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Influence of Ag_2SO_4 addition on the electrical conductivity of the $Li_2O:B_2O_3$ system

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Abstract. Glasses in the $Li_2O:B_2O_3:Ag_2SO_4$ system were prepared with varying silver sulphate contents. From the present results it can be said that the amorphous matrix accepts Ag_2SO_4 up to 5 mol% without any devitrification. The enhancement in conductivity with change in the structure of metaborate glass is due to Ag_2SO_4.

Keywords. Electrical conductivity; mobility; non-bridging oxygens.

1. Introduction

In recent years, a number of glasses, which support high ionic conductivity (Tuller *et al* 1980), have been studied and progress has been made towards the understanding of the complex phenomenology of transport in highly disordered systems (Garland and Tanner 1978). Large variations in conductivity with varying alkali oxide content have been observed in oxide glasses. Recently, more complex glasses have been synthesised by dissolving salts in oxide–base glasses (Ravaine 1980), which are suitable for solid state batteries.

A number of workers have reported fast ion conduction in lithium borate glasses (Otto 1966; Charls 1966; Audier *et al* 1976; Biefeld 1978; Takahashi and Yamamoto 1979; Levasseur *et al* 1979b; Malugani and Robert 1979; Button *et al* 1982; Ito *et al* 1983). As reported by Otto (1966), conventionally quenched $Li_2O:B_2O_3$ (42·5 : 57·5 mol %) is the best homogeneous glass-forming composition with maximum conductivity. Tuller and Button (1985) have suggested that an enhancement in the conductivity of the $Li_2O:B_2O_3$ system can be obtained by manipulating the glass structure, where the number of available sites for conduction are more than the concentration of mobile ions. The incorporation of SO_4^{2-} anion in the form of Li_2SO_4 in the macromolecular chain of lithium–borate glass, increases the conductivity (Levasseur *et al* 1979a).

Several glasses show high values of ionic conductivity in the silver–borate system. According to Øye (1963) the mobility of lithium ion increases in the presence of silver ion. Deshpande and Singh (1986) report enhancement in the conductivity with the addition of $AgI:Ag_2SO_4$ eutectic in lithium–borate glasses.

The effect of SO_4^{2-} ion added in the form of Ag_2SO_4, on the electrical conductivity of lithium–borate glass system has presently been studied.

2. Experimental details

B_2O_3 (99·9% pure, Germany), Ag_2SO_4 (E Merck, India) and Li_2CO_3 (99·9% pure, Moscow, USSR) were used as starting materials. The compositions investigated here are listed in table 1.

Table 1. Conductivity values at 473 K for various compositions.

Composition $Li_2O:B_2O_3:Ag_2SO_4$	σ at 473 K $(ohm\text{-}cm)^{-1}$
42·5:57·5: 0	$4{\cdot}21 \times 10^{-5}$
42·5:54·5: 3	$2{\cdot}11 \times 10^{-3}$
42·5:52·5: 5	$9{\cdot}44 \times 10^{-5}$
42·5:50·5: 7	$4{\cdot}21 \times 10^{-5}$
42·5:47·5:10	$9{\cdot}44 \times 10^{-6}$
$Li_2O:B_2O_3$ (40:60) + 10 mol% $AgI:Ag_2SO_4$ eutectic.	$5{\cdot}30 \times 10^{-4}$ (523 K)*

*– (Deshpande and Singh 1986).

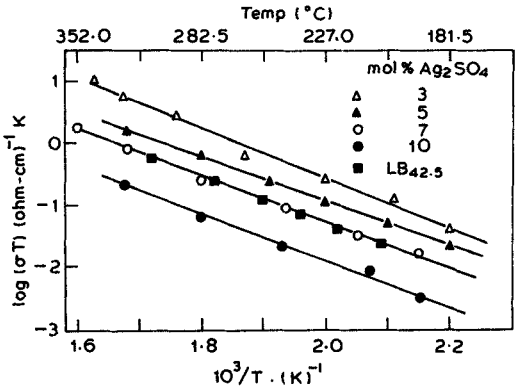

Figure 1. Variation of electrical conductivity of the $Li_2O:B_2O_3:Ag_2SO_4$ system with temperature.

About 12 g of the raw material of each batch were weighed and mixed thoroughly under acetone. The mixture was then heated in an electric furnace. It was maintained at 40 K above the melting point for 1 h to homogenize the melt. Glasses were cast by quenching the melt at room temperature in between two aluminium blocks. They were then characterised by XRD and DTA techniques.

The flat surfaces of the specimen were coated with silver paint and baked at 100°C for an hour to ensure good adhesion. Electrical conductivity was measured in the frequency range 5 Hz to 13 MHz at various temperatures ranging from 393 to 623 K by using a Hewlett–Packard 4192A LF impedance analyser. Temperature was controlled to ± 1°C accuracy with a Eurotherm temperature controller.

