# DC Conductivity and Density Measurements in Lithium Borate Glasses

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## Abstract

*DC electrical conductivity of glass system $30Li_2O$-$(70-x)B_2O_3$-$xAl_2O_3$, x = 0, 5, 10, 15 and 20 mol % prepared by a melt-quenching method were measured by two probe technique. The glassy phase was confirmed from XRD which shows a broad hump in between 20-25° and SEM. The influence of the substitution of $B_2O_3$ by $Al_2O_3$ in electrical conductivity and in activation energy was discussed. It is observed that conductivity decreases and activation energy increases with the addition of $Al_2O_3$. The molar volume decreases whereas density increases. The decrease in molar volume indicates the decrease in inter-atomic distances which increases the rigidity of the glass.*

**Keywords:** Conductivity; Thermal behaviour; Activation energy

## Introduction

Lithium batteries is one of the most widely accepted power sources for electronics and mobile devices due to better performance over other rechargeable batteries [1]. Most of the batteries use liquid electrolytes that are flammable and hazardous [2]. The solid state electrolytes (SSEs) would effectively eliminate the safety concern associated with the liquid electrolyte [3]. The low ionic conductivity and stability is main problem in the commercialization of lithium-ion batteries, sensors [4, 5]. The ion-exchange method is a crucial way to introduce metal cations into glass for improvement of the glass characteristics. The ion-exchange is usually carried out by immersing the alkali glass into molten salts containing the desired metal cations or the field-assisted ion exchange to accelerate the diffusion rate. The introduction of lithium ion into the glass is mainly used for the production of refractive index profiles in the glass [6].

Borate glasses are found to be very appealing amorphous materials because of its specific structure and physical properties. In these glasses, two groups of bands are obtained one due to trigonal $BO_3$ and another due to the tetrahedral $BO_4$ units. When transition metal ions added to these glasses, they show signs of specific physical properties [7]. Group III donor element, such as Al is added to improve electrical properties of glasses [8].

The present investigation might project a comprehensive study on the DC conductivity of $Li_2O$-$B_2O_3$-$Al_2O_3$ glasses in the temperature range 30 - 180 °C to correlate the dynamics of $Li^+$ ions with the

network structure of glasses. The systematic study on thermal and physical properties of glass samples is explained. The characterization technique, like X-ray diffraction (XRD), thermo gravimetric-differential thermal analysis (TG-DTA) and scanning electron microscope (SEM) is employed to study the structural properties of the glass samples.

## Experimental

The glass samples of the compositions of $30Li_2O$-(70-x) $B_2O_3$-$xAl_2O_3$, x = 0, 5, 10, 15 and 20 mol % were prepared by a melt-quenching method. The AR grade chemicals were weighed and mixed together. This mixture was homogenized and melted in silica crucible in a furnace at 1000 °C for 3 h. After melting, the mixture was poured onto a nonmagnetic stainless steel plate. The samples were characterized by using XRD, TG-DTA and SEM techniques. For the electrical measurements, the samples were polished and conducting silver paste was deposited on both sides. Measurements of DC conductivity as a function of temperature, in all the samples were made by two-probe technique in the temperature range of 30 - 180 °C. The density of the glass was determined at room temperature through Archimedes principle, by using xylene (ρ = 0.863 g/cc). The density was calculated by using Eq. (1)

$$\rho = \left( \frac{W_a}{W_a - W_l} \right) \times \rho_l \qquad (1)$$

Where ρ is density of the sample, $W_a$ is weight of the sample in air, $W_l$ is weight of the sample fully immersed in xylene and $\rho_l$ is density of the xylene.

The molar volume $V_m$ was calculated from Eq.(2).

$$V_m = \frac{M_T}{\rho} \qquad (2)$$

where $M_T$ is molecular weight of the glass calculated by multiplying x times the molecular weights of the various constituents.

## Result and Discussion

### XRD and SEM

XRD pattern of all samples shows amorphous nature (fig.1). The intense hump (amorphous hallow) appears at the same 2θ-position. Fig. 2 represent SEM image of 20 mol % of $Al_2O_3$ sample, which also hold the amorphous and homogeneous nature of glass sample [9].

