

Structural and lithium ion transport studies in borophosphate glasses

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Abstract

Lithium ion transport process and glass network modification upon the variation of network modifier (M) to former (F) ratio (M/F) in 30% LiBO₂–70% [(M Li₂O–F P₂O₅)] glasses have been investigated. The glasses with different M/F ratios (0.42–1.0) were prepared by melt quenching technique and characterized by X-ray diffraction (XRD), differential scanning calorimetry (DSC), Raman and impedance spectroscopy techniques. The glass transition temperature, T_g increased with increasing M/F ratio suggesting an increase in overall connectivity of the network structure. Dc conductivity showed an enhancement of three orders of magnitude with increasing M/F. The observed increase in T_g and dc conductivity with modifier concentration has been explained on the basis of the competition between network breaking/forming events, leading to an increase in overall connectivity of the network and the formation of continuous channels for ion migration. Ac conductivity data were analyzed by fitting the data to Almond-West type power law equation, $\sigma'(\omega) = \sigma(0) + A\omega^n$. The power law exponent, n , was found to be temperature dependent and exhibited a minimum, n_{\min} . The observation of n_{\min} has been explained in the light of diffusion controlled relaxation (DCR) model. Furthermore, the scaling of both ac conductivity and electrical modulus data showed an excellent collapse on to a single master curve indicating that there is a good time–temperature superposition and that conduction mechanism remains unchanged in this glass system.

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1. Introduction

Lithium based fast ionic conductors or electrolytes have gained much attention during last few decades because of their potential use in various technological applications such as lithium ion batteries, electrochromic displays, gas sensors, etc. [1–8]. Glass electrolytes have certain advantages over their crystalline counterparts like physical isotropy, absence of grain boundaries, better thermal stability and ease of compositional variation. Among the lithium based glass electrolytes, lithium phosphates are classical glass forming systems and have been studied extensively in the literature [9,10] because of their interesting structural and physical property changes upon network modification. The basic glass network structure consists of interconnected PO₄ tetrahedra. Lithium ions are introduced into such systems as Li₂O, which also acts as network modifier (M) in a way that breaks P–O–P bridges and introduces non-bridging oxygens (NBO) into the structure.

Depending upon the modifier content added to the glass former (F) P₂O₅, phosphate glasses are classified as ultraphosphates (Li₂O less than 50%), metaphosphate (Li₂O 50%) and polyphosphates (Li₂O more than 50%). This M/F ratio determines the glass structure, which in turn determines various physical properties. The structural evolution due to modifier addition in phosphate glasses can be described in terms of Q^{*i*} units, where *i* gives the number of bridging oxygens connected to P atom in PO₄ tetrahedra [11]. For example, vitreous P₂O₅ consists of interconnecting Q³ units and addition of Li₂O breaks the P–O–P linkages (giving NBOs) thereby converting Q³ units into Q² units. Thus, in the ultraphosphate composition range the structure consists of both Q³ and Q² units. In the metaphosphate composition (where M/F=1) all the Q³ units have been converted into Q² units and the structure thus consists of only Q² units. Further addition of Li₂O beyond metaphosphate composition converts Q² units into Q¹ units, thus polyphosphate structures consist of both Q² and Q¹ units. So, with addition of modifier the openness of the structure increases. As a result ionic conductivity increases with increasing M/F ratio [9]. The Li⁺ ions sit in the vicinity of these NBOs. The ionic

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conductivity is generally believed to arise from non-random hopping of Li^+ ion between these sites under the influence of an external field. Detailed structural studies on borophosphate glasses with different alkali dopant salts and multicomponent oxide glass formers, using Raman, IR and NMR techniques have been reported [12–21]. These studies gave insightful information about the glass structural modifications upon incorporation of borate in phosphate network and the effect of doping by different oxides such as PbO , ZnO and alkali salts.

