



STRUCTURAL AND ELECTRICAL CONDUCTIVITY STUDIES ON THE SOLID ELECTROLYTE SYSTEM $x\text{Li}_2\text{O}-(100-x)[0.5\text{B}_2\text{O}_3-0.5\text{P}_2\text{O}_5]$ WHERE $20 < x < 70$

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ABSTRACT

Lithium ion conducting glasses have been extensively investigated due to their potential application as solid state amorphous electrolytes in lithium rechargeable batteries. The use of glassy electrolytes in all solid state devices may provide numerous advantages like increased safety, facility of fabrication and miniaturization and having a higher conductivity than those of the crystalline counterparts. In this work, we prepared and studied the Lithium ion conducting glassy solid electrolytes of the composition $x\text{Li}_2\text{O}-(1-x)[0.5\text{B}_2\text{O}_3-0.5\text{P}_2\text{O}_5]$ where $20 < x < 70$, by melt quenching technique. The obtained solid material is characterized through X-ray diffraction (XRD), Differential thermal analysis (DTA), and Fourier transform infra-red spectrometry (FTIR) and impedance spectroscopy techniques. The conductivity obtained is of the order of 10^{-7}S/cm at room temperature and IR spectra reveal that the glass matrix undergoes structural modification with the addition of the glass modifier Li_2O .

Keywords: Lithium batteries, Glasses, solid electrolytes, conductivity

1.-Introduction

Lithium based solid electrolytes have gained much attention during the last few decades because of their potential use in various technological applications such as lithium ion batteries, electro-chromic displays, gas sensors etc.^{1, 2, 3} For practical use, solid electrolyte must have high ionic conductivity as well as chemical, thermal and electrochemical stability. Glass electrolytes have certain advantages over their crystalline counterparts like physical isotropy, absence of grain boundaries, better thermal stability and ease of compositional variation. Lithium oxide glasses can be divided into two types, oxide and sulfide glasses. Many research works have aimed at the preparation of glassy electrolytes with a very high conductivity, chemical and electrochemical stability for both oxide and sulfide glasses. The oxide glasses are easy to fabricate into thin film electrolyte for micro batteries and stable in air, however they show relatively low lithium ion conductivity in the order of 10^{-6} - 10^{-8} S/cm at room temperature.^{4, 5} On the other hand, lithium sulfide glasses show higher conductivity of the order of 10^{-3} - 10^{-4} S/cm compared to oxide glasses at room temperature due to the high polarizability of sulfide ions.⁶ These sulfide glasses are less stable in air and appear to be unstable in contact with lithium metal and its corrosive chemical nature resulting in a difficulty of in handling and managing the fabrication process. Due to these problems sulfide glasses have not yet been developed for real application. Among the lithium based oxide glass electrolytes, lithium phosphates are classical glass forming systems and have been studied extensively in the literature because of their interesting structural and physical property changes upon network modification. The phosphate glass network consists of interconnected PO_4 tetrahedra. The borate glass network consists of random network of boroxol rings and BO_3 triangles connected by a B-O-B linkages (bridging oxygen atom). Lithium ions are introduced into such systems as Li_2O which also act as network modifier in a way that breaks P-O-P bridges and modifies the boroxol ring, complex borate groups with one or two 4-coordinated boron atoms are formed and introduces non-bridging oxygen (NBO) into the structure.⁷ The Li^+ ions sit in the vicinity of these NBOs. The ionic conductivity is generally believed to arise from non-random hopping of Li^+ ion between these sites under the influence of an external field.

Different methods have been proposed in the literature for the design of highly conductive glasses like dissolve a lithium salt (LiI , Li_2SO_4 etc) in a conventional glass or to use several combinations of glass network forming oxides, often resulted in enhanced conductivity compared to binary systems, and is called 'mixed former effect'. Usually the mixed former glasses show promising characteristics such as high ionic conductivity coupled with good thermal stability. During the dissolution of ionic salt in these glasses, the conductivity is enhanced due to volume increasing effect of the dissolved ionic salt. When Li halides are used as doping salts, the halide ions remain independent in a sense that the halide ions do not go into the network

