

Lithium borosulphate glasses: an analysis of glass transition temperature results

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Abstract. Lithium borosulphate glasses have been prepared in three different series: (a) $(42.5 - x)\text{Li}_2\text{O} : 57.5 \text{ B}_2\text{O}_3 : x\text{Li}_2\text{SO}_4$; (b) $42.5\text{Li}_2\text{O} : (57.5 - x)\text{B}_2\text{O}_3 : x\text{Li}_2\text{SO}_4$ and (c) $42.5\text{Li}_2\text{O} : 57.5\text{B}_2\text{O}_3 : x\text{Li}_2\text{SO}_4$. The glass transition temperature (T_g) of these glasses has been analysed on the basis of the fraction of four coordinated boron which governs the glass structure. The analysis reveals that the addition of Li_2SO_4 in series (a) and (b) gives rise to increased value of N_4 whereas, in series (c) it increases the number of non-bridging oxygens.

Keywords. Glass transition; four coordinated boron fraction; lithium borosulphate glasses.

1. Introduction

Lithium conducting glasses are used as solid electrolytes in electrochemical devices such as solid state batteries, coulometers, timers etc. In the last few decades a number of papers have been published on lithium borate (LB) glasses (Otto 1966; Takahashi and Yamamoto 1979; Levasseur *et al* 1979b; Button *et al* 1982; Ito *et al* 1983). The main interest in these glasses has been two-fold: (i) to understand the macroscopic structural details and (ii) to enhance the ionic conductivity of these glasses at the lowest possible temperature.

LB glasses are characterized by the boron network in their trigonal and tetragonal forms associated with the non-bridging oxygens (NBO's) (Bray and O'Keefe 1963). IR, NMR and Raman studies have been carried out on these glasses to understand the geometry and distribution of conduction sites responsible for ionic migration (Konijnedijk and Stevels 1975; Kamitsos *et al* 1987; Soppe *et al* 1988). Apart from the above studies, T_g is the parameter that apparently gives the glass structure. This parameter and the conductivity results of LB glasses are found to be sensitive to the value of N_4 for these glasses.

Ionic conductivity in glass can be enhanced by manipulating its structure either by controlling the thermal history or by increasing the mobile ion concentration (Charles 1966; Button *et al* 1983). Addition of lithium salts has also been reported to increase the ionic conductivity of lithium borate glasses (Levasseur *et al* 1979a; Singh and Rokade 1984; Deshpande *et al* 1985; Tuller and Button 1985; Gandhi *et al* 1989). The nature of incorporation of LiCl in LB glass system has been studied in detail (Button *et al* 1982) on the basis of NMR, Raman, IR and T_g results. In this respect the role of lithium sulphate addition in LB glasses is still not well understood. Therefore in the present work a detailed analysis of the T_g results has been carried out in lithium borosulphate glasses.

2. Experimental

Otto (1966) reported that a glass with 42.5 Li₂O:57.5B₂O₃ gives maximum conductivity in the LB series. This composition has been taken as a base system in the present study. Lithium borosulphate glasses have been prepared in the following three different series:

- (a) (42.5 - x)Li₂O:57.5 B₂O₃:xLi₂SO₄;
- (b) 42.5Li₂O: (57.5 - x)B₂O₃: xLi₂SO₄ and
- (c) 42.5Li₂O:57.5B₂O₃: xLi₂SO₄

where x = 3, 5, 7, 10 and 15 mol%. B₂O₃ AR (purity = 99.9%) (SISCO, India), Li₂CO₃ (purity = 99.9%) (Moscow, Russia) and Li₂SO₄ AR (purity 99.9%) (SISCO, India) were used as starting materials. About 12 g of the raw material of each batch was weighed (with an accuracy of 0.01 mg using a Mettler AE 163 balance) and mixed thoroughly under acetone. The dried mixture was heated up to the melting temperature in a platinum crucible at moderate rate. The melting temperature for these glasses was in the range 973 to 1173 K depending on the composition. The temperature was maintained at 40 K above the melting point for an hour to homogenize the melt. The glasses were cast by quenching the melt at room temperature between two aluminium blocks. The glass formation was confirmed by XRD and the transition temperatures estimated with a Perkin Elmer TADS 1700 unit, employing a scanning rate of 10°C/min.

