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Electrical Conduction in Borophosphate Glasses Doped With CoO and Li_2O

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Abstract

Oxide glasses in the compositions, $(B_2O_3)_{0.2}$ - $(P_2O_5)_{0.3}$ - $(CoO)_x$ - $(Li_2O)_{0.5-x}$, where x = 0.05, 0.1, 0.15, 0.20, 0.25, 0.30, 0.40 and 0.50 were prepared at 1400K by the standard melt quenching method. The samples were confirmed to be noncrystalline through XRD studies By following Archimedes method, room temperature density was determined. Conductivity was measured for the temperature range from 350K to 625K. Molar volume was estimated using density. Density variation with x indicated that glass structure is sensitive to the changes in CoO content. The conductivity data was analyzed using Mott's small polaron hopping (SPH) model and activation energy was determined. The nature of change in conductivity and activation energy with CoO variation revealed switchover of conduction mechanism from predominantly ionic to electronic regimes around x=0.3. The conductivity data deviated from Mott's SPH model has been analyzed using variable range hopping models and density of states at Fermi level has been determined. The polaron hopping related quantities such as transition metal ion density, N, polaron hopping distance, r and polaron radius, r_p, were determined. For the first time borophosphate glasses doped with Li_2O and CoO were studied for conductivity variation with temperature and changeover of conduction mechanism from ioni cpredominane regime to electronic regime has been observed.

Keywords: Borophosphate glasses, density, conductivity, density of states.

Introduction

Phosphate, Borate and Tellurite glasses doped with alkali ions have been studied by several researchers for their novel technological applications such as solid electrolytes for lithium secondary batteries[1, 2]. Electrical studies of several oxide glasses of different compositions containing transition metal (TMI) and alkali ions are reported owing to interest in their conduction mechanisms and their other physical properties. The studies in pure borate and phosphate glasses have been limited by their hygroscopic nature despite the fact they have low melting temperatures. However, phosphate glass showed improved chemical durability when few boron atoms were incorporated into the network[3]. Borophosphate glasses have wide applications as optical devices, electrolytes in solid state electrochemical cells and in biomedical fields[4]. Sodium doped borophosphate glasses were measured for conductivity with temperature as a variable and it has followed Arrhenius behavior and was also confirmed to be due to hopping mechanism[5]. Conductivity in the temperature range from 293K to 393K has been studied in lithium doped borophosphate glasses of composition, 50 Li_2O. xB_2O_3. (50-x) P_2O_5[6]. Conductivity increased up to x = 0.2 and decreased for further higher values of x. The decrease of conductivity for x > 0.20 has been attributed to the crystallization of lithium. Mixed glass former effect has been observed in AgI doped silver borophosphate glasses[7]. Changeover of predominance of conduction mechanism from ionic to electronic has been observed in Dy_2O_3 doped borophosphate glasses[8]. Transition of conduction mechanism from electronic to ionic or vice-versa has been observed in different glass systems[9-11]. Glasses exhibiting transition of conduction mechanism from one type to another have always considered to be the potential candidates as electrodes in the solid state batteries. Few polaron hopping models viz., Mott's small polaron hoping (SPH), variable range hopping (VRH)[12,13] and Greaves VRH models[14] were invoked to understand temperature dependence of conductivity in the glasses.

Keeping in view of the fact that borophosphate glasses doped with alkali and transition metal ions have not been investigated for conductivity behavior with temperature by many authors though these glasses are known to be chemically more durable than pure phosphate and borate glasses and have attractive applications, we investigated conductivity with temperature as an input variable in borophosphate glasses of composition, $(B_2O_3)_{0.2}$ - $(P_2O_5)_{0.3}$ - $(CoO)_x$ - $(Li_2O)_{0.5-X}$, where x=0.05, 0.1, 0.15, 0.20, 0.25, 0.30, 0.40 and 0.50 labeled as BPCL1, BPCL2, BPCL3, BPCL4, BPCL5, BPCL6, BPCL7 and BPCL8 respectively.

