Hinthada University Research Journal, Vol. 1, No. 1, 2009

DC Conductivity Studies on Lithium Alumino Phosphate Glasses

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Abstract

Glass system $yLi_2O.(1\text{-}y)\ P_2O_5.0.01Al_2O_3$ in the composition range ($0.1 \leq y \leq 0.5$) is prepared by melt-quenching technique. The dc electrical measurements were made over a temperature range (353K- 673K). The results of a systematic study of the influence of lithium ions on the conductivity of lithium alumino phosphate glasses was reported. The addition of lithium ions (Li^+) to the phosphate glasses system affects the electrical conductivity . It has been found that the conductivity increases with temperature and with the increase in the lithium content. The activation energy is found to be concentration and temperature dependent.

Key words: DC conductivity, alumino phosphate glasses, activation energy

Introduction

Glass is an amorphous solid in which the atoms form a random network. Glasses do not have the rigidity of crystals and have a viscosity that increase as the temperature as lowered. At very low temperature, when the viscosity is very large, glasses can become elastic and brittle.

The basic unit is a tetrahedral or triangular co-ordination of a glass former with oxygen. The basic building block in phosphate glasses and crystals is the phosphorous-oxygen tetrahedron. However, in contrast to the four-valent glass formers, the phosphorous has a double bond to one of its surrounding oxygen atoms. The structure of glass P_2O_5 is a three dimensional network of these phosphorous-oxygen tetrahedra as in vitreous silica.

The basic structural P_2O_5 unit is assumed to be made up of two PO_4 tetrahedra with common oxygen and each tetrahedron has 3 bridging and one non-bridging oxygen atoms in it.

The properties of glass are due to the strong intensity of interatomic bonds which form its structure (Chowdari & Kumari, 1996). Though pure P_2O_5 is extremely unstable, the alkali oxide modified glasses are quite stable. Therefore the electrical conductivity of the glass has been employed for the structural characterization of these glasses (Dwivedi *et al.*,1992).

Experiment

The starting materials (Li_2CO_3, $NH_4H_2PO_4$ and Al_2O_3) were mixed thoroughly in amounts which after heating and loss of CO_2 and H_2O produced a glass of composition $yLi_2O.(0.99\text{-}y)P_2O_5.0.01\ Al_2O_3$ ($0.1 \leq y \leq 0.5$) .

The mixture was kept at about 400˚C for 18 hours and 800˚C for an hour to convert Li_2CO_3 into Li_2O and $NH_4H_2PO_4$into P_2O_5 according to the chemical reactions.

$$Li_2CO_3 \rightarrow Li_2O + CO_2$$

$$2NH_4H_2PO_4 \rightarrow P_2O_5 + 3H_2O + 2NH_3$$

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The temperature of the crucible containing the mixture was raised to 1100ºC for three hours in an electric furnace. The samples are made by pouring the bubbles free melt in between the copper mold kept at room temperature. The samples are cut and then they are made to have a thickness of 1mm. The reaction scheme for the formation of lithium-alumino phosphate glass using melt quenching method is shown in Figure 1.

X-ray powder diffraction, revealed the glassy structure. Due to the disordered structure, the X-ray diffraction pattern of the glass consists of a few broad diffuse haloes. The XRD pattern has a broad hump peak at about 20-30 degree, as in generally observed in several oxide glasses with an "amorphous" structure. It will not produce diffraction sharp peaks except a broad peak in the background. Figure (2) shows the XRD pattern for $yLi_2O.(0.99-y)P_2O_5. 0.01 Al_2O_3$ glasses (Van Black, 1975).

