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ENHANCEMENT OF THE IONIC CONDUCTIVITY OF LITHIUM BOROPHOSPHATE GLASS: A MIXED GLASS FORMER APPROACH

R. V. SALODKAR, V. K. DESHPANDE and K. SINGH

Department of Physics, Nagpur University, Nagpur 440010 (India)

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Summary

The electrical conductivity of the lithium borophosphate system has been studied. An enhancement in the ionic conductivity has been obtained via the mixed glass former effect. Two maxima have been observed in the conductivity and have been explained by using a thermodynamic approach. The highest conductivity at 30 °C is 1×10^{-6} (ohm cm)$^{-1}$, corresponding to a Li/P ratio of unity. Glass with this composition may find useful application in electrochemical power sources.

Introduction

Research activities in the field of solid electrolytes have long been dominated by studies of crystalline materials. In recent years, however, glassy solid electrolytes have become the focus of interest because these materials have certain advantages over their crystalline counterparts [1]. Since lithium is the lightest and most electropositive metal, lithium-conducting glasses [2 - 9] offer good prospects for application in high energy density batteries and other electrochemical systems. The development of lithium conducting glasses has proceeded in several directions:

- replacement of oxygen in oxide glasses by sulphur (the latter being more polarizable than the former) [10 - 12]
- addition of alkali salts, such as halides, sulphates, etc., to increase the carrier concentration [13 - 16]
- use of rapid quenching techniques to obtain glasses of higher lithium content [17 - 19].

Although considerable attention has concentrated on obtaining glasses that are rich in modifier content, little effort has been devoted to the mixing of glass formers as a means of achieving an enhanced conductivity. With competitive network formation (using more than one glass former), it has been shown [2, 3, 20, 21] that technologically interesting products can be obtained. In particular, when the molar fraction of the modifier is kept constant, the conductivity and glass transition temperature (T_g) of boro-

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phosphate glasses are highly non-linear functions of the $B_2O_3/B_2O_3 + P_2O_5$ ratio [6, 21].

Chiodelli *et al.* [22] have reviewed the published data on the relationship between properties of glasses using a single glass former and those having a competitive network formation. The authors conclude that the latter systems cannot be characterized by the same rules that appear to hold for systems produced with one glass former.

The properties of borophosphate glasses have been studied by several workers [20, 23 - 26]. Takahashi [27] showed that the glasses have relatively good chemical durability and a comparatively high T_g on account of the presence of BPO_4 groups. Tsuchiya and Moriya [20] have also examined various properties of borophosphate glasses (namely, density, hardness, thermal expansion and Raman spectra) and have related their behaviour to the BPO_4 and BO_4 groups in the glasses.

A detailed study of lithium borate glasses (in the range 40 - 50 mol percent. Li_2O*) has revealed that a 42.5% Li_2O:57.5% B_2O_3 composition yields maximum conductivity for conventionally prepared samples [28]. Thus, with a view to increasing further the conductivity of this optimized composition, the electrical conductivity of the 42.5% Li_2O:$(57.5 - X)$% B_2O_3:X% P_2O_5 series has been investigated in the work reported here.

Experimental

The Li_2O:B_2O_3:P_2O_5 glass systems were prepared by keeping the Li_2O content constant and varying the ratio

$$Y_P = \frac{P_2O_5}{B_2O_3 + P_2O_5} \quad \text{(Table 1)}.$$

The starting materials Li_2CO_3 (A.G. Fluka), P_2O_5 and B_2O_3 (E'merk, Darmstadt) were of high purity (99.9%). The materials were mixed thoroughly in the required proportions and the dried mixture was then heated in a platinum crucible. The temperature was maintained at 20 °C above the melting point of the mixture for 1 h.

The clear and bubble-free melt was quenched between two aluminium slabs at room temperature. The resulting glasses were polished to obtain a specimen of regular shape. The electrical measurements were carried out at various temperatures using a Hewlett Packard 4192 A LF impedance analyser in the frequency range 5 Hz - 13 MHz. The amorphous nature of the glasses was confirmed by X-ray diffraction analysis.

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*All subsequent mole percentages are written as %.

