in the system Li_2O-$LiCl$-Al_2O_3-B_2O_3 and obtained a maximum conductivity of 7×10^{-3} ohm^{-1} cm^{-1} at 300°C. High lithium ion conduction has also been observed in the glass system $Al(PO_3)_3$-LiF-Li_2O (Evstrop'ev *et al* 1974; Jagla and Israd 1980). Glasses could be made in this system containing upto 80 mol% LiF + Li_2O. A more detailed investigation on the system has been recently carried out (Kulkarni *et al* 1981). Malugani *et al* (1978) studied glasses in the system $LiPO_3$-Li_2SO_4 and room temperature conductivity of the order of 10^{-7} ohm^{-1} cm^{-1} has been reported. Systematic studies are being intensively pursued in various glass systems so as to increase the conductivity as much as possible. In this paper, the results obtained from the system Li_2O-B_2O_3-Li_3PO_4 are reported.

2. Experimental

The raw materials used for glass preparation were of Analar grade H_3BO_3 and Li_2CO_3. Li_3PO_4 used was prepared in the laboratory.

2.1 *Preparation of Li_3PO_4*

Lithium ortho-phosphate was prepared in the laboratory by solid state reaction between Li_2CO_3 and $(NH_4)_2HPO_4$ at 800°C. Stoichiometric amounts of Li_2CO_3 and $(NH_4)_2HPO_4$ were mixed in acetone as a slurry, dried overnight in an air-oven at 110°C, heated slowly in an alumina crucible to drive out CO_2, combined with water and ammonia, finally brought to 800°C, and kept for 2 hr. The mixture was cooled, ground and the procedure repeated to ensure thorough mixing and complete chemical reaction. X-ray powder diffraction spectrum, using Cu-K_α radiation was taken to confirm the presence of the desired phase only.

2.2 *Glass melting*

Appropriate amounts of dry reagents (H_3BO_3, Li_2CO_3, and Li_3PO_4) were mixed and melted in a platinum crucible at 950°C, for about 30 min till a clear bubble-free liquid was formed. The resultant melts were poured on to a brass mould and subsequently annealed at 450°C. The compositions of the different glasses melted are shown in figure 1. X-ray powder diffraction was used to check the formation of any crystalline phase.

2.3 *Electrical conductivity*

For measurement of conductivity, specimens were prepared in the form of rectangular tablets (approximately 10 × 5 × 2 mm) or circular discs (radius 5 mm thickness 2 mm both approximately).

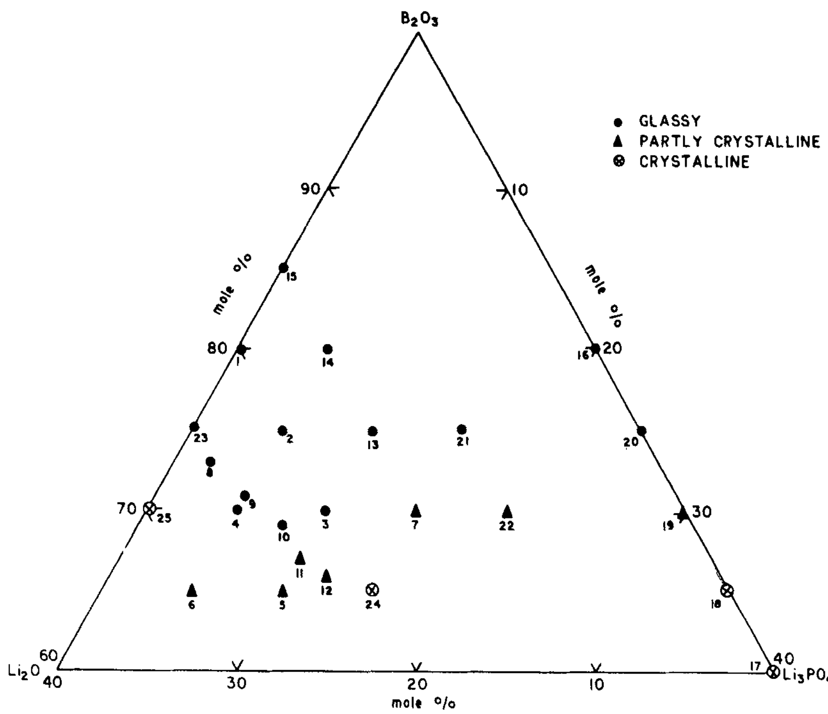

Figure 1. Glass formation region for the system B_2O_3-Li_2O-Li_3PO_4.