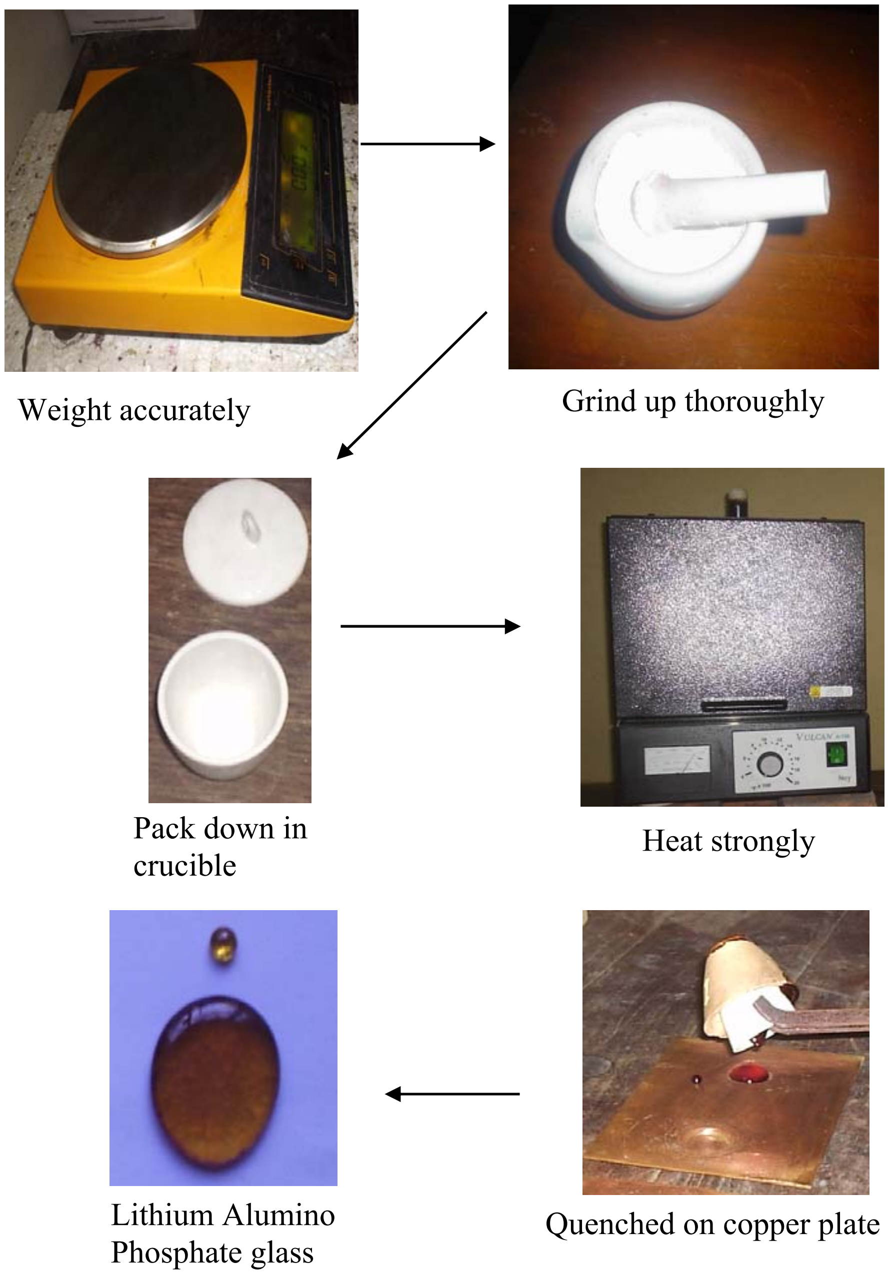

Figure 1 Reaction scheme for the formation of Lithium Alumino Phosphate glasses using the melt-quenching method.