structure.⁸ In the case of Li_2SO_4 as doping salt in phosphate glasses, a weak interaction between SO_4^{2-} ions and metaphosphate ions, resulting in a small dynamic concentration of dithiophosphate units.⁹ Phosphate glasses are thermally unstable and hygroscopic in nature which imposes limitations to its practical applications. The properties of this glass can be modified by mixing another glass former, borate to it, to have a mixed former effect. The present paper reports the effect of the addition of glass modifier Li_2O to the mixed glass former system of the series, $x\text{Li}_2\text{O}-(1-x)[0.5\text{B}_2\text{O}_3-0.5\text{P}_2\text{O}_5]$ where $20 \leq x \leq 70$.

2.- Experimental techniques

The glass samples of the series $x\text{Li}_2\text{O}-(100-x) [0.5\text{B}_2\text{O}_3-0.5 \text{P}_2\text{O}_5]$ where $20 < x < 70$ were synthesized by melt quenching technique. Appropriate amount of the dried precursors Li_2CO_3 (Aldrich 99.99%), $(\text{NH}_4)_2\text{HPO}_4$, H_3BO_3 (Spectrochem chemicals) were ground and mixed in an agate mortar and pestle. The mixture was then placed in a platinum crucible and placed in an electric furnace and heated to 1200-1400°C for 2 hrs depending on the samples. The molten mixtures at high temperatures were rapidly poured out on to stainless steel plate held at room temperature and immediately covered by a second stainless-steel plate.

The amorphous state of all the quenched samples were checked by powder X-ray diffraction (XRD) using Philips X'Pert diffractometer using a Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda=1.5418\text{\AA}$). Differential thermal Analysis (DTA) and thermogravimetric analysis (TGA) was carried out using alumina crucibles for ground glass batches of about 10K/min by Perkin Elmer TG/DTA Analyzer in the range of 25-700°C. Fourier transform infrared (FTIR) absorption spectra of all the samples were recorded in $150\text{-}1500\text{cm}^{-1}$ range at room temperature using Nicolet, Avatar 360FTIR. Electrical conductivity measurements were done by using a frequency response analyzer (PC14-750, Gamry Instruments, where an AC voltage of 10mV was applied at a frequency range of 0.1Hz-1kHz. Measurements were carried out on the temperature range 298K -348K on samples in the form of pellets. The pellets were prepared from the powdered samples which uniaxially pressed at a pressure of 5000kg/cm^2 .

3.- Results and Discussion

The glassy nature of the sample was checked by X-ray diffraction and is shown in Figure 1 for the samples of the series $x\text{Li}_2\text{O}-(100-x) [0.5\text{B}_2\text{O}_3-0.5 \text{P}_2\text{O}_5]$ where $20 \leq x \leq 70$. For $x= 30$ to 50 gives transparent and colourless, where $x= 20, 60, 70$ gives white solid material. Glass forming region in the series $x\text{Li}_2\text{O}-(100-x) [0.5\text{B}_2\text{O}_3-0.5 \text{P}_2\text{O}_5]$ ranges from $x=30$ to 50 and the composition with $x=60$ and 70 is with optimum dispersion of Li_3PO_4 crystallites in the glass matrix and could be attributed to the glass-crystal interface effect. The presence of BPO_4 peaks in the sample with $x=20$ makes the glass heterogeneous and could produce a weak binding area

around the strong structure of BPO_4 , where a conduction pathway for the ions is formed.¹⁰ For $x=20, 60$ and 70 were partially crystalline or crystalline states. The quenching method employed here is air quenching and the glass forming region could be slightly widened if a faster quenching technique such as oil quenching or splat quenching is employed.

