DC conductivity of Li$_2$O and SrO doped borophosphate glasses

Anand Thipperudra,$^{1,2}$ S Manjunatha,$^{3,6}$ H L Pushpalatha,$^{2}$ M Prashanth Kumar$^4$ and Y T Ravikiran$^5$

$^1$Department of Physics, VTURC, Rao Bahadur Y. Mahabaleswarappa Engineering College, Ballari, 583104 India,
$^2$Department of Physics, Cambridge Institute of Technology, Bengaluru 560036, India,
$^3$Department of Physics, V. V. Sangha’s Independent PU College Ballari, 583104 India,
$^4$Department of Physics, Government First Grade College, Kalaburagi, 585101, India,
$^5$Department of PG Studies in Physics, Govt. Science College, Chitradurga, 577501, India.

$^6$E-mail: manjusballari@gmail.com

Abstract. Borophosphate glasses with dopants SrO and Li$_2$O in the composition of 20(B2O3) + 30(P$_2$O$_5$) + (50-x) (SrO) + x (Li$_2$O) where x = 10, 20, 30, 40 and 50 were synthesized by standard melt quenching technique. All the glass samples were annealed to extract the thermal strains presence in it if any, its amorphous nature was evidenced by XRD characterization, density of the as synthesized glass series has been calculated at the ambient temperature using Archimedes’ principle and also its molar volume was estimated. With increase in mole fraction of Li$_2$O, density of the glass samples found deceasing and the molar volume observed to be increasing as per the trends. Using Nernst-Einstein equation, high temperature dc activation energy has been calculated.

Keywords: DC conductivity, Borophosphate, Glass.

1. Introduction

Ion conducting glasses doped with alkali and alkaline metal oxides found to be potential applications in solid state ionic devices [1], like electro chromic displays, lithium-ion batteries, etc. Warburg et al. in 1984 explored ion transport glasses by applying DC voltage [2–4]. The ionic conductivity in oxide glass systems doped with alkali and alkaline earth ions is due to migration of ions from one ionic site to another ionic site by hopping [5,6]. However, the amorphous structure and non-equilibrium nature of the oxide glasses are to be fundamental in understanding their ionic transport mechanism [7].

Normally in fast ion conducting glasses, network formers are oxide materials containing covalent bonding [8]. In ion conducting glasses the electron donation to the total conductivity is normally weak, this is due to the periodic potential fluctuations imposed by the disordered structure [9]. The electrical conductivity in these glasses is by the hopping of polarons from one state to other states [10]. The presence of alkali ions (singly charged) in a variety of alkali and alkaline earth glass systems and in doubly charged alkaline earth cations proved to exhibit higher diffusivities than in two alkaline earth
glasses [11]. The experimental results from XRD studies, molar volume, density, DC conductivity and activation energy studies on borophosphate glass systems doped with SrO and Li$_2$O in the composition range 20(B$_2$O$_3$) + 30(P$_2$O$_5$) + (50-x) (SrO) + x (Li$_2$O) where x = 10, 20, 30, 40 and 50 are presented in this work.

2. Experimental

The required AR grade chemicals such as Boric acid (H$_3$BO$_3$) Ammonium dihydrogen orthophosphate (NH$_4$H$_2$PO$_4$) Lithium carbonate (Li$_2$CO$_3$) and Strontium oxide (SrO) were taken in silica crucible. The chemical mixture was heated to a high temperature at 1253 K in a muffle furnace. A homogeneous transparent melt was formed, then the melt was rapidly quenched using two stainless steel plates. The synthesized samples were annealed by heating them up to 573 K and later allowed for slow cooling for 4 hours. Borophosphate glasses doped with SrO and Li$_2$O with composition of 20(B$_2$O$_3$) + 30(P$_2$O$_5$) + (50-x) (SrO) + x (Li$_2$O) where x = 10, 20, 30, 40 and 50 were synthesized by melt quench process and represented as BPSL. X-ray diffraction (XRD) studies were done for all the glass samples. Density (ρ) was determined by using Archimedes principle. DC conductivity measurements were carried out by two-probe technique for the temperature range 308-503 K. Conductivity (σ) of the samples were determined using $\sigma = (1/\rho)$ where $\rho$ is the electrical resistivity which is given by, $\rho = (R A/t)$, R- resistance, A- cross-sectional area and t- sample thickness.