Methodology

The glasses were prepared by melt-quenching technique using Himedia make AR grade chemicals, H_3BO_3, $NH_4H_2PO_4$, CoO and Li_2Co_3. The mixture of chemicals in desired weight ratios were taken in silica crucibles and melted in an electric furnace at 1400K. After maintaining the melt at 1400K for an hour, it

was suddenly quenched to room temperature. Samples of varied sizes and shapes thus formed were collected. To remove thermal strains built up in the samples, they were annealed at 450K and were subjected to XRD studies for the confirmation of non-crystallinity.

By following Archimedes principle, room temperature density of the glasses was determined using a single pan balance of Citizen make (Model cy204) of precision 0.0001gm and Toluene as an immersion liquid[10]. Glasses were prepared for conductivity study by shaping them to the size of 3 mm in thickness and cross sectional area in the range from 20 mm^2 to 40 mm^2. Silver paint was applied to the two major surfaces of the samples. Resistance in the temperature range from 350K to 625K was measured by two probe method in a computer interfaced Danbridge make (DB502) Resistance Bridge. DB502 is capable of measuring resistance from few ohms to Giga ohms with an error limit of 0.05%. Temperature was measured using a Chromel-Alumel thermocouple with an accuracy of ± 0.5K. Data of resistance and temperature were simultaneously collected using the Labview software through computer at equal intervals of temperature.

The resistivity, ρ, and conductivity, σ, were determined using the relations, $\rho = (rA/t)$ and $\sigma = (1/\rho)$ respectively with t being thickness, r the resistance and *A* the cross sectional area of the glass. The experimental uncertainities on conductivity, Δσ, and resistivity, Δρ were estimated as per, $\Delta\sigma = (\Delta\rho/\rho^2)$ and $\Delta\rho = \Delta r\,(A/t)$ respectively by taking into account of error on resistance, Δr.. The errors on conductivity were found to lie with in 2%.

Results and Discussion

XRD: A typical XRD spectrum of the BPCL4 glass is shown in figure-1. No peaks are observed in the spectrum, which indicates non-crystalline nature of the sample. Similar nature of spectra was obtained for other samples of the present series.

Density: The Density, D, of the present glasses is found to be in the range from 2.101 gm cm^{-3} to 3.997 gm cm^{-3}. Density variation is observed to be non-systematic with CoO content. This indicates that the glass network of the present series is dynamic and sensitive to the CoO content. It can also understood that there is no orderly tightening or loosening of the network with increasing concentration of CoO. These density values are in the range of reported values for vanadium iron tellurite glasses and vanadium cobalt tellurite glasses[10].

The molar volume, V_m, was calculated using the relation[15,16], V_m=M/D Where M is the molecular weight of the glass given as $M = (0.2)M_{B_2O_3} + (0.3)M_{P_2O_5} + (x)\,M_{CoO} + (0.5 - x)M_{Li_2O}$. These values of V_m are in the range from 32.802 cm^3/mol to 62.256 cm^3/mol (table-1). Molar volume also varied non-systematically with CoO content. This imply that with increasing CoO concentration, there is no continuous orderly change in the structure and topology of the glass network taking place.

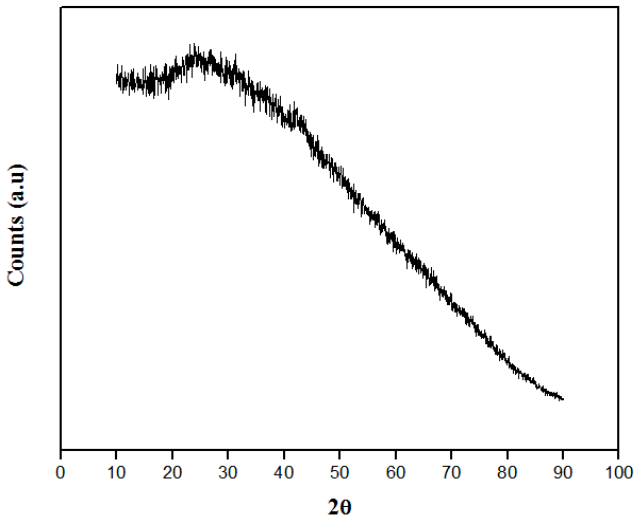

Figure-1
X-Ray diffraction pattern of BPCL4

The transition metal ion density, N, was estimated using the relations given in references[10, 15, 16],