3. Results and discussion

Figure 1 shows the variation of conductivity with temperature for various mol% Ag_2SO_4 added to the $Li_2O:B_2O_3$ (42·5:57·5 mol%) system. The conductivity increases with increase in temperature for all the samples.

It is well-known that binary $Li_2O:B_2O_3$ (42·5:57·5 mol%) gives maximum conductivity when prepared by the conventional quenching technique. This glass is characterized by the boron network in its trigonal and tetrahedral form associated with non-bridging oxygens (NBO). Here, lithium ion conductivity in this glass is governed by the NBO and by the concentration of mobile ions. Thus, in the present case the above system is considered to be a prime system.

Figure 2 demonstrates the variation of log σ as a function of mol% Ag_2SO_4 at three different temperatures. Here it can be seen that the conductivity increases with Ag_2SO_4 concentration up to 5 mol% and beyond that it decreases.

From figure 3, it is seen that the glass transition temperature (T_g) determined from DTA is minimum for 3 mol% Ag_2SO_4, where the maximum conductivity is observed. As the concentration of Ag_2SO_4 increases from 3 to 5 mol%, the T_g increases and the conductivity decreases. Beyond 5 mol% Ag_2SO_4 the glass transition temperature decreases due to crystallization (which is evident from XRD analysis) which in turn decreases the conductivity.

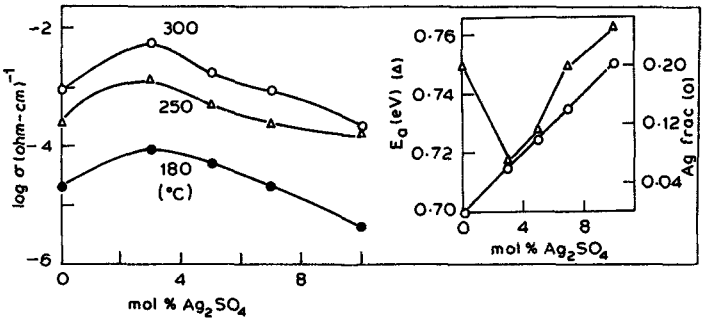

Figure 2. Variation of conductivity, activation energy and $Ag_{fraction}$ with mol% of Ag_2SO_4 in the $Li_2O:B_2O_3:Ag_2SO_4$ glass system.

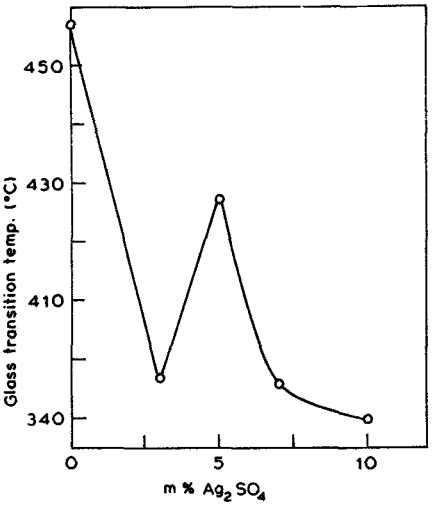

Figure 3. Variation in the glass transition temperature with mol% Ag_2SO_4 in the $Li_2O:B_2O_3:Ag_2SO_4$ system.

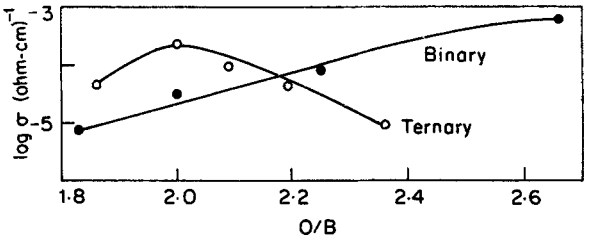

Figure 4. Variation of conductivity with O/B ratio for binary and ternary glass system at 200°C.

Maximum conductivity for 3 mol% Ag_2SO_4 is further supported by the minimum in the activation energy seen in the inset of figure 2. Here the SO_4^{2-} ion being tetrahedral might extend the BO_3/BO_4 glass network. The Ag^+ ion being large in size expands the B_2O_3 lattice which in turn enhances the mobility of mobile ions. In this case the silver ion might also contribute to the conduction.

From figure 4, the value of O/B ratio for metaborate glass and glass with 3 mol% Ag_2SO_4 is seen to be the same. Thus we can say that on addition of Ag_2SO_4 the structure gets manipulated and thus is responsible for the maximum value of conductivity obtained.

4. Conclusion

It can be concluded from the present study that 3 mol% Ag_2SO_4 addition to the 42·5 Li_2O : 57·5 B_2O_3 glass system, where the lithium metaborate structure is manipulated by Ag_2SO_4, shows maximum conductivity.

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