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Study of Electrical Conductivity of Lithium Borate Ionically Conducting Glasses

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Abstract – *Alkali ion conductors are of considerable interest because of their possible applications in solid state battery systems. The highly electropositive alkali ion provides the possibility of large cell voltage and very high energy densities. In general, particular material will be required to act as either an electrode or an electrolyte. Both application required high ionic conductivity, preferably at ambient or relatively low temperature. Lithium has a lower equivalent weight than sodium or potassium. It is also more electropositive and thus, provides the greater cell voltage than other two ions. Lithium has additional advantage that it can be handling more easily at room temperature than other alkali metals. On the basis of theoretical background and considering the advantage of amorphous solid electrolyte it was thought imperative to develop a lithium borate glass base solid electrolyte.*

Keywords- *Alkali ion conductors, solid state battery, ionic conductivity, electropositive ion, amorphous solid electrolyte, lithium borate glass base solid electrolyte.*

INTRODUCTION

The recognition of fast lithium conduction in solids dated from 1921, when Benrath and Deokopf [1] discovered high temperature alpha phase of Li_2SO_4 until the 1940.New emphasis has been given to this area in 1967 as a result of discovery of the higher Li^+ conductivity in the alumina type layered structure. The state of knowledge of Sodium lithium ion conductors up to 1970 has been reviewed by Pizzine [2].About the same time it become evident that lithium is potentially a highly attractive element to use in kind of energy storage system. Its light weight and high electro positivity as well as relative ease with which it may be handled have led to the proposal of many lower battery configurations utilizing both liquid and solid electrolyte. During the sane decades, glasses electrolyte with high ionic conductivity have been found accidentally Kunze in 1973 [3].which where refer as super ionic conducting glasses. The current interest in glassy solid electrolytes is due to two main reasons.[a].Since they are X-ray amorphous, there is wide scope for structural investigation on microscopic level leading to theoretical understanding of these of these materials.[b] Due to their advantage [4] over their crystalline counter parts, they have good prospects for being used in technological applications. The ionic transport in amorphous solid electrolyte has been reviewed by Souquet [5] in 1981.The fast ion conducting lithium glasses have been reviewed by Kulkarni et al [6]. Progress in fast ions glasses has been given by Minami[7] several glassy electrolyte system has been discusses

I.1 Lithium Borate Glass Systems

These glasses are comprised of a network former B_2O_3 in which the covalent bond structure ensured the rigidity of the macromolecular structure and network modifier (Li_2O,Na_2O,K_2O,Ag_2O,CaO,BaO etc) which introduce ionic bond giving rise to cationic conduction. All oxygen remain covalently bonded to cations of the forming oxides in the elementary units. The micromolecular are thus formed by the assembly of three units in which at least one of the oxygen ions, called bridging ion is shared with other non-bridging oxygen carrying effective negative charge and therefore maintain in their vicinity alkali or alkaline cations of the network modifier oxide. These ionic bonds are generally assumed to be randomly distributed over the macromolecular chain [5-6].Otto [8] was the first to report glasses with high lithium ion conductivity at relatively low temperature in M_2O:B_2O_3:SiO_2 (M=Li,Na) system. He also suggested that high lithium ion conductivity could be obtained in borate glasses if more that 40 mole% lithium compounds could be incorporated in the glass without diversification. As a general rule, the conductivity of oxide glasses increases with increasing amount of network modifier such as Li_2O,Na_2O and K_2O [9-11].

I.2 Mixed Alkali Glass Systems:

The NMR investigation for the borate glass added with different alkali oxide modifier shows different structural variation for each oxide [8].In general the properties exhibiting the mixed alkali effect typically reach either minimum or maximum depending upon the specific property with substitution of second alkali e.g. electric resistivity .This behavior for properties related to alkali ion movement found essentially independent of glass forming oxide being observed in silicate [12-16], borate [17-20],borosilicate [21],Phosphate [22-24] and germinate [25-26] glasses. For mixed alkali glasses, the large maximum in electrical resistivity has been reported [27].Han et al [28] have studied the diffusion of Na^+ and Ag^+ in binary Na_2O:B_2O_3 glasses. The electrical conductivity for 4-24 mole% of Na_2O has been measured from 373 °C to the temperature slightly below T_g. Matusita et al [29] have measured the electrical conductivity of [a] (1 – X) Li_2O :XbaO : $2SiO_2$ [b] (1 – X) Li_2O :XmgO : $2SiO_2$ [c] (1 – X) Li_2O :XcaO : $2SiO_2$ [d] (1 – X) Li_2O :XBaO : $2SiO_2$ in the temperature rang from room temperature to 725K. The mixed alkali effect on the spectra of Ni2+ and Cu2+ on borate glasses has been reported by Ahmed et al[30].

