TEMPERATURE DEPENDENCE ELECTRICAL CONDUCTIVITY IN LITHIUM BORATE GLASSES DUE TO MIXED FORMER EFFECT

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ABSTRACT

The ionic conducting glasses of modifier ratio (η = 2.333) *and former ratio y*($0.71 \leq y \leq 1$) *have been prepared with various composition by using melt quenching technique. The nature of glass samples were confirmed by XRD and SEM. The dc electrical conductivity of glass samples were measured by using four probes method at different temperature (323K-623K). It has revealed that dc conductivity obeys Arrhenius behavior and electrical conductivity of glass increases with increase in mole percent of aluminum oxide and temperature.*

Keywords: *dc conductivity, XRD, SEM, Arrhenius behavior*

Introduction

Electrical properties of glasses have been studied extensively for number of years due to their use in solid state devices and batteries. Introduction of metal oxide or alkali ions into glasses exhibit high conductivity as like semiconductor and can be used as solid electrolytes high energy density batteries (Fu.J.1996). In the literature, it has been reported that Bi_2O_3 occupy both network forming and network modifier. Therefore physical properties and electric properties of these glasses exhibit discontinuous changes due to role of structural cations changes (Baia. L.et al, 2003, Bale S. & RahmanS. 2008). It is reported that it shows significant change in the electrical properties of glasses with change in composition and temperature (Dalal.S.et al, 2015,2016).The electrical conductivity of lithium borate glasses has been investigated and special attention has been devoted to describe dielectric relaxation on the basis of dielectric parameters (Dongare D.T & Lad A.B., 2015).Aim of present work is to study the temperature dependence electrical conductivity in lithium borate glasses due to mixed former effect

Preparation of Material and Experimental

The starting material lithium carbonate, boric acid and aluminum oxide of AR grade purchased from Merc laboratory were used. The aluminum lithium borate glasses of composition were prepared by melt quenching technique. A homogeneous mixture of different composition has melted in ceramic crucible by keeping it into Muffle furnace equipped with digital temperature controller. The materials were melted at1150^{0}C for two hours with heating rate 30^{0}C/min and molted material is quenched in aluminum mould at room temperature (27^{0}C). The samples were annealed at 200^{0}C for 2Hrs in hot air oven. These samples were stored in desiccators and taken only at the time of measurement. These samples were prepared for keeping modifier ratio (η = 2.333) and different former ratio.

Modifier ratio $\eta = \frac{B_2O_3 + Al_2O_3}{Li_2O}$

Former ratio $y = \frac{B_2O_3}{B_2O_3 + Al_2O_3}$

The structure of sample was confirmed by the measurements of XRDusing XPERT PRO DIFFRACTOMETER and SEM by using ZEISS Ultra SEM instrument. The samples were in circular disc shapes, polished by using sand paper. The good quality paint was applied on both flat surfaces of sample and after drying it was loaded in the sample holder of four probe method for conductivity measurement.

The DC conductivity of samples has been calculated by using following relation.

$$\sigma_{dc} = \frac{d}{RA} \qquad \ldots\ldots\ldots\ldots (1)$$

Where , d is the thickness of sample and A is the area of cross section.

Activation energy of glass material was determined by using Arrhenius equation

$\sigma_{dc} = \sigma_0 \exp[-Ea/KT]$ …………… (2)

Result and Discussion

The XRD spectra of investigated samples have been found as shown in Fig.1. Only broadpeak has been observed for glass samples, indicating that these glass samples are composed glassy phase. However, glass samples shows peaks superimposed on weak halo pattern in XRD, indicating partial crystallization.XRD and SEM confirmed the amorphous nature of sample. Fig.2 shows SEM of L1BA sample.

