

ELECTRICAL CONDUCTION IN LITHIUM BOROPHOSPHATE GLASSES

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Abstract

Electrical conductivity of ternary glass system 30mol%B₂O₃-(70-x) mol% P₂O₅-x mol% Li₂O is carried out using two-probe method. The samples are fabricated using the well known melt quench technique. The measurements are undertaken at room temperature and also in the temperature range 293-473K. The conductance is found to increase by the addition of Li₂O. The conductivity switches from a low voltage ohmic type to the field emitted exponential type for high enough fields. This can be explained on the basis of the Pool-Frenkel phenomenon. The dc activation energies E_a and the refractive indices n are also evaluated.

Keywords: Activation energy, Pool-Frenkel conduction, phosphate glasses.

INTRODUCTION

Ever since the discovery of semi conducting nature of phosphate glasses by Deuton *et al.* [1954] many studies on the electrical properties of P₂O₅ glasses have been reported [Moustafa 1999, Almeida *et al.* 2001, Abid *et al.* 2003, Lee *et al.* 2004]. Phosphate glasses have relatively low melting point compared with silicate and borate glasses. Their high conductivity makes them potentially applicable to supersonic conductors, solid electrolyte etc. Borophosphate glasses are among the multi component glasses studied for the interesting applications. Such glasses are useful as their properties can be effectively controlled by changing their composition. However, little is known about the conduction mechanism of lithium borophosphate glasses, their basic structure unit and effect of lithium on electrical behavior. The composition studied is the mixture of two formers (B₂O₃ and P₂O₅) and one alkali-modifier (Li₂O). This research work is performed to determine the conduction behavior of these glasses and to investigate the temperature dependence of the conductivity thus evaluating the activation energy E_a of the system from Arrhenius equation [Bose and Thangandurai 2006]:

$$\sigma = \sigma_0 \exp (- E_a / kT).$$

MATERIALS AND METHODS

The desired Lithium-borophosphate glasses were prepared using relevant amounts of lithium carbonate (Li_2CO_3), boron trioxide (B_2O_3) and phosphoric oxide (P_2O_5) by melt-quench technique for 6 gm samples using molar weight percentage formula bearing four different compositions 30mol% B_2O_3 -(70-x)mol% P_2O_5 -x mol% Li_2O with x = 35, 37.5, 40 and 42.5. To avoid thermal stresses, samples were annealed at 473 K for two hours. Grinding them on silicon carbide paper produced polished disc shaped glass samples. For fine polishing the silicon carbide papers of grads 320 to 1000 were used. The samples were cleaned by an industrial glint before the evaporation of electrodes. In order to undertake the electrical measurements metallic electrodes (Cu-electrodes) were evaporated using thermal evaporation technique on either side of the glass samples. The electrode evaporation was carried out using Edwards 306A Coating Unit. Two-probe method was used to carry out the d.c. conductivity measurements. These measurements (current, I versus voltage, V) were taken at room temperature and in the temperature range 293-473 K (for Arrhenius plots). The voltage applied range was from 20 to 2000 volts using KEITHLEY 247 High Voltage Supply. The current was measured using KEITHLEY 610C Electrometer.

RESULTS AND DISCUSSION

Fig. 1 illustrates the initial electrical measurements on the as prepared lithium borophosphate glass systems in various compositions. This is the I-V data plotted on logarithmic scale. An increasing conductance level with the Li_2O contents is noticed. This is attributed to the increase of NBOs (non-bridging oxygens) [Deuton *et al.* 1954, Moustafa 1999, Almeida *et al.* 2001, Lee *et al.* 2004]. Li_2O working as modifier cleaves the glass network structure thereby increasing the NBOs which enhances the conductivity of a glass. This is because the Li^+ ions are weakly bonded to the NBOs and can migrate easily with applied voltage.

Two regions of conductance i.e. at low applied bias and the high field conduction can easily be differentiated. The low voltage region is the ohmic range as is expected due to the presence of thermally generated carriers. The high voltage range doesn't seem to follow any single power law straight behavior indicating some field assisted exponential barrier conduction. This field assisted exponential conduction is controlled by either Schottky or Poole-Frenkel mechanisms [Simmons 1967]. Schottky conduction is analogous to thermionic emission over a field lowered barrier, which arises from electrode image-force interaction with the field at metal-insulator interface. This conduction is described by the relation (current density J versus applied field F):

