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

V K DESHPANDE and K SINGH
Department of Physics, Nagpur University, Nagpur 440 010, India

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Abstract. Addition of three eutectics, $Li_2SO_4:Li_2CO_3$, $3Li_2O{\cdot}Nb_2O_5:LiNbO_3$ and $AgI:Ag_2SO_4$ has been tried in the $Li_2O:B_2O_3$ glass system. The electrical conductivity increases with the addition of eutectic. The amount of lithium fraction and the melting point of the eutectic govern the conductivity.

Keywords. Eutectic; lithium fraction; electrical conductivity.

1. Introduction

In recent years, considerable research has been devoted to electrolytes based on Li ion conducting glasses suitable for solid state batteries. Non-crystalline solid electrolytes have definite advantages over their crystalline counterparts, like isotropic properties, ease of thin film formation, flexibility of size and shape (at satisfactory cost) etc. One of the important features of glass as a solid electrolyte is the possibility of continuous change of the composition over a wide range. A major characteristic of oxide glasses concerns the large variation in the conductivity with alkali oxide content. Recently, more complex glasses have been synthesized by dissolving salts in an oxide based glass (Smedley and Angell 1978; Levasseur *et al* 1979a).

A number of workers have reported fast ion conduction in lithium borate glasses (Otto 1966; Charls 1966; Levasseur *et al* 1979b; Biefeld *et al* 1978; Audier *et al* 1976; Malugani and Robert 1979; Glass *et al* 1978). As reported by Singh and Rokade (1984), conventionally quenched $Li_2O:B_2O_3$ (40:60 m%) is the best homogeneous glass-forming composition with maximum conductivity. Tuller and Button (1985) have suggested that an enhancement in the conductivity of $Li_2O:B_2O_3$ system can be obtained by increasing the alkali ion concentration. According to Øye (1963) the mobility of Li ion increases in the presence of silver ions. Low melting point is one of the important criteria responsible for high ionic conductivity (Reau *et al* 1978). In a binary system, an eutectic is the lowest melting point composition.

By considering the above factors, an attempt has been made to study the influence on the electrical conductivity of $Li_2O:B_2O_3$ (40:60) system by the addition of $Li_2SO_4:Li_2CO_3$, $3Li_2O.Nb_2O_5:LiNbO_3$ and $AgI:Ag_2SO_4$ eutectics. It is expected that the presence of these eutectics in the glass system under study will provide an enhancement in the conductivity.

2. Experimental details

In the present work, the starting materials, Li_2SO_4, Li_2CO_3, B_2O_3, AgI, Ag_2SO_4 and Nb_2O_5 of 99·9% purity were used for the synthesis of the glasses. For preparing

$Li_2SO_4:Li_2CO_3$ eutectic, about 10 g of raw material in eutectic ratio (60:40) m% was weighed to an accuracy of 0·0001 g and mixed under acetone. The mixture was then heated in an electric furnace. It was maintained at a temperature of 20 K above the melting point for 2 hr to homogenize the melt. Then the melt was quenched in an aluminium mould at room temperature. This eutectic was then crushed to a fine powder and added in the host $Li_2O:B_2O_3$ system.

Similarly, other eutectics of $3Li_2O.Nb_2O_5:LiNbO_3$ and $AgI:Ag_2SO_4$ were prepared. Later, these eutectics were added in different concentrations to the lithium borate glass. In all these compositions, the ratio of $Li_2O:B_2O_3$ was maintained to be 40:60 m%. After quenching the glasses in aluminium mould, they were immediately transferred to an annealing furnace maintained at 473 K. After 4 hr of annealing, the samples were subjected to furnace cooling.

The glasses thus obtained were polished flat. Silver paint was used to ensure the ohmic contact before loading the sample in the sample holder which has been described elsewhere (Deshpande and Singh 1982). The conductivity of these samples was measured at 1 kHz as a function of temperature.

3. Results and discussion

Figure 1 shows the variation of log σT vs $10^3/T$ for $Li_2O:B_2O_3$ glass system with addition of three eutectics; Li_2SO_4:Li_2CO_3, $3Li_2O.Nb_2O_5:LiNbO_3$ and $AgI:Ag_2SO_4$. In general, the conductivity increases with increase in temperature. Typical conductivity values at two different temperatures, lithium fraction and the melting point of the dopant eutectic, are given in table 1 and it is evident that the addition of all the