For glasses in which very small portions of crystallized inclusion (figure 1, solid triangle) was observed, only the transparent glassy part was used for conductivity measurements. The polished surfaces of each sample were coated with silver paste and platinum foil electrodes were placed on either sides of the sample. The whole arrangement along with a thermocouple was assembled in a quartz tube which was maintained at a pressure of the order of 10^{-2} mm of Hg. The temperature was controlled to within $\pm$ 1°C, by a temperature controller over the range 30-350°C. AC electrical conductivities were measured using a standard AC bridge (Wayne Kerr, model B224) at a frequency of 1592 Hz (the internal frequency of the bridge).

3. Results and Discussion

3.1 *Glass formation region*

Ten grams of the glass were melted at a time. The melt was cast in a brass mould and allowed to cool freely in air till, it was rigid enough to be transferred to the annealing furnace. Glass formation region under such experimental conditions in the Li_2O-B_2O_3-Li_3PO_4 system is shown in figure 1. Table 1 gives the chemical composition, density and other data for these glasses.

In the calculation of the total Li_2O content, both the lithia added as Li_2CO_3 and that present in Li_3PO_4 was taken into account. It may be seen from table 1 and figure 1 that under the present experimental conditions, glasses could be made with a maximum of about 36 mol% of the total Li_2O content.Concentration of lithium ion per unit volume was calculated from the chemical composition and density of these glasses. Figure 2 shows a plot of concentration of lithium ion against total Li_2O content of the glasses. Despite extra complexity in structure caused by the addition of Li_3PO_4 to Li_2O-B_2O_3

Table 1. Composition, total Li_2O content, density and Li-ion concentration of the Glasses studied in the system B_2O_3 - Li_2O - Li_3PO_4.

Glass No.	Composition (mol%)			Total Li_2O content (mol %)	Density (cm^{-3})	Li-ion concentration ($\times 10^{22}$) (cm^{-3})
	B_2O_3	Li_2O	Li_3PO_4			
1	80	20	0	20.0	2.116	0.845
2	75	20	5	26.19	2.170	1.12
3	70	20	10	31.82	2.231	1.55
4	70	25	5	30.95	2.243	1.42
5	65	25	10	36.36	2.273	1.70
6	65	30	5	35.70	2.294	1.73
8	73	25	2	27.45	2.199	1.22
10	69	23	8	32.41	2.256	1.48
12	66	22	12	35.71	2.268	1.65
14	80	15	5	21.43	2.146	0.88
16	80	0	20	25.0	2.148	0.98