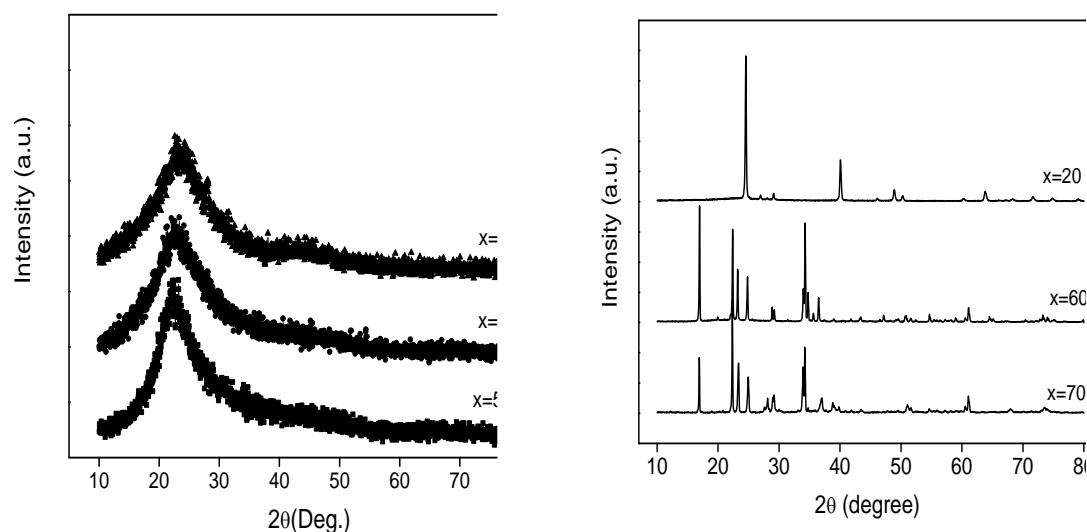


Figure1. X-ray diffraction pattern for the series of composition $x\text{Li}_2\text{O}-(1-x)0.5\text{B}_2\text{O}_3-0.5\text{P}_2\text{O}_5$

DTA measurements was carried out to find out the glass transition temperature of the system $x\text{Li}_2\text{O}-(1-x)0.5\text{B}_2\text{O}_3-0.5\text{P}_2\text{O}_5$. Figure 2 shows the DTA-TGA profile obtained from $50\text{Li}_2\text{O}-25\text{B}_2\text{O}_3-25\text{P}_2\text{O}_5$ glass system. The TGA Curve exhibits a weight loss in the temperature range from $100-400^\circ\text{C}$, due to the evaporation of molecular water combined in H_3BO_3 . An endothermic peak around 100°C in the DTA curve is also due to the evaporation of water molecule. The huge peak reveals that the strong hygroscopic nature of P_2O_5 and B_2O_3 , which suggest that the specimen produced by the method employed in this study, must be kept in dry atmosphere, at least, before high temperature heat treatment. The glass transition was observed around 400°C . The first weight loss in the TGA curve is associated with a large endothermic peak in the DTA curve which is due to the evaporation of water molecule and the second weight loss corresponds to glass transition temperature, T_g .

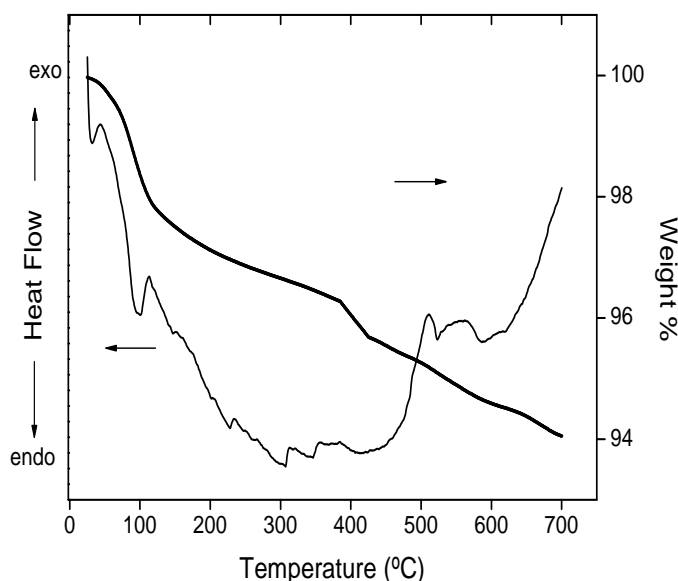


Figure 2. The DTA-TGA profile obtained from 50Li₂O-25B₂O₃-25P₂O₅ glass system.