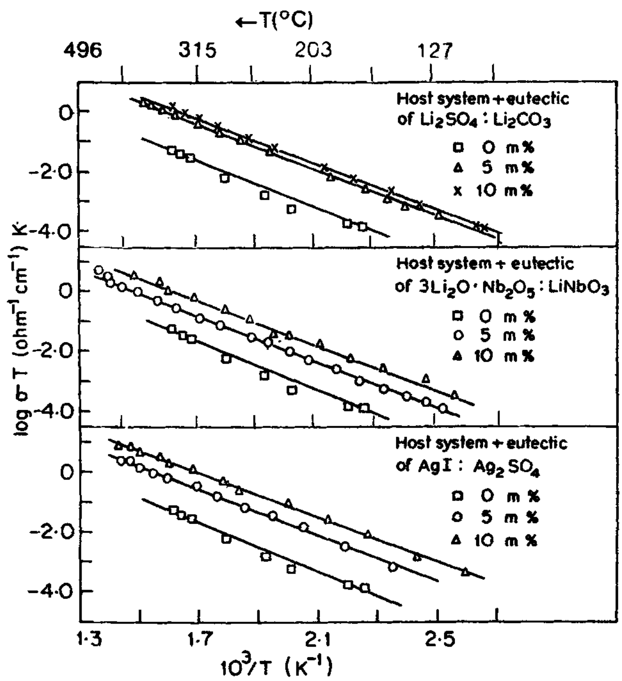

Figure 1. Variation of log σT vs $10^3/T$ for $Li_2O:B_2O_3$ host system with the addition of three different eutectic.

Table 1. Conductivity values at 623 and 523 K, lithium fraction and melting point of the dopant eutectic.

$Li_2O:B_2O_3$ (40:60) + 10 m% of eutectic	σ in ohm^{-1} cm^{-1} at 623 K	523 K	$*f_{Li^+}$	Melting point of the eutectic
	1.15×10^{-4}	5.70×10^{-5}	0·80	
$Li_2SO_4:Li_2CO_3$	2.02×10^{-3}	1.51×10^{-4}	0·92	530°C (Amadori 1912)
$3Li_2O{\cdot}Nb_2O_5:LiNbO_3$	1.60×10^{-3}	1.35×10^{-4}	0·84	1160°C (Reismen 1958)
$AgI:Ag_2SO_4$	4.03×10^{-3}	5.3×10^{-4}	0·72	158°C (Takahashi *et al* 1972)

$$*f_{Li^+} = \frac{2n_{Li_2O} + 2n_{Li_2SO_4} + 2n_{Li_2CO_3}}{n_{Li_2O} + n_{B_2O_3} + n_{Li_2SO_4} + n_{Li_2CO_3}}$$

where n_i is the number of moles of constituent i in the mixture.

three eutectics enhances the conductivity of the host system by more than an order of magnitude. The enhanced conductivity for higher concentration of the first two eutectics is due to increased Li^+ fraction. Similar enhancement in the conductivity with increasing Li^+ fraction has been reported earlier (Deshpande *et al* 1985).

Among the three eutectic samples, the conductivity for $3Li_2O.Nb_2O_5:LiNbO_3$ is minimum. This is because of its higher melting point and lower lithium fraction than that for $Li_2SO_4:Li_2CO_3$. The lithium fraction for 10 m% $Li_2SO_4:Li_2CO_3$ containing sample (0·92) is higher than that observed for 7 m% Li_2SO_4 containing $Li_2O:B_2O_3$ glass (0·88) (Deshpande *et al* 1985). Also the conductivity in this case is higher than what was reported earlier for 7 m% Li_2SO_4 added sample. Thus, the melting point of the eutectic and the lithium fraction governs the conductivity for eutectic of lithium salts.

For 10 m% $AgI:Ag_2SO_4$ eutectic, maximum conductivity is observed. This is because of the lowest melting point of this sample over all the others studied in the present investigation. This sample was a homogeneous glass without any crystallization in it suggesting that, upto 10 m%, $AgI:Ag_2SO_4$ gets adjusted in the amorphous matrix of the host system. The SO_4, being tetrahedra might extend the BO_3/BO_4 glass network. Due to the larger size of the iodine, it expands the lattice which enhances the mobility of the mobile ion. In this case, silver ions might also contribute to the conduction. However, due to non-availability of the experimental facilities, it was not possible to separate out the contribution of silver and lithium ions. The study of AgX (X = I, Br) containing borate glasses suggests that AgI containing glasses give more conductivity (Minami *et al* 1982). According to Minami (1983), those Ag ions surrounded by halide ions in the glass contribute to the conduction. In B_2O_3 containing glasses, Ag ions interacting with BO_4 groups also contribute to the conduction as well as the Ag ions surrounded by halide ions.

4. Conclusion

From the present investigation it can be concluded that, lower the melting point of the eutectic, higher is the conductivity of the system. The maximum value of conductivity, $\sigma \simeq 4.03 \times 10^{-3}$ ohm^{-1} cm^{-1} at 623 K obtained for sample with 10 m% $AgI:Ag_2SO_4$ eutectic can be used for technical applications.

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