$$J = A T^2 \exp(-\phi_0 / kT) \exp(\beta_S F^{1/2} / kT) \quad (1)$$

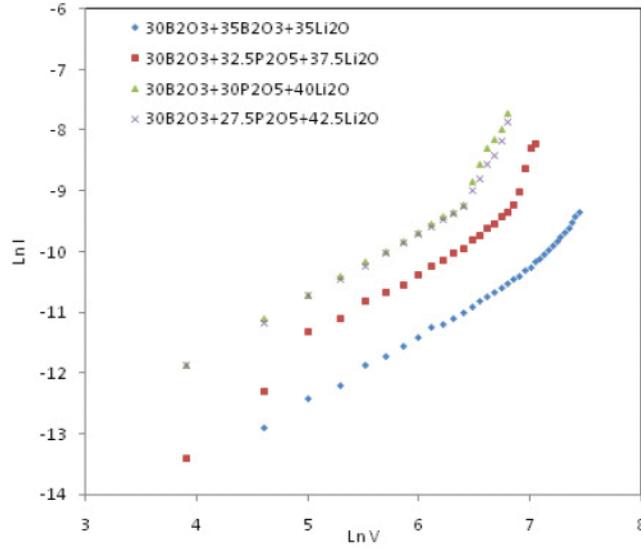


Fig.1. Logarithmic Current against logarithmic Voltage.

where β_S (Schottky coefficient of barrier lowering) is given by

$$\beta_S = \left[\frac{e^3}{4\pi \epsilon_0 K^*} \right]^{1/2} \quad (2)$$

$A = 120$ (in conventional units) is the Richardson constant, K^* is the high frequency dielectric constant and ϕ_0 is the barrier height at zero applied field. In Poole-Frenkel conduction, electrons are thermally emitted from traps inside the bulk of the material to the conduction band by lowering of a Coulombic potential when it interacts with the external electric field. The J-F relation is:

$$J = J_0 F \exp[\beta_{PF} F^{1/2} / 2kT] \quad (3)$$

$$\beta_{PF} = \left[\frac{e^3}{\pi \epsilon_0 K^*} \right]^{1/2} \quad (4)$$

where J_0 is the low field current density and other symbols have their usual meanings. An analysis based on the field assisted barrier lowering involves essentially, plotting $\ln(I)$ versus $V^{1/2}$ as shown in Fig. 2 for all the prepared compositions of the glass system. From these curves, slopes of linear portion are calculated. The experimental value of coefficient of barrier lowering β is calculated using the following relation [Simmons 1967]:

$$\beta_{exp} = m d^{1/2} kT \quad (5)$$

where $m = m_s$ (Schottky slope) is the slope of high voltage regions of the curves, d the sample thickness, k the Boltzmann constant and T the room temperature.

Comparing the experimental values of coefficient of barrier lowering with the theoretical values of β_S or β_{PF} (Eqs. 2 and 4) may guide authors to estimate the dominant conduction phenomenon in present glass networks.

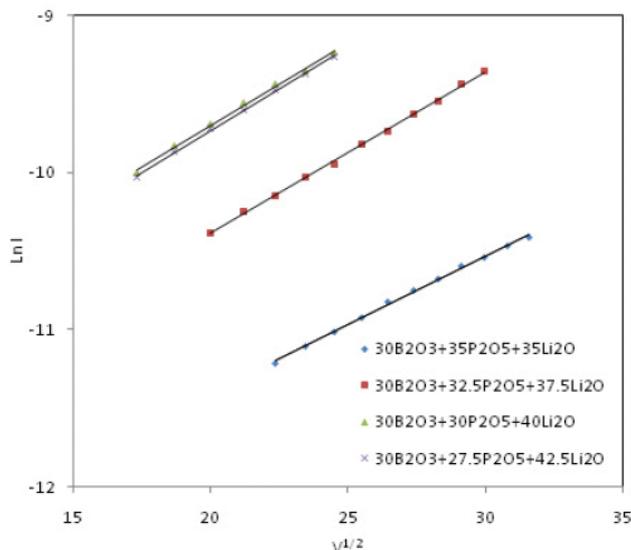


Fig. 2. The $\ln(I)$ plotted against $V^{1/2}$ (for Schottky conduction).

The high frequency dielectric constant K^* is estimated using the relation [Simmons 1967] $K^* = n^2$ where n is the refractive index of the glass obtained through optical measurements on the samples. The theoretical values of β_S , β_{PF} and n are given in Table 1 using Eq. 5. The experimental values of β_S are also given in Table 1 using the slopes m_s of the curves of various compositions of the fabricated glass samples. A wider difference between the experimental and the theoretical values is noticed here thus eliminating the possibility of the Schottky conduction.

Turning to the possibility of Poole-Frenkel conduction, plots of $\ln(I/V)$ versus $V^{1/2}$ based on the Poole-Frenkel equation (Eq. 3) are drawn in Fig. 3. The slopes of these plots $m = m_{PF}$ (Poole-Frenkel slope) used in Eq. 5 provide values of the experimental β_{PF} for all the glass compositions.