TABLE 1

Properties of lithium borophosphate glasses of various compositions

Composition (mol.%)			$Y_P = \frac{P_2O_5}{B_2O_3 + P_2O_5}$	log σ* (ohm cm)$^{-1}$	E_a (eV)	Li/B	Li/P	log σ_o
Li_2O	B_2O_3	P_2O_5						
42.5	57.5	0	0	−7.82	0.755	0.73	–	4.86
42.5	51.75	5.75	0.1	−7.22	0.75	0.82	7.3	5.37
42.5	46	11.5	0.2	−7.02	0.72	0.92	3.6	5.07
42.5	40.25	17.25	0.3	−6.22	0.58	1.0	2.4	3.52
42.5	34.5	23	0.4	−6.77	0.66	1.2	1.8	4.37
42.5	28.75	28.75	0.5	−6.92	0.64	1.4	1.4	3.83
42.5	23	34.5	0.6	−6.62	0.67	1.8	1.2	4.63
42.5	17.25	40.25	0.7	−6.0	0.61	2.4	1.0	4.22
42.5	11.5	46	0.8	−7.97	0.82	3.6	0.92	5.80
42.5	5.75	51.75	0.9	−8.57	0.79	7.3	0.82	4.70
42.5	0	57.5	1.0	−8.027	0.795	–	0.73	5.32

*At 30 °C.

Results and discussion

Figure 1 shows the conductivity (σ) of the glasses as a function of Y_p at three different temperatures, namely 100 °C, 150 °C and 200 °C. In each isotherm, two maxima in conductivity are observed, at $Y_p = 0.3$ and $Y_p = 0.7$. The maximum at $Y_p = 0.7$ is more pronounced than that at $Y_p = 0.3$. The conductivity isotherm at 30 °C and the variation of activation energy (E_a) as a function of Y_p is shown in Fig. 2. It can be clearly seen that the activation energy exhibits minima at the Y_p values that correspond to maxima in the conductivity.

Typical values of the conductivity at 30 °C, the activation energy, the Li/P and Li/B ratios, and the pre-exponential factor (σ_o) for different compositions are given in Table 1. It is interesting to note that for $Y_p = 0.3$, the Li/B ratio is unity, whereas for $Y_p = 0.7$ the Li/P ratio is unity.

The existence of two maxima in the conductivity has been reported for oxide glass systems such as Li^+, Na^+ and Ag^+ conducting borophosphate and borotellurate [19 - 21, 29]. Deshpande *et al.* [30] have also reported an enhancement in the conductivity of the sulfide glass system, Li_2S:SiS_2:GeS_2. This was attributed to the mixed glass former effect. The two maxima generally observed (one being more prominent that the other) in the conductivity curves of borophosphate and borotellurate glasses have been explained on thermodynamic grounds [20, 29 - 31]. The ternary glass system is considered to be a mixture of two binary limiting compositions, and the formalism of a regular solution model is taken to be valid. If the enthalpy of mixing (ΔH_m) is assumed to be positive, *i.e.*,

$$\Delta H_m = -\alpha x(1 - x) \tag{1}$$

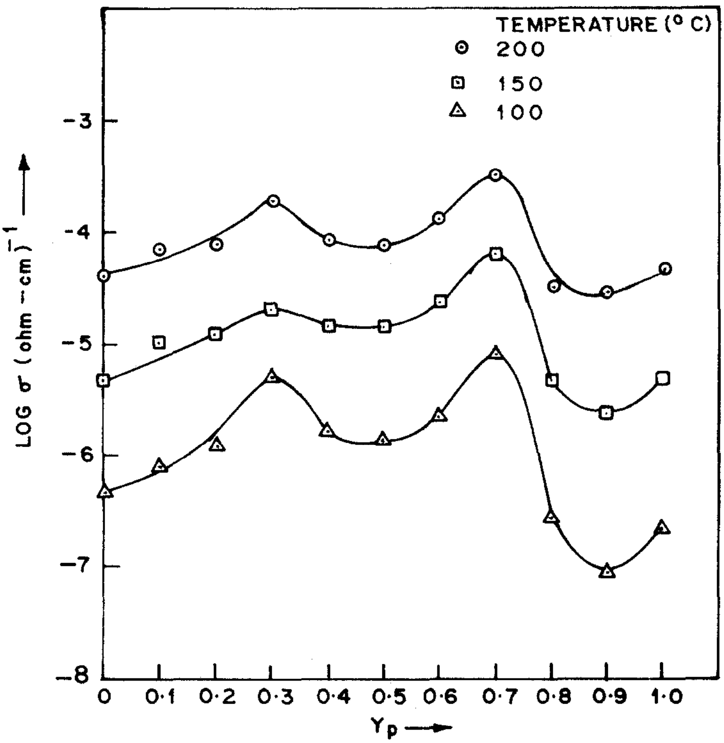

Fig. 1. Variation of conductivity with Y_p at three different temperatures.

then immiscibility is expected for the glasses. For kinetic reasons, however, this may not occur. In this case, the modifier activity can be calculated giving two maxima in the curve. The maxima will be close to the limiting compositions, as the parameter α (which is indicative of the bond rearrangement resulting from the reaction of the mixture) is negative, as shown by Kone [31] for the Na_2O:B_2O_3:P_2O_5 system, and Herving and Navrotsky [32] for the Na_2O:B_2O_3:SiO_2 system. According to weak electrolyte theory, the activity and conductivity vary in the same sense — and therefore two maxima in the conductivity are expected.