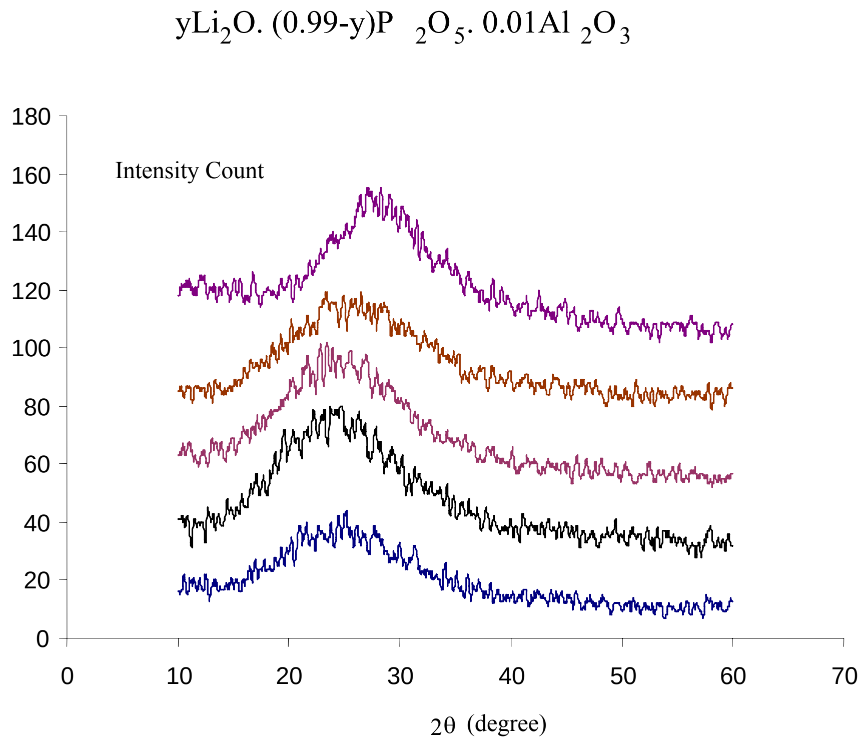

Figure 2 XRD Pattern for $yLi_2O.\ (0.99\text{-}y)P_2O_5.\ 0.01Al_2O_3$ Glasses

Electrical Conductivity Measurement

The dc electrical conductivity measurements on the glasses were carried out over the temperature range from 353 K to 673 K in steps of 20 K. To measure the temperature variation of conductivity, a simple home-made apparatus was developed in the laboratory. The apparatus consists of a sample holder attached with the 150W heater and the steel chamber (Kishore *et al.,* 1982). The desired temperature of the samples was maintained with the help of a temperature controller (J type, Model No 8528-21). The variation of the temperature was sensed by J type thermocouple. The experimental arrangement for temperature dependent electrical conductivity is shown in Figure 3.

The detailed procedure of mounting the sample in the sample holder for the measurement includes the following steps. The sample was sandwiched between two copper plates that are in contact with two copper rods. These two copper rods serve as two electrodes. To ensure better electrical contact, silver paste was applied evenly on both surfaces of the sample. The sample in the sample holder was placed on the copper cylinder that was heated by 150 W heater. Thermal conducting mica shield is used between the sample holder and the copper cylinder to protect from electrical conduction. The apparatus was immersed in a heating steel chamber surrounded by asbestos to reduce the thermal flow from the environment.

The resistances were measured using FLUKE 1520 mega-ohm meter. The J type thermocouple was inserted near the sample to record its temperature. The copper block holder was heated by 150 W heater coil. Photograph of the experimental setup for the measurement of dc conductivity is shown in Figure 4.

The conductivity has been calculated using the formula $\sigma = l / RA$ where l the thickness of the sample, A the area of cross-section of the electrodes and R is the resistance. The conductivity was measured over a temperature range from 353 K-673 K at intervals of 20 K.

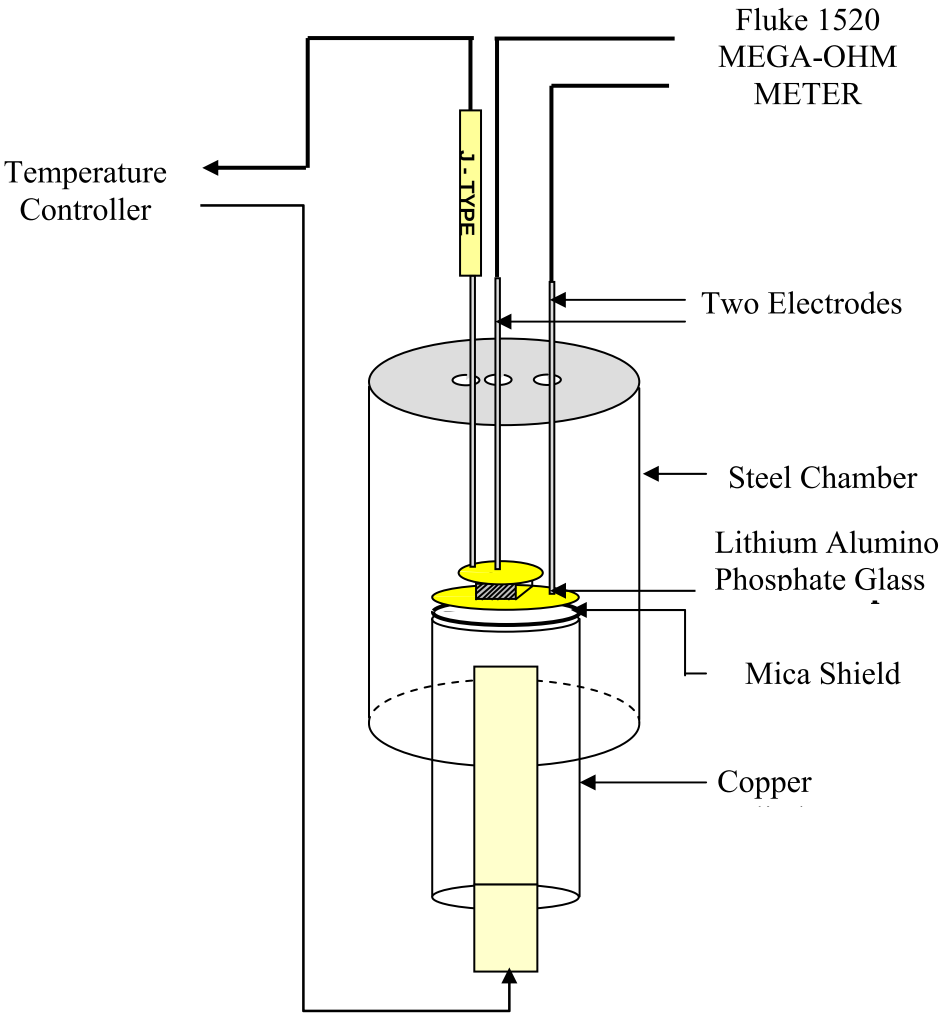

Figure 3 Experimental arrangements for conductivity measurement

Figure 4 Photograph of the experimental setup for the measurement of DC conductivity

Results

In ion conducting glasses, the arrhenious formula $\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$ (where σ the conductivity, the σ_0 pre-exponential factor which is temperature dependant, E_a, the activation energy for conduction, k the Boltzmann constant and T the absolute temperature) is the most suitable relation for studying the variation of conductivity.