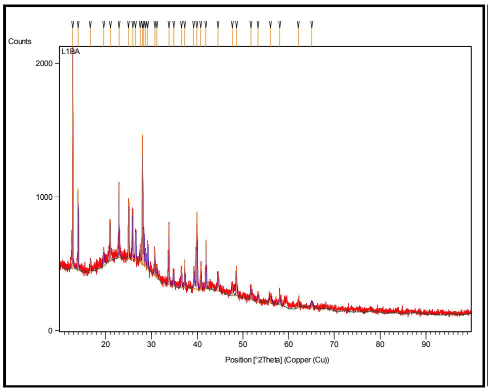

Fig.1: XRD of L1BA sample

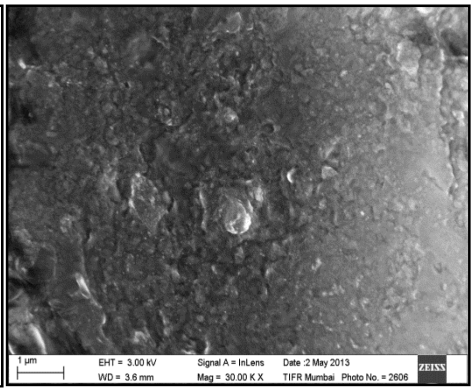

Fig.2: SEM of L1BA sample

The variation of conductivity as a function of $10^3/T$ for the glass samples of different former ratio with modifier ratio (η = 2.333) is depicted in Fig.3. For all the samples, it is observed that the dc conductivity (σ_{dc}) obeys Arrhenius behavior. The activation energy calculated from the graph is listed in the Table.1. The compositional dependence of dc conductivity (σ_{dc}) at 323K and the activation energy (E_{dc}) of glass is shown in Fig.4. The dc conductivity (σ_{dc})for glasses containing Al_2O_3 exhibits lower values than that for Al_2O_3 free glass whereas E_{dc} increases with increasing Al_2O_3 content. Such behavior is related to structural modifications observed with the addition of Al_2O_3 as a result of interlinking between borate chain and aluminum tetrahedral unit. The decrease of conductivity is due to network regulation by formation B-O-Al and Al- O –Al bond and presence of the large amount of Al_2O_3 increases an ionic character therefore it reduces Li^+ ions mobility and breaks conduction path.

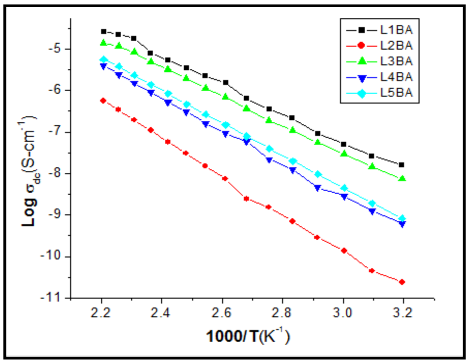

Fig.3: Temperature dependent conductivity

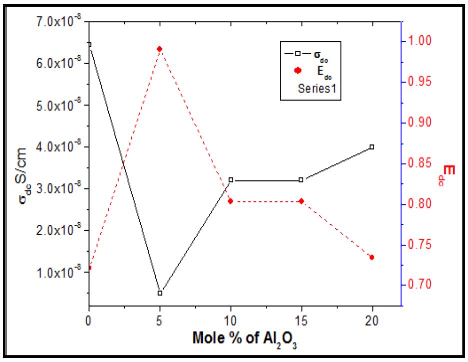

Fig 4: E_{dc}&σ_{dc} modifier ratio (η = 2.333)

The results are parallel with the report(Gedam R.S.&Deshpande V.K.2009). No glass composition in the system presents higher conductivity than conductive binary glass ($30Li_2O:70B_2O_3$) therefore it shows that there is no evidence of existence of mixed former effect in the system. It is observed that glass sample L_1BA exhibits high conductivity and low activation energy. The conductivity of sample L1BA has been found to be 6.64 x10^{-8}S/cm (323K). The activation energy calculated from the slope of fitted line has been found to be 0.85±01 eV for this series.

Table.1: *Activation energy and dc conductivity of series I (L1BA-L5BA)*

Sample code	Mole % of Li_2O	Mole % of Al_2O_3	Mole % of B_2O_3	Modifier ratio (η)	Former ratio (y)	σ_{dc}S/cm (323K)	E_{dc}(eV)
L1BA	30	0	70	**2.333**	**1**	6.44E-8	0.7214
L2BA	30	5	65	**2.333**	**0.9285**	4.92E-9	0.9911
L3BA	30	10	60	**2.333**	**0.8571**	3.2E-8	0.8036
L4BA	30	15	55	**2.333**	**0.7857**	3.2E-8	0.8036
L5BA	30	20	50	**2.333**	**0.7143**	3.99E-8	0.7343

Conclusion

The effect of compositional changes by addition of second former Al_2O_3 into Li_2O:B_2O_3 glass on electrical conductivity has been investigated. It was observed that dc conductivity decreases with addition ofAl_2O_3which is attributed to structural modification and formation of Al-O-B linkage, resulting in hinders the migration ofLi+ ions. The maximum conductivity was observed for Al_2O_3 free glass and it indicates that the mixed former effect doesnot exist in .

these compositions. The conductivity of glass increases with increase in temperature and Arrhenius behavior has observed for all samples.

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