The conductivity of the lithium borophosphate glasses investigated here is compared in Table 2 with that reported elsewhere for analogous systems of high conductivity. The data show that the lithium borophosphate glasses have the highest conductivity. This may be due to the fact that the basic composition (42.5% Li_2O:57.5% B_2O_3) of the present system yields the best conductivity for the entire binary series. Table 3 presents a comparison of the present results with those previously reported for binary borate and phosphate glasses containing high lithium concentrations. The data show that despite the decrease in lithium content, an improved ionic conductivity

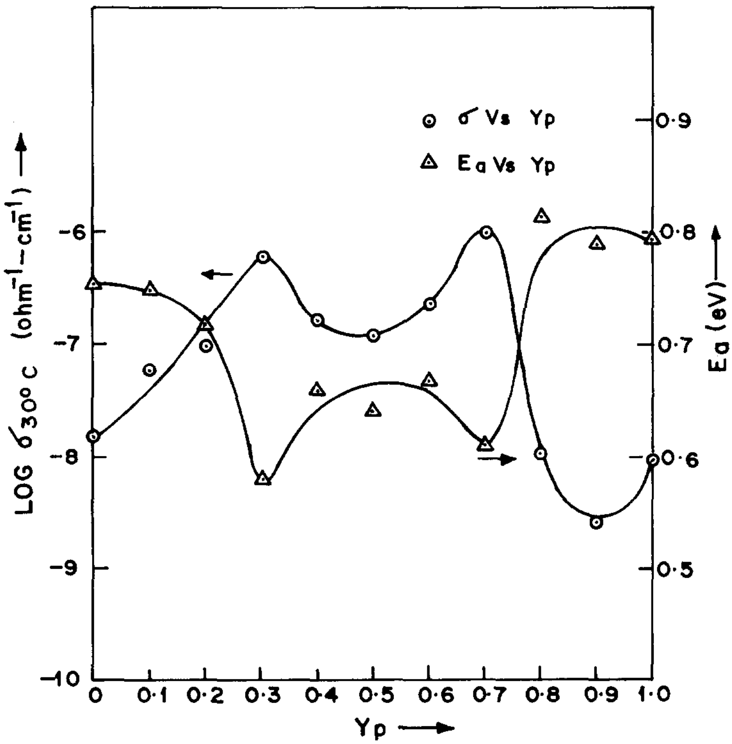

Fig. 2. Variation of conductivity at 30 °C and activation energy with Y_p.

TABLE 2

Conductivity (σ) of lithium borophosphate glasses of various compositions

Composition (mol.%)	σ (ohm cm)$^{-1}$	Temp. (°C)	Ref.
$50Li_2O:30B_2O_3:20P_2O_5$	1.4×10^{-7}	22	6
$33.4Li_2O:33.3B_2O_3:33.3P_2O_5$	6.3×10^{-10}	22	6
$40Li_2O:20B_2O_3:40P_2O_5$	6.3×10^{-9}	30	20
$40Na_2O:40B_2O_3:20P_2O_5$	3.5×10^{-9}	30	20
$30Li_2O:40B_2O_3:30P_2O_5$	5×10^{-8}	30	20
$40Li_2O:48B_2O_3:12TeO_2$	4×10^{-11}	25	29
$40Li_2O:18B_2O_3:42TeO_2$	2×10^{-10}	25	29
$42.5Li_2O:40.25B_2O_3:17.25P_2O_5$	5.9×10^{-7}	30	*
$42.5Li_2O:17.25B_2O_3:40.25P_2O_5$	1×10^{-6}	30	*

*Present study.

can be achieved by using two glass formers. Clearly, this procedure modifies the structure of the glass and thereby causes an enhancement in the ionic mobility and, in turn, the conductivity.

TABLE 3

Comparison of the present results with binary borate and phosphate glasses containing high lithium concentrations reported elsewhere

Composition (mol.%)			σ (ohm cm)$^{-1}$	Temperature (°C)	Reference
Li_2O	B_2O_3	P_2O_5			
75	25	0	1×10^{-7}	25	8
63	37	0	6.3×10^{-11}	25	33
63	0	37	1.2×10^{-7}	25	34
42.5	57.5	0	1.5×10^{-8}	30	*
42.5	0	57.5	9.4×10^{-9}	30	*
42.5	17.25	40.25	1×10^{-6}	30	*

*Present study.

Conclusions

The mixing of two glass formers is effective in improving the ionic conductivity of lithium borophosphate glass. Glass with a composition of 42.5% Li_2O:17.25% B_2O_3:40.25% P_2O_5 has a conductivity of 1×10^{-6} (ohm cm)$^{-1}$ and could prove useful in power source applications.

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