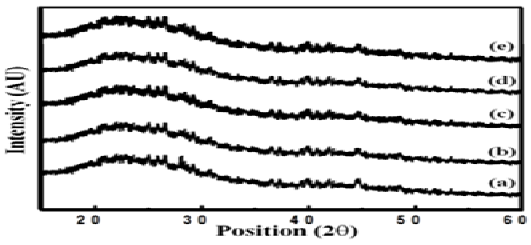


**Fig.1.** XRD of $30Li_2O$-(70-x) $B_2O_3$-$xAl_2O_3$, for (a) x=0 mol%, (b) x=5 mol%, (c) x=10 mol%, (d) x=15 mol% and (e) x=20 mol%.

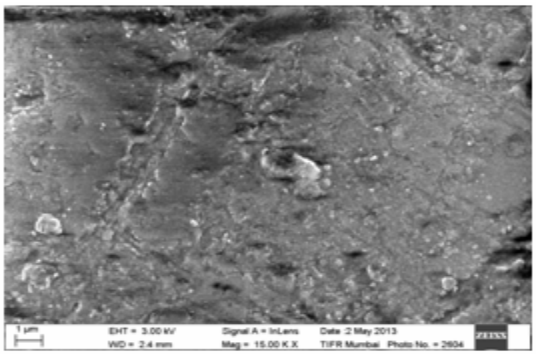

**Fig.2.** SEM Image of 20 mol % of $Al_2O_3$ glass sample.

**Thermal analysis**

Thermal analysis (TG/DTA) was conducted and the representative thermogram of sample (20 mol % of $Al_2O_3$) is shown in fig. 3. The weight loss 6 % was observed in first step (up to 254 °C) which is due to the loss of water molecules. In the second step (up to 350°C) weight loss is 19 % is observed. A total weight loss 25 % was observed after heating up to 500 °C. From the DTA profiles, it is identified that endothermic peak appears in between 250-280 °C which represents the glass transition (Tg). The Tg of this glass is found to be 267 ºC [10].

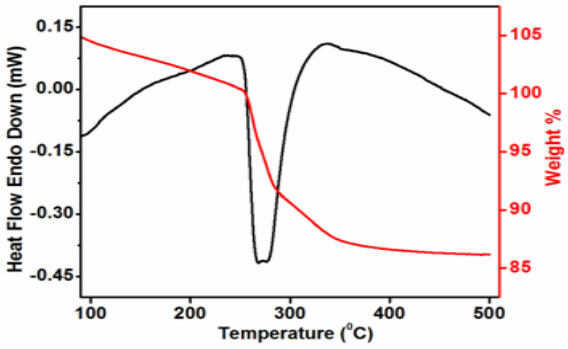


**Fig. 3** TG-DTA plot for 20 mol % of $Al_2O_3$.

**DC Conductivity**

The variation of DC conductivity as a function of temperature for studied glass system is as shown in fig. 4. For all the glass systems, conductivity shows Arrhenius behavior. Fig. 5 shows the variation of conductivity and activation energy as a function of mol % of $Al_2O_3$ at 453 K. It is observed that initially conductivity decreases with the addition of $Al_2O_3$ up to 5 mol % and beyond this conductivity increases. The maximum in conductivity corresponds with minimum in activation energy. The decrease in conductivity for 5 mol % of $Al_2O_3$ may be due to creation of bridging oxygens. The creation of bridging oxygens makes the structure rigid and hence the conductivity decreases. Beyond 5 mol % of $Al_2O_3$ increase in conductivity explains on the basis of Anderson and Stuart model. With the further addition of $Al_2O_3$ the structure becomes loose and hence the conductivity increases [11, 12].