The lithium ion conductivity is determined mainly by the concentration of lithium ion in glass network and the structural modification of glass formers induced by the addition of modifier, Li₂O.¹¹ The combination of these two effects increases the ionic conduction of glass electrolyte. The modification of glass network structure can be induced by changing the composition of glass formers and this alters the free volume of glass network. The free volume within the glass network is expected to free up more immobile Li ions trapped in the deep energy level and converts these immobile ions into mobile charge carrier. Therefore the conductivity increases as a result of increase in the number of effective mobile ions and the reduction of the activation energy of mobility. Non-bridging oxygen generated by the introduction of Li₂O is known to offer the hopping site for ionic conduction in oxide glass network.¹² The formation of non-bridging oxygen is also contributing to the formation of relatively open network structure with large free volume for ion drift. Fig.3. shows the complex impedance plot obtained for the 70Li₂O-15P₂O₅-15B₂O₃ electrolyte system at room temperature. The conductivity calculated from this result is of the order of 10⁻⁷S/cm at room temperature. The impedance spectra of all the samples exhibited a high frequency semi circle and a low frequency spur, which emanated from ion migration in the glass and electrode polarization respectively. The bulk resistance of the glass was varied to a large extent with the variation of Li₂O content.

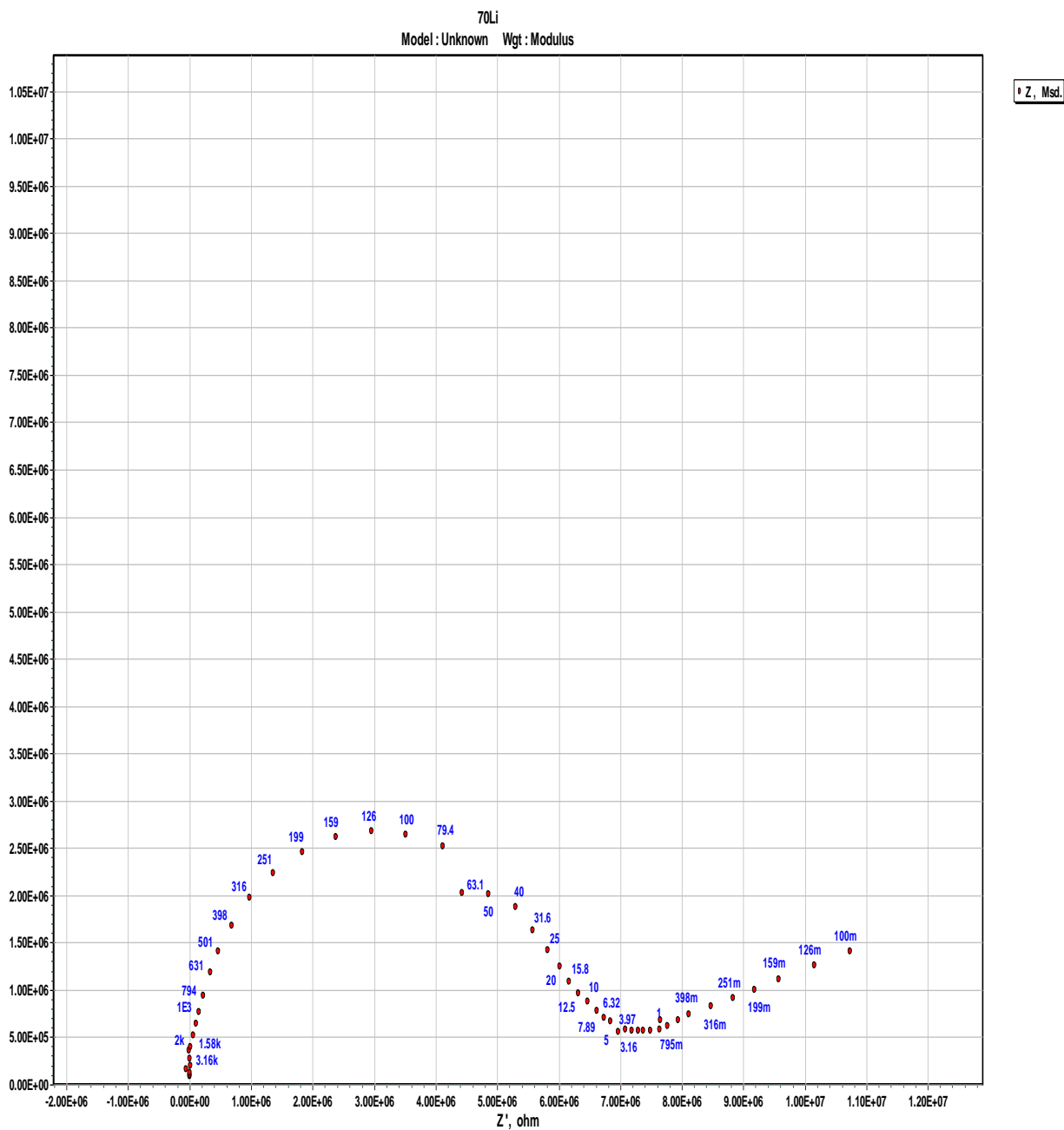


Figure 3. Impedance spectra for the sample with $x\text{Li}_2\text{O}-(1-x) (0.5\text{B}_2\text{O}_3-0.5\text{P}_2\text{O}_5)$ with $x=70$.

The ionic conductivity increases with modifier concentration Li_2O in the present study and is attributed due to the formation of continuous ion conducting channels arising from the competition of network breaking or forming events resulting in easy migration of Li^+ ions along these channels. The conductivity is found to increase in all the samples with increase of temperature. The conductivity studies are still under progress.

The infra red spectra of the sample system $x\text{Li}_2\text{O}-(1-x) (0.5\text{B}_2\text{O}_3-0.5\text{P}_2\text{O}_5)$ show broad absorption bands which indicate an amorphous structure of the samples and are shown in Figure 4 extending from 400-1800 cm^{-1} .

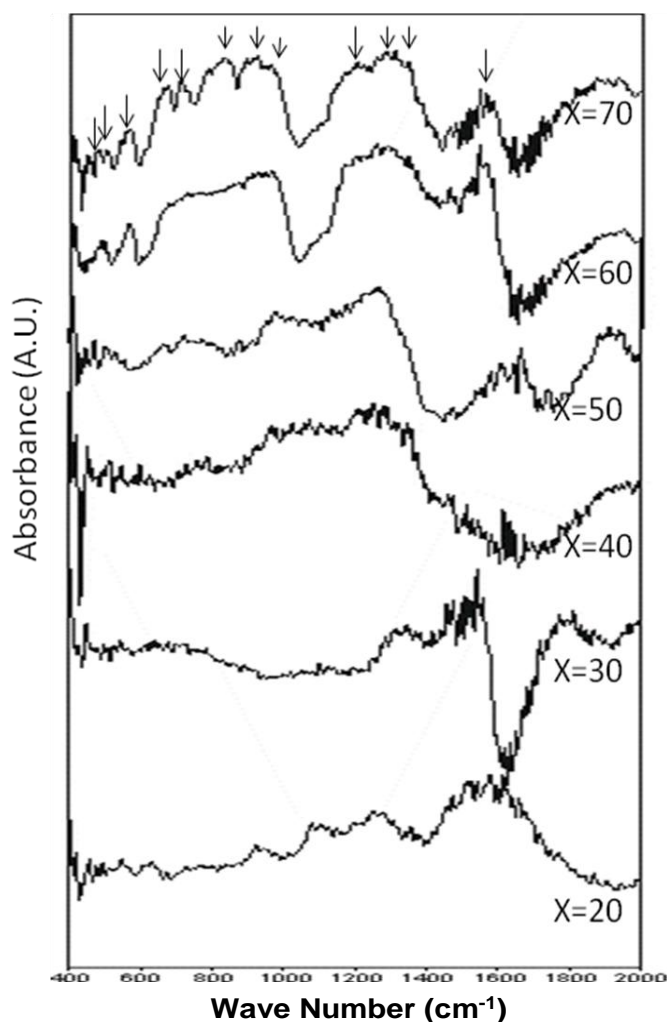


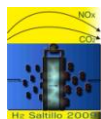
Figure 4. The variation of IR spectra of $x\text{Li}_2\text{O}-(1-x) (0.5\text{B}_2\text{O}_3-0.5\text{P}_2\text{O}_5)$ samples by the addition of Li_2O .