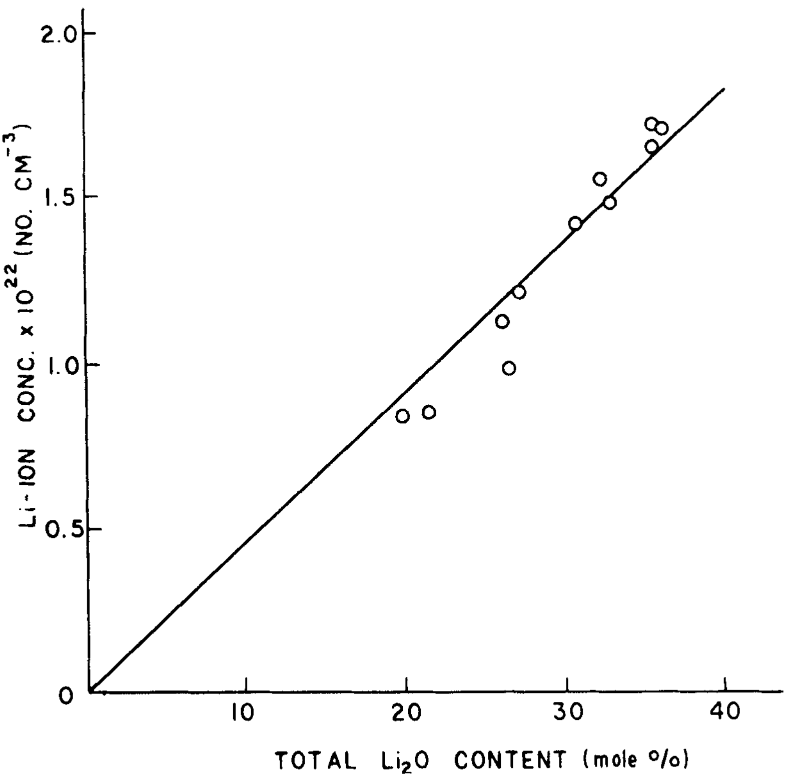

Figure 2. Variation of Li-ion concentration with total Li_2O content.

glasses, the volume concentration of lithium ion increases almost linearly with total Li_2O content of these glasses. Figure 3 shows a plot of the molar volume of the glasses 23, 8, 9, 10, 11 and 12 against mol% of Li_3PO_4 present in them. All these six glasses are on the pseudo-binary line joining the two end components (Li_2O, 3 B_2O_3) and Li_3PO_4. It is interesting to note that the plot is linear and thus partial molar volumes of (Li_2O, $3B_2O_3$) and Li_3PO_4 in mixtures within the composition range studied, do not change.

Under the experimental conditions of the present investigations, binary lithium borate melts containing more than 27 mol% Li_2O devitrified very quickly during casting. However, under the same experimental conditions, the limit of glass formation could be extended to around 36 mol% Li_2O (total) in the Li_2O-B_2O_3-Li_3PO_4 system with a consequent increase in the lithium ion concentration per unit volume.

3.2 *Temperature dependence of conductivity*

Electrical conductivity of all the glasses was measured in the temperature range 30–350°C. The conductivity σ followed the Arrhenius relation :

$$\sigma = A_0 \exp(-E_c/kT),$$

where T is the absolute temperature, A_0 is a constant, k is the Boltzmann constant and E_c is the activation energy for conduction. Some typical plots of $\log \sigma$ against T^{-1} are shown in figure 4. Activation energy for conduction E_c for various glasses was calculated from

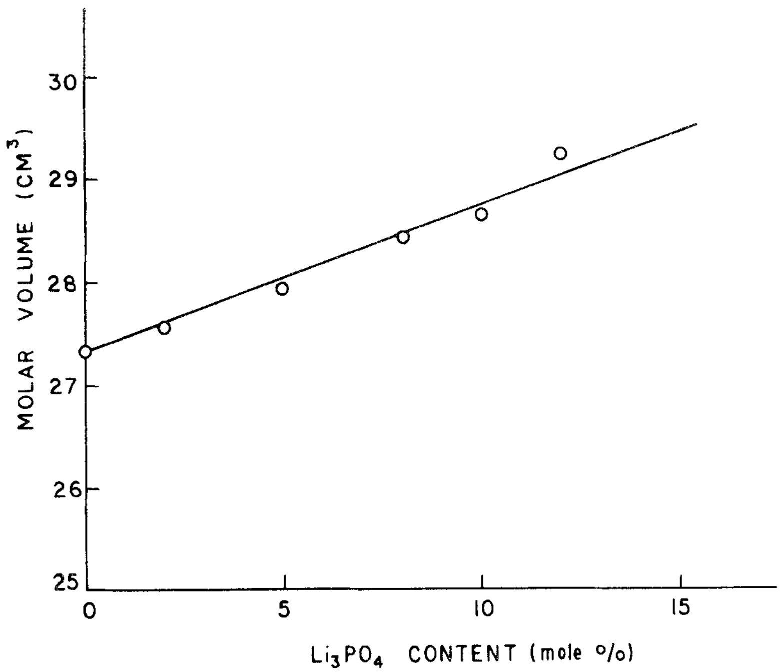

Figure 3. Variation of molar volume with Li_3PO_4 content.