3. Results and discussion

Figure 1 depicts the variation of T_g as a function of mol% Li₂SO₄ for all the three series. It was observed that in series (a) T_g decreases up to 3 mol% of Li₂SO₄ and remains constant with further increase in Li₂SO₄. For (b) T_g decreases gradually with the increasing Li₂SO₄ content. Interestingly, in (c) a prominent decrease in T_g is observed up to 10 mol% of Li₂SO₄.

This variation of T_g observed in three different series can be analysed on the basis of NMR and DTA results of LB glasses by Bray and O'Keefe (1963) who reported the fraction of four coordinated boron ($N_4 = BO_4/BO_3 + BO_4$) and T_g both are functions of $R = Li_2O/B_2O_3$ as shown in figures 2a and 2b respectively. It has been assumed that

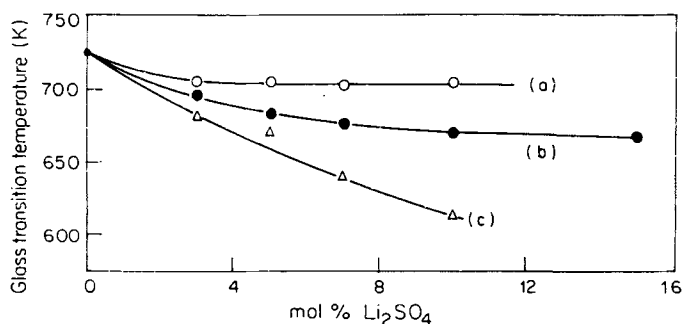


Figure 1. Variation of glass transition temperature with mol% Li₂SO₄ for lithium borosulphate glasses.

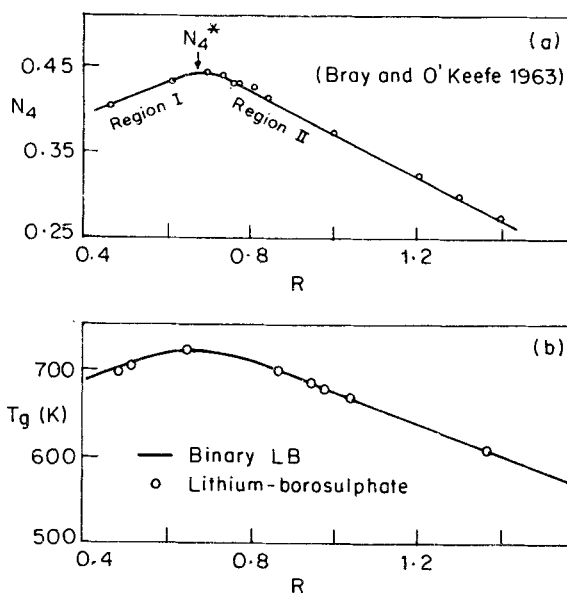


Figure 2a, b. Variation of fraction of four co-ordinated boron (N_4) and glass transition temperature for LB glasses.

Table 1. Composition, R , glass transition temperature, N_{4A} , N_{4B} and ΔN_4 for lithium borosulphate glasses.

Composition (in mol %) $\text{Li}_2\text{O}:\text{B}_2\text{O}_3:\text{Li}_2\text{SO}_4$	R	T_g (in K)	N_{4A}	N_{4B}	ΔN_4
42.5:57.5:0	0.73	726.0	0.442	0.442	0
39.5:57.5:3	0.68	704.6	0.446	0.415	0.031
37.5:57.5:5	0.65	704.5	0.441	0.415	0.026
35.5:57.5:7	0.61	702.7	0.43	0.410	0.02
42.5:54.5:3	0.77	698.2	0.432	0.41	0.022
42.5:52.5:5	0.80	683.8	0.425	0.385	0.04
42.5:50.5:7	0.84	678.8	0.415	0.38	0.035
42.5:47.5:10	0.89	670.3	0.402	0.365	0.037
42.5:42.5:15	1.00	669.2	0.375	0.365	0.01
41.225:55.775:3	0.73	681.3	0.442	0.38	0.062
40.375:54.625:5	0.73	669.0	0.442	0.365	0.077
39.525:53.475:7	0.73	641.8	0.442	0.315	0.127
38.25:51.75:10	0.73	612.8	0.442	0.28	0.162

N_4 for ternary glass system (i.e. glasses prepared in the present study) is also a function of R and varies similarly as that for the binary LB glasses. Thus N_4 for three series are calculated from figure 2a and denoted as N_{4A} .