The ionic conductivity in the glass electrolyte is closely related to the network structure and the local environment where a lithium ion is located, and especially on the existence and the structure of the non-bridging oxygens. Due to close and overlapping bands, the obtained infrared absorption spectra appear more complex. In borate glasses, the non-bridging oxygen is generated by the conversion of a BO_4 unit (four coordinated boron) to $[\text{BO}_3]^-$ (three coordinated boron with a non-bridging oxygen). Therefore, the formation of $[\text{BO}_3]^-$ units promotes the ionic mobility and increases the ionic conductivity. The vibrational modes of the borate network are mainly active in three infra red spectral regions, which are similar to those reported by several workers.¹³ The occurrence of first band is at $1200\text{-}1600\text{cm}^{-1}$ is due to the asymmetric stretching relaxation of the B-O band of trigonal BO_3 units and phosphoryl group. The second band between $800\text{-}1200\text{cm}^{-1}$ is due to the B-O bond stretching of the tetrahedral BO_4 units, and the third has a strong and wide absorption band in the region of $1200\text{-}700\text{cm}^{-1}$ is due to the bending of B-O-B linkages in the borate network. The IR spectra of these samples show a number of sharp, medium and broad absorption peaks. The broad absorption band observed in the region $1400\text{-}1200\text{cm}^{-1}$ is connected with the B-O(B) stretching vibrations of BO_3 units.

The maximum of this band is found at 1375 cm^{-1} . With the increasing Li_2O amount, the intensity of the peak near 1000 cm^{-1} increases, followed by a decrease in intensity of the peak near 1500 cm^{-1} , which attribute the conversion of BO_3 to BO_4 groups. The conversion from four co-ordinated boron to three co-ordinated boron with a non-bridging oxygen can be verified by the growth of the peak around 1200cm^{-1} , which is unfortunately not so clear due to the broad absorption band in the region $1200\text{-}1400\text{cm}^{-1}$. However, the growth of 1200cm^{-1} peak is seen with increasing amount of Li_2O . The absorbance peak around 1170 cm^{-1} is assigned to B-O bond stretching of trigonal BO_3 with a non-bridging oxygen. In the figure, we can see that the peak becomes evident as the concentration of Li_2O increases. The increase of non-bridging oxygen is accompanied by the formation of BO_3 trigonal unit since, at high Li concentration; the addition of Li_2O converts the BO_4 tetrahedral unit to BO_3 trigonal unit with a non-bridging oxygen. The peak around 690cm^{-1} and 1170cm^{-1} corresponds to the symmetric P-O-P and O-P-O stretching vibration in $(\text{PO}_3)_n^{n-}$ chain and PO_4 tetrahedra respectively.^{14,15} The peaks at 660cm^{-1} indicate that B_2O_3 units link to form chain like metaborate $(\text{BO}_2)^{1-}$ units and the phosphate chain $(\text{PO}_3)_n^{n-}$ links with BO_4 units. The peak at 1116cm^{-1} at $x=20$ is due to the formation of BPO_4 units (as seen from the X-Ray diffraction patterns).

4.- Conclusions

Solid State electrolytes with the composition $x\text{Li}_2\text{O}\text{-(}1\text{-}x\text{)}\text{ (}0.5\text{B}_2\text{O}_3\text{-}0.5\text{P}_2\text{O}_5\text{)}$ were prepared by melt quenching technique and characterized by XRD, DSC, IR and impedance techniques. In the above the ionic conductivity at room temperature obtained is of the order of 10^{-7}S/cm . The glass forming region has been



identified in the series, $x\text{Li}_2\text{O}-(1-x) (0.5\text{B}_2\text{O}_3-0.5\text{P}_2\text{O}_5)$ as $30 \leq x \leq 50$. IR spectra show the structural modifications with the addition of Li_2O on the glass formers, B_2O_3 and P_2O_5 . The ionic conductivity increases with modifier concentration Li_2O could be attributed due to the formation of continuous ion conducting channels arising from the competition of network breaking or forming events resulting in easy migration of Li^+ ions along these channels.

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