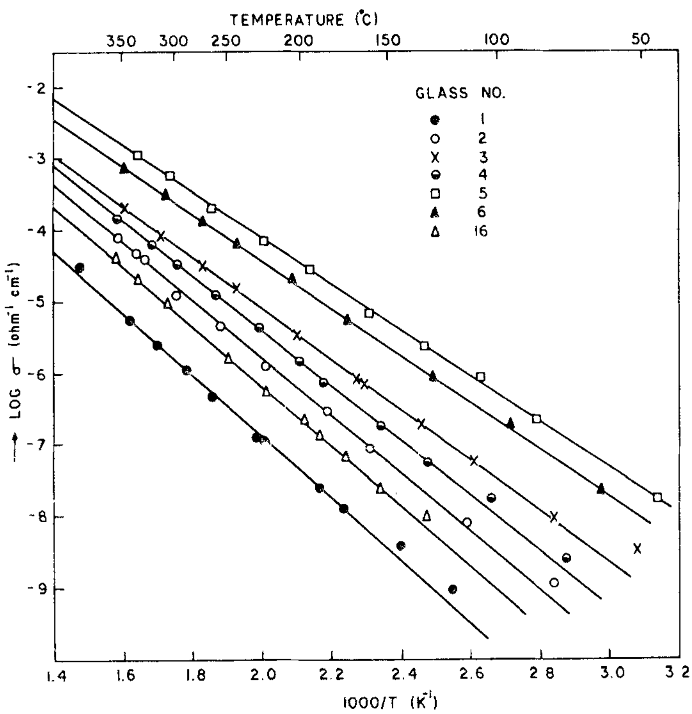

Figure 4. Typical plots showing temperature dependence of conductivity in the B_2O_3-Li_2O-Li_3PO_4 glasses.

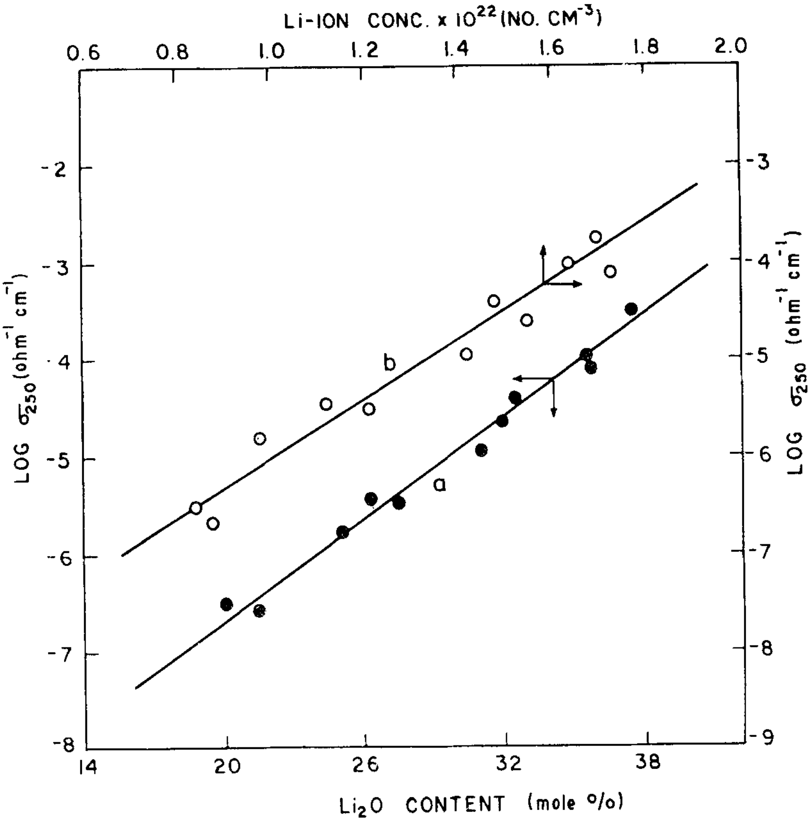

Figure 5. Variation of conductivity at 250°C with (a) total Li_2O content and (b) Li-ion concentration for the B_2O_3-Li_2O-Li_3PO_4 system.

the slope of such linear plots. Figure 5(a) shows the variation of conductivity at 250°C, with total Li_2O content of those glasses where a satisfactory linear relationship may be observed. A similar linear relationship exists between log σ_{250} and lithium ion concentration per unit volume of these glasses as shown in figure 5(b). The maximum conductivity obtained in this system is in the glass containing largest Li_2O (total) content, *i.e.* 36.36 mol% Li_2O having conductivity of the order of 10^{-4} ohm^{-1} cm^{-1} at 250°C.