I.3 Mixed Glass Former Systems:

It has been reported [31-32] that for the some molar ration between lithium oxide glass former (B_2O_5+ P_2O_5), the ionic conductivity, at room temperature substantially higher in borophosphate glasses than in pure borate or phosphate.Tatsumisago et al have studied the glass forming conductivity and thermal properties of glasses containing high amount of Li_2O in Li_2O: SiO_2 : B_2O_3 , Li_2O: B_2O_3 :P_2O_5, Li_2O: P_2O_5 : SiO_2 systems. According to them, the widest glass forming region has been observed in Li_2O: SiO_2: B_2O_3 system. The composition dependence of conductivity has been found to be closely related to Tg. The enhancement in conductivity, mixing of two glass forming oxide, also observed in Li_2O: SiO_2: B_2O_3 glasses containing large amount of Li_2O. Tsai and Greenblatt have investigated the conductivity,IR and TMA for Li_2O: SiO_2 : P_2O_5 system. These glasses have been prepared by Solgel technique.The enhancement in the conductivity in sulphide glasses (Li_2O: SiO_2 : GeS_2) has been represented by Deshpande et al and phenomenon called as mixed glass former effect (MGFE).

I.4.Glasses With Addition Of Salts:

For increasing the ionic conductivity of glasses,different approaches have been adopted .Of all the approaches, the addition of lithium salt viz. halides,sulphates,to lithium conducting glasses has been well established and widely studied one.In 1966 Otto [9] has reported that considerable amount of LiF,LiCl or Li_2SO_4 could be incorporated in lithium glasses without devitrifying them.Shue and Tuller have examined the effect of CaO addition to Li_2O : LiCl : B_2O_3 glasses, since such addition have been believed to improve the durability in contact with lithiumCaO additions systematically decreases ionic conductivity in boroacite nad metaborate glass systems,the lithium choride, which systematically increases the conductivity,widens to calcium doping.The glass in ternary system Li_2O : ($LiCl_2$):B_2O_3 (LCB) have been examine by Raman and NMR [technique.The enhancement of the lithium conduction in borate glasses by addition of LiCl has also been observed by Muller et al .

II EXPERIMENTAL TECHNIQUE

Material Preparation:

For the glass preparation compositional parameter ‘n’ and ‘y’ are defined to have systematic variation in former and modifier.

$$n = \frac{Mix.Former}{Modifier} = \frac{B2O3+SiO2}{Li2O}$$

$$Y = \frac{Former}{Mixed\ Former} = \frac{SiO2}{B2O3+SiO2}$$

In the present work two different series are prepared with general composition $42.5Li_2O$ – (57.5-X) B_2O_3 – $XSiO_2$. The series is specified with constancy of Li_2O content given in table I and II

S. No	Glass No	Y	Composition of mole%			Specification
			Li_2O	B_2O_3	SiO_2	
1	I1	0	42.5	57.5	0	For fixed n=1.35 y is varied
2	I2	0.08695	42.5	52.5	5	
3	I3	0.1739	42.5	47.5	10	
4	I4	0.3478	42.5	37.5	20	
5	I5	0.05217	42.5	27.5	30	

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The initial ingredient were kept at kept at 100°C for 24 hours to remove the moisture and were weighted as per molar ration with an accuracy of 0.00001 g using AE136 mettler (Switzerland) monopan electronic Balance. After grinding them thoroughly in acetone for homogeneity, then dried mixture kept furnace at 400°C for 2 hour, then temperature increase to 600°C and maintain at 1 hour. After evolution of decomposition product the melt was kept at 900-1050 °C for 30 minute then viscous melt was quenched in aluminum block kept at room temperature .The quenching rate offered by the two blocks was found to be approximately 10^2C/s .The prepared sample were studied by electrical characterization.

III RESULTS AND DISCUSSION

I] AC Conductivity:

For the electrochemical device, bulk conductivity (σ_{bulk}) is very important. σ_{bulk} of each sample excluding electrode effect, was determined from the real axis intercept of the complex impedance analysis. It is also excludes the contribution of displacement current.

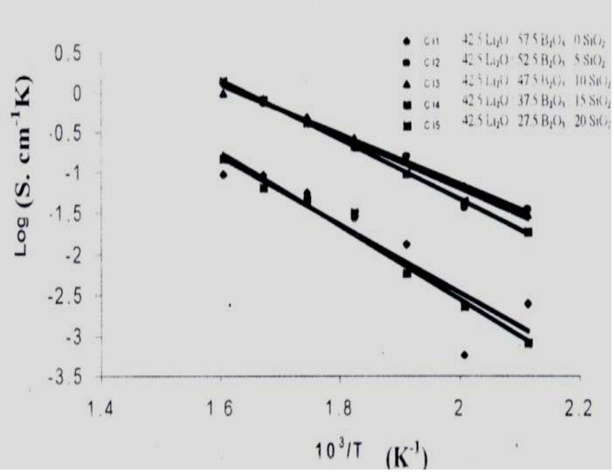

Fig.1 Arrhenius plots for Li_2O: B_2O_3: SiO_2 mixed former system (Series-I)