ISSN:2319-6602
International Journal of Chemical and Physical Sciences

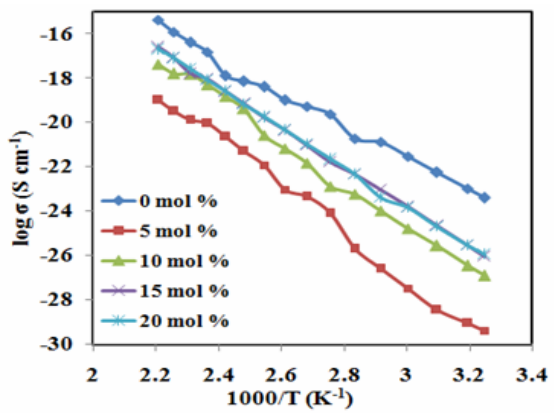


**Fig. 4** Variation of conductivity as a function of temperature.

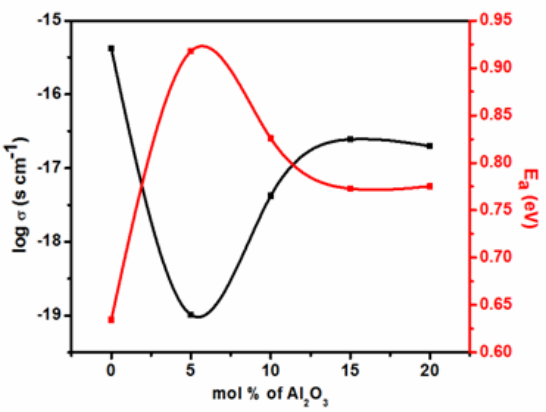


**Fig. 5** Variation of conductivity and activation energy with mol % of $Al_2O_3$.

### Density and molar volume

The density is a prevailing tool capable of exploring the changes in the structure of glasses. In the studied glasses, it is observed that the density increases from 2.32 to 2.62 g/cm$^3$, while molar volume decreases from 24.81 to 24.46 cm$^3$ mol$^{-1}$ with increase in $Al_2O_3$ content as shown in fig. 6. It is expected that the density and molar volume should show opposite behavior to each other, and so in the studied glasses the molar volume decrease with the increase in density [13]. In general the decrease in molar volume indicates the decrease in inter-atomic distances. Hence the compactness of the glass increases and more bridging oxygens will be created which increases the rigidity of the glass [14].

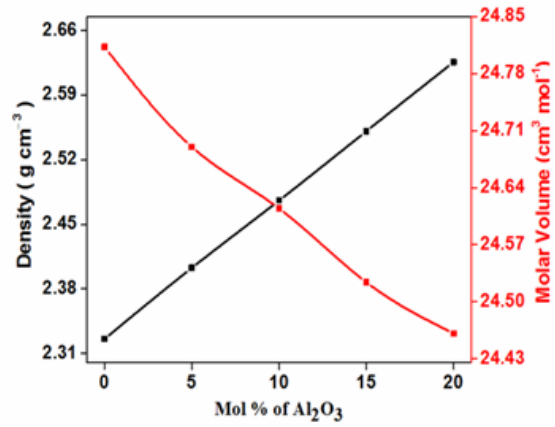


**Fig. 6** Variation of density and molar volume with mol % of $Al_2O_3$.

## Conclusion

The amorphous structure of the samples was confirmed from XRD and SEM. The DC conductivity shows Arrhenius-type temperature dependence. The maximum value of conductivity and minimum value of activation energy were found to be in the range of $10^{-7}$ Scm$^{-1}$ at 453 K and 0.6–0.7 eV respectively. It is realized that the structural modification is depends on density and molar volume. The density was found to be increases from 2.32 to 2.62 g/cm$^3$, congruent with decreased in the molar volume

from 24.81 to 24.46 $cm^3$ $mol^{-1}$ with $Al_2O_3$ content indicates increase in compactness of the glass bridging oxygens.

## Acknowledgements

Authors are thankful to Principal, S.S.S.K.R. Innani Mahavidyalaya, Karanja Lad, Secretary, Indira Gandhi Kala Mahavidyalaya, Ralegaon and Principal, Amalokchand Mahavidyalaya, Yavatmal for providing necessary facilities.

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