The functional dependence of T_g on R for LB glasses follows that of N_4 as can be seen from figure 2b. It is evident from this figure that the T_g values for lithium borosulphate glasses (marked by open circles) lie on the same curve for LB glasses. Thus for a particular value of T_g , it is logical to calculate R from figure 2b and the corresponding N_4 from figure 2a. N_4 thus calculated are denoted by N_{4B} . The values of N_{4A} , N_{4B} along with those of T_g and R for different series are given in table 1. The difference in values of

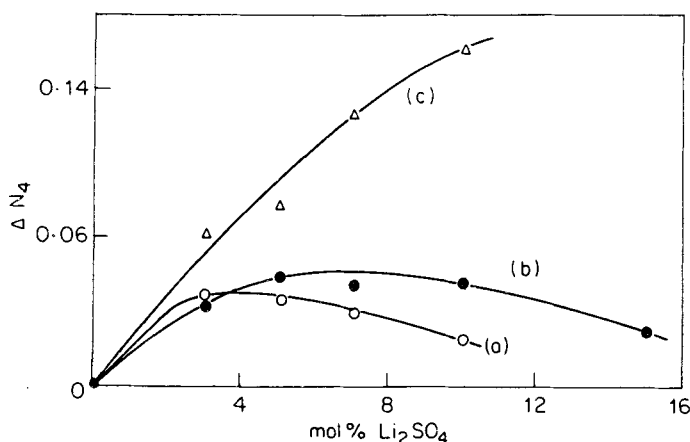


Figure 3. ΔN_4 variation with mol% Li_2SO_4 .

N_4 i.e. N_{4A} and N_{4B} suggests that the N_4 is not only a function of R but also gets influenced by Li_2SO_4 . This is justified because, according to Kamitsos *et al* (1987), the incorporation of Li_2SO_4 in lithium borate glasses gives rise to polar groups viz. BO_4 or NBO 's. Thus it can be considered that the obtained N_{4B} is the contribution of Li_2SO_4 to N_4 for ternary glasses.

In order to understand the role of Li_2SO_4 in LB glasses and the T_g variation in lithium borosulphate glasses (figure 1), the difference in the two N_4 values ΔN_4 ($\Delta N_4 = N_{4A} - N_{4B}$) is plotted as a function of mol% of Li_2SO_4 in figure 3. The variation of T_g in different series can be interpreted in the light of figures 2a and 3 as follows.

In figure 2a, the maximum value of N_4 (say N_4^*) corresponds to $R = 0.73$ (for $42.5\text{Li}_2\text{O}-57.5\text{B}_2\text{O}_3$ composition). From this figure one can distinguish two regions of N_4 : region-I on the left side of N_4^* where N_4 decreases with decreasing R and region-II on the right side of N_4^* , where N_4 decreases with increasing R . For series (a) with addition of Li_2SO_4 one moves in region-I (since $R < 0.73$) and thus the corresponding N_4 and T_g should decrease. However, the observed result is not so. This has been attributed to the contribution of N_{4B} due to the added Li_2SO_4 which strengthens the glass structure and hence enhances the T_g . It is also evident from figure 3 that the ΔN_4 increases for 3 mol% Li_2SO_4 but then decreases with further increase in Li_2SO_4 . Thus the contribution of N_{4B} is less for 3 mol% Li_2SO_4 and it increases with further addition of Li_2SO_4 . This explains the observed results for series (a).