Modified network glasses can be doped with Li salts to achieve higher conductivities. There have been several studies of doping with lithium halides and lithium oxysalts in the literature [1,10,12–26]. Enhancement of conductivity by introduction of LiX ($\text{X}=\text{Cl}$, Br , I) and Li_2SO_4 has been reported. The conductivity enhancement is attributed to a volume increasing effect of the dissolved ionic salts [1,22,23,27]. However, introduction of LiF has been reported to decrease Li^+ ion conductivity and is attributed to the formation of local columbic traps of F^- ions, which impede Li^+ ion motion [28,29]. When Li halides are used as doping salts, the halide ions remain independent in a sense that the halide ions do not get into the network structure [1,22,23]. In the case of Li_2SO_4 as doping salt, a weak interaction between SO_4^{2-} ions and metaphosphate ions, resulting in a small dynamic concentration of dithiophosphate units has been proposed [30,31]. Furthermore, in most of the glasses studied, the glass network modification has been reported in the metaphosphate–polyphosphate region ($1 < \text{M}/\text{F} < 2$) and similar studies in the region $0 < \text{M}/\text{F} < 1$ is very scant [13]. It would therefore be very interesting to examine the network structural modifications and the resulting conductivity changes in ultraphosphate ($0 < \text{M}/\text{F} \leq 1$) region to gain more insights into the physical properties of lithium phosphate glass system. Further we used LiBO_2 as doping salt in the present study, because the salt LiBO_2 is an interesting one in the present context in a sense that it could be considered as if the glass former B_2O_3 has been modified by equal mol% of the modifier, Li_2O . So, the anion, BO_2^- is expected to behave differently from other simpler anions, like halide ions. Thus it would be interesting to study the LiBO_2 “doped” ultraphosphate glass ($\text{M}/\text{F} < 1$) system in order to understand how the network structure gets modified by the glass former modified anion, BO_2^- and its role in ion transport and relaxation behaviors of lithium borophosphate glass system.

In this paper we report the results of structure, glass transition, and conductivity relaxation behaviors in LiBO_2 – Li_2O – P_2O_5 glass system over a range of temperature and frequency in

the ultraphosphate ($0 < \text{M}/\text{F} < 1$) region, where Li ions are present in an anion matrix of complex phosphate and metaborate ions. Interestingly, it is found that the dc conductivity enhancement of three orders of magnitude is observed with increasing M/F . The observed increase in dc conductivity and glass transition temperature has been rationalized based on the competition between network breaking/forming events due to the replacement of phosphate units by borate units into the glass network structure with increasing Li_2O . Furthermore, the ac conductivity and its temperature dependence are discussed in the context of existing theoretical models [32–34].

2. Experimental

Lithium borophosphate glasses of different M/F ratio listed in Table 1 were prepared by melt quenching technique. Appropriate amounts of the starting materials, Li_2CO_3 (Alfa Aesar), $(\text{NH}_4)_2\text{HPO}_4$ (Alfa Aesar) and LiBO_2 were mixed and ground. The mixture was heated at 300°C for 5 h to decompose Li_2CO_3 and $(\text{NH}_4)_2\text{HPO}_4$ into Li_2O and P_2O_5 , respectively. The resulting mixture was melted at 1000°C for 30 min; at this stage the melt was stirred frequently for homogeneity. The melt was then quenched in liquid nitrogen to form transparent glass samples. The glass nature of the samples was characterized by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The ground glass powder was used for XRD and DSC (10mg) measurements. The XRD pattern was recorded (Siemens, D5000 using Cu K_α radiation) at a scanning rate of 3°min^{-1} from 5° to 50° in the 2θ scale. The glass transition temperatures were determined using differential scanning calorimeter (Shimadzu, DSC-50) over the temperature range from 20°C to 500°C at a scanning rate of $10^\circ\text{C min}^{-1}$ using dry nitrogen as purge gas. Raman data at room temperature was collected in backscattering geometry (Jobin Yvon T64000) using 514.5 cm^{-1} radiation (Coherent Innova 99 argon ion laser) as excitation line. A charge-coupled device (CCD) system collected and processed the scattered light. The samples for electrical conductivity measurements were prepared by cutting the glasses into circular discs with $\sim 10 \text{ mm}$ diameter and $\sim 2 \text{ mm}$ thickness. Both faces of the samples were polished and silver paint was applied as top and bottom electrodes. The impedance $|Z|$ and phase angle (θ) were measured directly in the frequency range from 50 Hz to 1 MHz, using HP4294 impedance analyzer. The impedance measurements were carried out at an interval of 25°C from room temperature to 600 K and the temperature was controlled with an accuracy of

Table 1
Initial compositions of the glasses studied, glass transition temperature, T_g , dc conductivity, σ_{dc} , conductivity pre-exponential, $\sigma(0)$, activation energy for dc conductivity, E_{dc} , activation energy for conductivity relaxation, E_τ and pre exponential relaxation time, t_0

Composition (%)			T_g ($^\circ\text{C}$)	σ_{dc} (425 K) (S cm^{-1})	$\sigma(0)$ (425 K) (S cm^{-1})	E_{dc} (eV)	E_τ (eV)	t_0 (s)
Li_2O	P_2O_5	LiBO_2						
14.0	56.0	30.0	318	1.01×10^{-8}	9.5×10^{-9}	0.918	0.923	0.30×10^{-14}
23.3	46.7	30.0	375	2.98×10^{-6}	2.8×10^{-6}	0.661	0.705	0.40×10^{-14}
30.0	40.0	30.0	372	1.74×10^{-5}	2.0×10^{-5}	0.618	0.682	0.16×10^{-14}
35.0	35.0	30.0	400	4.79×10^{-5}	4.1×10^{-5}	0.519	–	–

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