Comparing the theoretical and the experimental values of β_{PF} , as given in Table 1, a much smaller discrepancy is noticed. The Poole-Frenkel phenomenon can thus be recommended playing dominant role in the electrical conduction of present glass systems.

For any further evidence in favor of the Poole-Frenkel effect, activation energy E_a is investigated. The lower limit of E_a observed for the Schottky conduction is 0.8 eV [Maissel and Glang 1970]. The experimental values of the activation energy for the present glass samples are obtained from the Arrhenius plots drawn in Fig. 4 and are given in Table 1 for various compositions. It is noted that calculated values of the activation energy (0.07 to 0.35eV) are much smaller than the lower limit (0.8eV) observed for the Schottky conduction. It is, therefore, claimed that the Poole-Frenkel phenomenon is responsible for the electrical conduction of the present lithium borophosphate glasses.

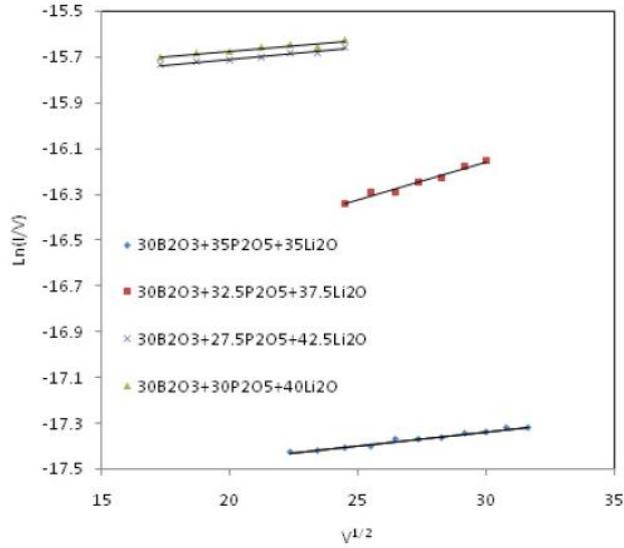


Fig. 3. The $\ln(I/V)$ plotted against $V^{1/2}$ (for Poole Frenkel conduction).

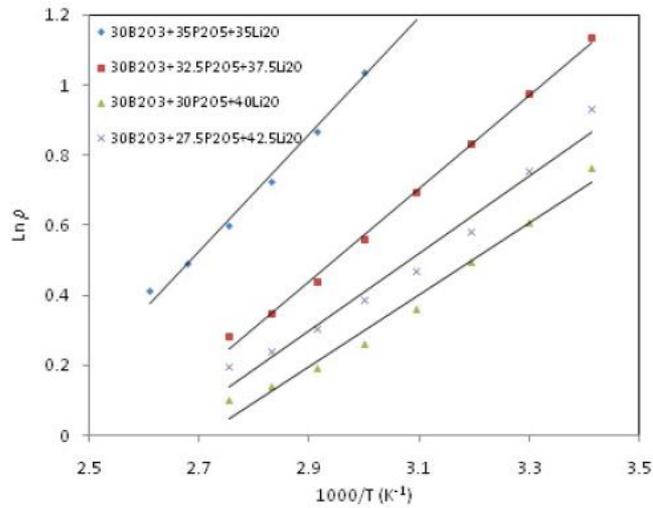


Fig. 4. Arrhenius plot (Logarithmic resistivity plotted against $10^3/T$) for activation energy calculations.

Table 1: Various optical and electrical parameters of lithium-borophosphate glasses.

Composition (mole %)	n	K^*	Barrier lowering coefficient ($10^{-5} \text{ eV m}^{1/2} \text{ V}^{-1/2}$)				E_a (eV)
			Theoretical		Experimental		
			β_S	β_{PF}	β_S	β_{PF}	
$30\text{B}_2\text{O}_3\text{-}35\text{P}_2\text{O}_5\text{-}35\text{Li}_2\text{O}$	1.79	3.20	2.12	4.24	8.46	6.99	0.35
$30\text{B}_2\text{O}_3\text{-}32.5\text{P}_2\text{O}_5\text{-}37.5\text{Li}_2\text{O}$	1.78	3.17	2.13	4.26	9.40	2.58	0.26
$30\text{B}_2\text{O}_3\text{-}30\text{P}_2\text{O}_5\text{-}40\text{Li}_2\text{O}$	1.76	3.10	2.15	4.30	10.81	1.34	0.24
$30\text{B}_2\text{O}_3\text{-}27.5\text{P}_2\text{O}_5\text{-}42.5\text{Li}_2\text{O}$	1.73	3.00	2.19	4.38	10.07	0.95	0.22

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