3. Results and Discussion

3.1. X-Ray Diffraction

XRD is an important experimental tool widely used for materials characterization, specifically, determination of structure, grain size, lattice strains etc. It is confirmed that as prepared samples are amorphous in nature and no sharp peaks have been observed which suggests the non-crystalline nature of the samples. XRD patterns of sample BPSL 10 and BPSL 20 is shown in figure 1(a) [12].

![Figure 1. (a) XRD Patterns of BPSL 10 & BPSL 20 samples. (b) Variation of compositional density ‘$\rho$’ and the molar volume, ‘$V_m$’ of BPSL glasses.](image)

3.2. Density and molar Volume

Estimated density ‘$\rho$’ of the glass samples ranges from 1.64-2.70 g/cm$^3$ which are presented in Table 1. It is found that with the increase in mole fraction of Li$_2$O, density of the samples decreased smoothly till x=30 mole fraction, after that there was a steep decrease in density as depicted in figure 1(b). This gives the effect of substitution of Li$_2$O with SrO on the density of the glass samples. The insertion of Li$_2$O enhanced the rate of degradation of these glass samples. The total ion concentration of the strontium and lithium ions in this series of glass samples were kept constant. These values are comparable with those of many reported alkali and alkaline earth ion doped borate, phosphate and
borophosphate glasses [13]. The topology of glass network is not same for all compositions in the present series. When the Li$_2$O ion concentration goes on replacing at the cost of SrO the molar volume increases and hence the glass network found to be loosely packed. In the present series of as synthesized glass samples, the linear decrease in density ($\rho$) and the linear increase in molar volume ($V_m$) with Li$_2$O ion concentration shows the higher reticulation in the glass network [14].

### Table 1. Density and conductivity data for the borophosphate glasses doped with SrO and Li$_2$O

| Glass sample | $\rho$ (in g/cm$^3$) | $V_m$ (in cm$^3$) | $\sigma$ (in ohm$^{-1}$) | $W_{DC}$ (in eV) |
|--------------|----------------------|-------------------|-------------------------|-----------------|
| BPSL 10      | 2.43                 | 142               | 4.24 x 10$^{-8}$        | 1.22            |
| BPSL 20      | 2.41                 | 146               | 6.88 x 10$^{-7}$        | 1.21            |
| BPSL 30      | 2.36                 | 149               | 2.89 x 10$^{-6}$        | 1.20            |
| BPSL 40      | 1.79                 | 165               | 6.92 x 10$^{-5}$        | 0.83            |
| BPSL 50      | 1.52                 | 197               | 7.60 x 10$^{-5}$        | 0.77            |

### Figure 2. (a) Variation of DC conductivity $\sigma$ and the activation energy $W_{ac}$ of BPSL glasses with respect to x-mole fractions of Li$_2$O, (b) Variation of ln($\sigma T$) with 1/T. Solid lines represent least square fits to the high temperature data.

3.3. DC Conductivity

DC conductivity ($\sigma$) Studies for the varied glass compositions is depicted in figure 2 (a). It is found that the conductivity increases linearly with increasing temperature, inferring that the conduction mechanism in the samples is similar to that of in alkali and alkaline earth doped borophosphate glasses [15]. Behaviour of activation energy $W_{ac}$ and conductivity $\sigma$ of BPSL glasses were plotted and are shown in figure 2(a). Variation of ln($\sigma T$) with (1/T) were plotted and are as shown in figure 2(b). From the plots it is found that the curves are linear in the high temperature region and the linear plots were fit to the data at high temperature. The degree of fits was found to be in the range 0.9998 - 0.9995 for all the samples. The slopes of linear fits were found from the figure 2(b). The temperature independent DC activation energies, $W_{ac}$ values were determined which 0.77-1.22 eV is in the range. DC conductivity values at 500 K were found in the range 4.248 x 10$^{-8}$-7.608 x 10$^{-5}$ ohm$^{-1}$m$^{-1}$, which are summarized in Table 1. These results are similar to those obtained in the similar studies available in the literature [16]. From the above studies it is clear that the activation energy observed to decrease and conductivity found to increase slightly up to x=30 mole fractions of Li$_2$O. For further increase in
Li$_2$O ion concentration, the conductivity increases rapidly and activation energy decreases abruptly [17].