The variation of activation energy with total Li_2O content of these glasses is shown in figure 6. As in many other alkali containing binary oxide glasses (Otto 1966; Owen 1963), the activation energy decreases with incresing Li_2O (total) content of these glasses.

In binary Li_2O-B_2O_3 glasses, addition of Li_2O predominantly changes the oxygen co-ordination of boron from 3 to 4 up to about 40 mol% Li_2O (Bray and O'Keefe 1963) breaks P-O-P bond with the formation of so-called non-bridging oxygen (Westman and Gartaganis 1957) P-O^-Li^+. Li_3PO_4 contains 75 mol% Li_2O and 25 mol% P_2O_5 whereas the highest Li_2O content in binary lithium borate glass used in the present investigation contained only 25 mol% Li_2O. Although standard-free energy of formation of ($3Li_2O$, P_2O_5) is much more negative (stable) than that of (Li_2O, $3B_2O_3$) (Jeffes 1975) in mixtures,

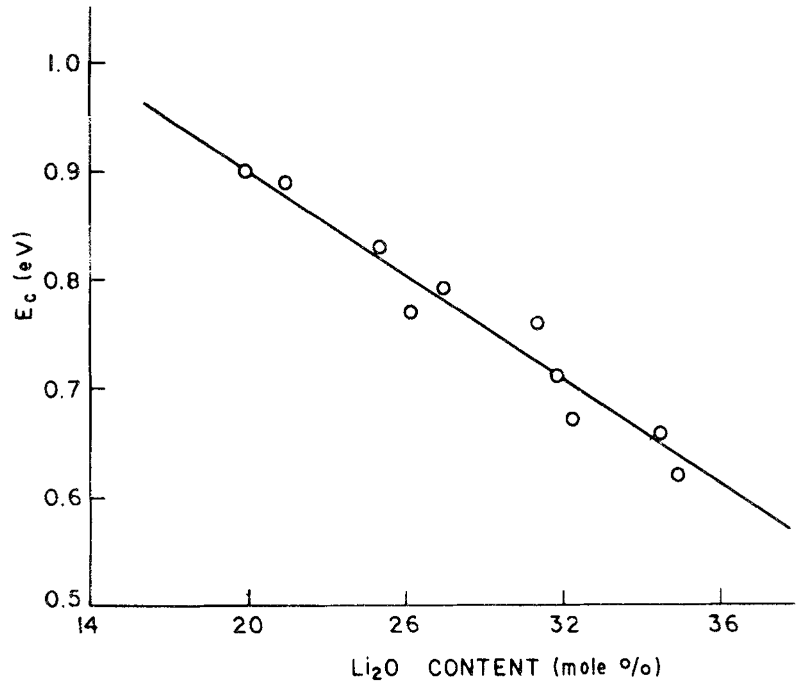

Figure 6. Variation of the activation energy for conduction (E_c) with total Li_2O content in B_2O_3-Li_2O-Li_3PO_4 glasses.

transfer of Li_2O from phosphate matrix to borate matrix is still theoretically possible provided the chemical potential of lithium oxide is lowered by that process. Unfortunately, data for free energy of mixing in this system are not available and no definite suggestions can be made. However, the constancy of partial molar volume (this can be estimated from figure 3 by drawing tangents at individual compositions) does not indicate any such Li_2O transfer.

Formation of borophosphate group with cristobalite type of structure in mixtures of borate and phosphate particularly containing low alkali oxide concentration is well known. Such borophosphate group formation involves co-ordination change of boron and π bonding of phosphate group and is thus expected to alter the molar volume. As discussed before, no such significant change of molar volume was observed in the present system probably indicating absence of borosphate group in these glasses.

From all these evidences, it appears that (Li_2O + B_2O_3) and Li_3PO_4 mixes almost ideally without any major structural change. However, by mixing Li_3PO_4 with lithium borate, glasses can be made with substantially larger concentration of Li^+ per unit volume and a consequent increase of lithium ion conductivity.

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