In case of series (b) with the addition of Li_2SO_4 one moves to the right of N_4^* ($R > 0.73$) in region-II, hence again N_4 and T_g should decrease. A critical look at figure 2a reveals that the fall in N_4 and T_g for series (b) should be of higher magnitude than that for series (a), since the slope in region-II is greater than in region-I. From figure 3 it can be seen that ΔN_4 increases for this series i.e. N_{4B} in this case is less than that in series (b). Thus the gradual decrease in T_g for this series can be understood. In this series for 15 mol% of Li_2SO_4 the ΔN_4 decreases compared to that for 10 mol% Li_2SO_4 . Hence the T_g for 10 and 15 mol% Li_2SO_4 containing glasses are almost the same. This also means that for the glass with 15 mol% Li_2SO_4 the contribution of N_{4B} has increased maintaining the same T_g .

For series (c), with addition of Li_2SO_4 , R remains constant at N_4^* . A prominent decrease in T_g observed in this case can be understood on the basis of a remarkable enhancement in ΔN_4 (figure 3). This suggests that the addition of Li_2SO_4 does not contribute much to N_{4B} . On the other hand it may increase the NBO's and thereby decrease T_g drastically.

4. Conclusion

On the basis of the analysis of T_g results of lithium borosulphate glasses the following conclusions can be drawn:

- (i) When Li_2SO_4 is substituted for Li_2O (not site to site) (series a) and B_2O_3 (series b) in LB glasses it contributes to the formation of four coordinated boron.
- (ii) The number of four-coordinated boron contributed by Li_2SO_4 is more in series (a) than in series (b). Hence the variation of T_g in series (a) is less than that in (b).
- (iii) When Li_2SO_4 is added to LB glasses by keeping $\text{Li}_2\text{O}/\text{B}_2\text{O}_3$ ratio constant (series c) it gives rise to NBO's which lowers T_g drastically.

References

- Bray P J and O'Keefe J G 1963 *Phys. Chem. Glasses* **4** 37
- Button D P, Tandon R P, King C, Velez M H, Tuller H L and Uhlmann D R 1982 *J. Non-Cryst. Solids* **49** 129
- Button D P, Moon P K, Tuller H L and Uhlmann D R 1983 *Glastech. Ber.* **56** K Bd 2 856
- Charles R J 1966 *J. Am. Ceram. Soc.* **49** 55
- Deshpande V K, Rokade S and Singh K 1985 *Proc. Sixth Riso. Int. Symp. on transport-structure relationship in fast ion and mixed conductors*, Denmark (eds) F W Poulsen, N H Andersen, K Clusen, S Skaarup and O T Sorensen; GH-Tryk 1/S Odense, 129
- Gandhi P R, Deshpande V K and Singh K 1989 *Solid State Ionics* **36** 97
- Ito Y, Miyauchi K and Oi T 1983 *J. Non-Cryst. Solids* **57** 389
- Konijnendijk W N and Stevels J M 1975 *J. Non-Cryst. Solids* **18** 307
- Kamitsos E I, Kavakassites M A and Chryssikos G D 1986 *J. Phys. Chem.* **90** 4528
- Kamitsos E I, Kavakassites M A and Chryssikos G D 1987 *J. Phys. Chem.* **91** 5807
- Levasseur A, Kabala M, Brethous J C and Hagenmuller P 1979a *Solid State Commun.* **32** 839
- Levasseur A, Brethous J C, Reau J M and Hagenmuller P 1979b *Mater. Res. Bull.* **14** 921
- Otto K 1966 *Phys. Chem. Glasses* **7** 29
- Singh K and Rokade S 1984 *J. Power Sources* **13** 159
- Soppe W, Marcel C V D and Hartog H W D 1988 *J. Non-Cryst. Solids* **101** 101
- Takahashi T and Yamamoto O 1979 *Chem. Lett.* 135
- Tuller H L and Button D P 1985 *Proc. Sixth Riso. Int. Symp. on Transport-structure relationship in fast ion and mixed conductors*, Denmark (eds) F W Poulsen, N H Andersen, K Clusen, S Skaarup and O T Sorensen; GH-Tryk 1/S Odense, 119