4. Conclusion
Borophosphate glasses with dopants of SrO and Li$_2$O have been prepared. Amorphous nature of the as synthesized glass samples was given by XRD. The high temperature DC activation energy was determined by fitting the measured experimental data. The conductivity and activation energy observed to behave in opposite way and hits maximum and minimum peaks respectively.

References

[1] Ravaine D 1985 Ionic transport properties in glasses \textit{J. Non. Cryst. Solids} \textbf{73} 287–303
[2] Govindaraj G, Baskaran N, Shahi K and Monoravi P 1995 Preparation, conductivity, complex permittivity and electric modulus in AgI-Ag$_2$O-SeO$_3$-MoO$_3$ glasses \textit{Solid State Ionics} \textbf{76} 46–55
[3] Saito T, Torata N, Tatsumisago M and Minami T 1996 Ionic conductivities of rapidly quenched AgI-Ag$_2$O-B$_2$O$_3$ glasses containing large amounts of AgI \textit{Solid State Ionics} \textbf{88} 491–5
[4] Tatsumisago M and Hayashi A 2008 Preparation of lithium ion conducting glasses and glass-ceramics for all-solid-state batteries \textit{J. Non. Cryst. Solids} \textbf{354} 1411–7
[5] Kaushik R and Hariharan K 1987 Silver phosphovanadate vitreous electrolytes \textit{Solid State Commun.} \textbf{63} 925–7
[6] Coppo D, Duclot M J and Souquet J L 1996 Silver ionic conductivity enhancement by network former mixed in oxide-based glasses \textit{Solid State Ionics} \textbf{90} 111–5
[7] Elliott S R 2016 A.c. conduction in amorphous chalcogenide and pnictide semiconductors \textit{Adv. Phys.} \textbf{87} \textbf{32} 135–218
[8] Zachariasen W H 1935 The vitreous state \textit{J. Chem. Phys.} \textbf{3} 162–3
[9] Belostotsky V 2010 Defect model for the mixed mobile ion effect revisited: An importance of deformation rates \textit{J. Non. Cryst. Solids} \textbf{356} 129–31
[10] Austin I G and Mott N F 1969 Polarons in Crystalline and Non-crystalline Materials \textit{Adv. Phys.} \textbf{18} 41–102
[11] Natrup F, Bracht H, Martiny C, Murugavel S and Roling B 2002 Diffusion of calcium and barium in alkali alkaline-earth silicate glasses \textit{Phys. Chem. Chem. Phys.} \textbf{4} 3225–31
[12] Cullity B D 1978 \textit{Elements of diffraction quasi-optics} (Addison-Wesley Publishing Company INC.)
[13] Prashant Kumar M and Sankarappa T 2009 DC conductivity of rare earth ions doped vanadotellurite glasses \textit{J. Non. Cryst. Solids} \textbf{355} 295–300
[14] Doweidar H and Saddeek Y B 2009 FTIR and ultrasonic investigations on modified bismuth borate glasses \textit{J. Non. Cryst. Solids} \textbf{355} 348–54
[15] Belostotsky V 2007 Defect model for the mixed mobile ion effect \textit{J. Non. Cryst. Solids} \textbf{353} 1078–90
[16] Abou Neel E A, Chrzanowski W, Pickup D M, O’Dell L A, Mordan N J, Newport R J, Smith M E and Knowles J C 2009 Structure and properties of strontium-doped phosphate-based glasses \textit{J. R. Soc. Interface} \textbf{6} 435–46
[17] Kamitsos E I 2003 Infrared studies of borate glasses \textit{Phys. Chem. Glas.} \textbf{44} 79–87