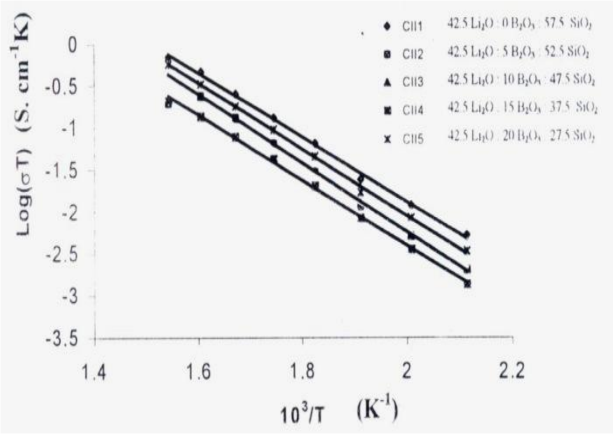

Fig.2 Arrhenius plots for Li_2O: B_2O_3: SiO_2 mixed former system (Series-II)

A detailed structure characteristic of entire LB series has revealed the complete amorphousness of the composition. The study of an temperature dependent conductivity for this glasses, measured during heating and cooling, so as to see the thermal hysteresis shown in fig.3

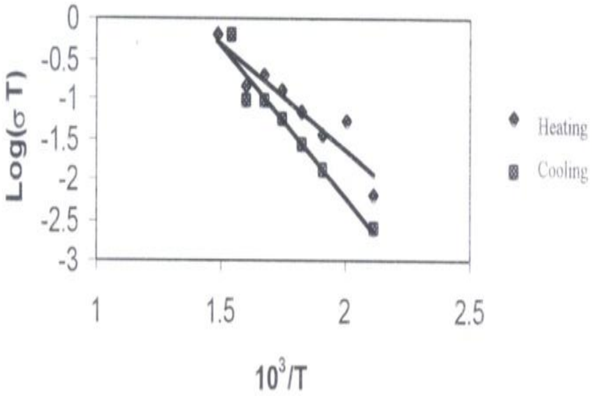

Fig.3 The plot of log (σT) Vs 10^3/T for 42.5 Li_2O : 57.5 B_2O_3 : 0 SiO_2

From the above result it is clear that the conductivity does not follow the same path during heating and cooling cycle, moreover they exhibit different slop indicating attenuation in activation enthalpy.

II] CONCENTRATION DEPENDENT CONDUCTIVITY:

The variation of conductivity as a function of Y for series I and II are given in figure 4 and 5

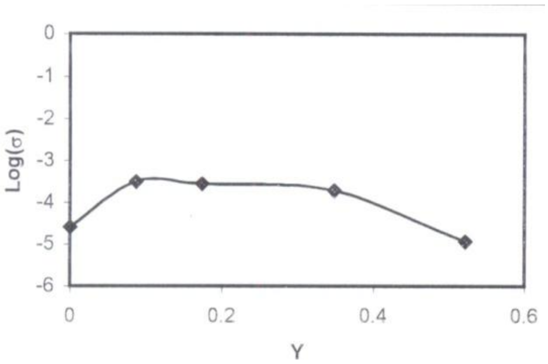

Fig4 Variation of conductivity as a function of Y for series (I) at (250 °C)

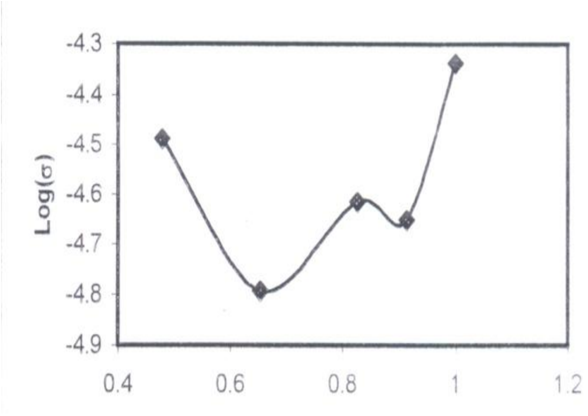

Fig.5 Variation of conductivity as a function of Y for series (II) at (250 °C)

It is seen from these curve that for each series, characterize by a specific values of n , the sample with y = 0.1 gives the maximum conductivity. For the y ≥ 0.2 the conductivity decreases.

IV CONCLUSION

The glasses prepared by quenching technique are found to be ionic conductors. Amongst the entire sample studied the glass with $42.5Li_2O:57.5B_2O_3:0SiO_2$ composition exhibits maximum conductivity. Also, this composition may find potential application as solid electrolyte in electrochemical devices.

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