Arrhenious plots of the variation of DC conductivity the prepared glass samples (Table 1) with temperature (353 K- 673 K) as shown in Figure 4. The activation energies have been determined from the slopes of the best fit lines obtained by least square methods. The results are presented in Table 2.

Table 1 Chemical composition of the prepared glasses

Sample No	(mol%) P_2O_5	Li_2O	Al_2O_3
1	0.89	0.1	0.01
2	0.79	0.2	0.01
3	0.69	0.3	0.01
4	0.59	0.4	0.01
5	0.49	0.5	0.01

Table 2 Activation energy of the prepared glasses

Sample No	$yLi_2O.\ (0.99\text{-}y)\ P_2O_5.\ 0.01\ Al_2O_3$ content	Activation energy (E_a) (eV)
1	0.1 Li_2O 0.89 P_2O_5 0.01 Al_2O_3	0.92
2	0.2 Li_2O 0.79 P_2O_5 0.01 Al_2O_3	0.86
3	0.3 Li_2O 0.69 P_2O_5 0.01 Al_2O_3	0.79
4	0.4 Li_2O 0.59 P_2O_5 0.01 Al_2O_3	0.72
5	0.5 Li_2O 0.49 P_2O_5 0.01 Al_2O_3	0.63

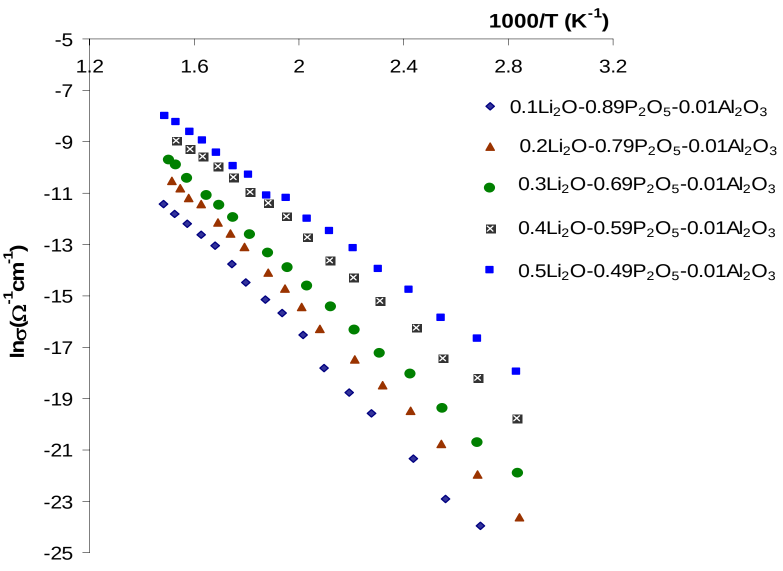

Figure 4 The result for temperature dependent conductivity measurement on yLi_2O. (0.99-y) P_2O_5. 0.01 Al_2O_3 glasses

Discussion

From the plot, it is obvious that the conductivity increases with concentration of Li_2O and also with temperature expected. The increase in conductivity with the increase in the concentration of Li_2O must be due to the transport of Li^+ ions.

According to the model proposed by Anderson and Stuart the activation energy must decrease with an increase of the alkali content resulting in an enhanced conductivity. Our results of measurement of conductivity in lithium alumino phosphate glass system strictly agree with this model.

Conclusion

The influence of Li+ ions on the dc electrical of lithium alumino phosphate glasses has been investigated. It is found that the conductivity increase with temperature as well as with concentration of Li_2O. It is concluded that the enhanced conductivity is due to the effect of alkali ions. From the experimental results, the conductivity increases and the activation energy decreases with increasing in ion concentration.

Acknowledgements

I would like to express my heartfelt thanks to Dr Tin Tun Myint, Pro-Rector of Hinthada University, for his kind permission to carry out this project and overall supporting during the project.

I am also greatly indebted to Dr Si Si Hla Bu, Pro-Rector, Hinthada University, for all her valuable guidance and helpful advice.

I would like to thank Professor Dr Mya Mya Win, Head of Department of Physics, Hinthada University, for her kind permission to carry out this research.

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