$$N = 2\left[\left\{\frac{\rho(m_{CoO} + m_{Li_2O})}{M_{CoO} + M_{Li_2O}}\right\}N_A\right] \quad (1)$$

Table-1
Physical properties of BPCL glasses

Sl. No.	Glass	Mol. Fraction of CoO	D□±□0.002 (gm/cm^3)	V_m ± 0.002 (cm^3/mol)	N ± 0.01 (x$10^{21}$$cm^{-3}$)	R ± 0.01 (nm)	θ_D (K)
1	BPCL1	0.05	2.893	45.194	11.71	4.40	836
2	BPCL2	0.1	2.101	62.256	8.51	4.90	866
3	BPCL3	0.15	2.681	48.807	10.85	4.52	946
`4	BPCL4	0.2	2.776	47.155	11.24	4.46	836
5	BPCL5	0.25	2.681	48.846	10.85	4.52	886
6	BPCL6	0.3	3.609	36.300	14.61	4.09	966
7	BPCL7	0.4	3.997	32.802	16.18	3.95	906
8	BPCL8	0.5	2.726	48.135	11.04	4.49	946

Where ρ is the density of glass, m_{CoO} and m_{Li_2O} are the mole fractions of CoO and Li_2O respectively, M_{CoO} and M_{Li_2O} are the molecular weights of CoO and Li_2O, respectively and, N_A the Avogadro number. The calculated values of transition metal ion density, N and mean spacing between TMI, R, are tabulated in table-1. The errors on N values were estimated to be of the order of ± 0.01 x 10^{21}. Mean spacing between the TMI are of obtained to be of the order of few nanometer which is in agreement with those reported in refeence[15].

DC conductivity: In the experimental range of temperature range, the electrical conductivity was found to vary in the range from 10^{-3} to 10^{-4} ohm^{-1}m^{-1}. The increase of conductivity with temperature indicates semiconducting nature of the glasses. The plots of σ versus T for all the glasses are shown in Figure-2.

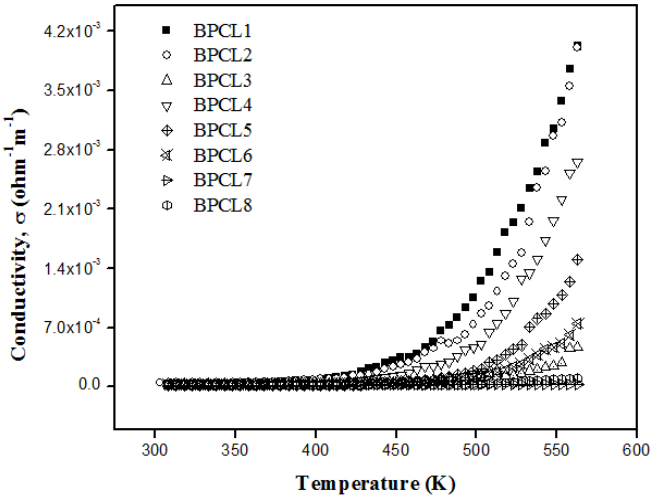

Figure-2
Plots of conductivity, σ, versus Temperature, T(K) for BPCL glasses

Mott's SPH model[10] has been used to analyze conductivity data. According to this model σ can be expressed as,

$$\sigma = \left(\frac{\sigma_0}{T}\right)\exp\left(\frac{-W}{k_B T}\right) \qquad (2)$$

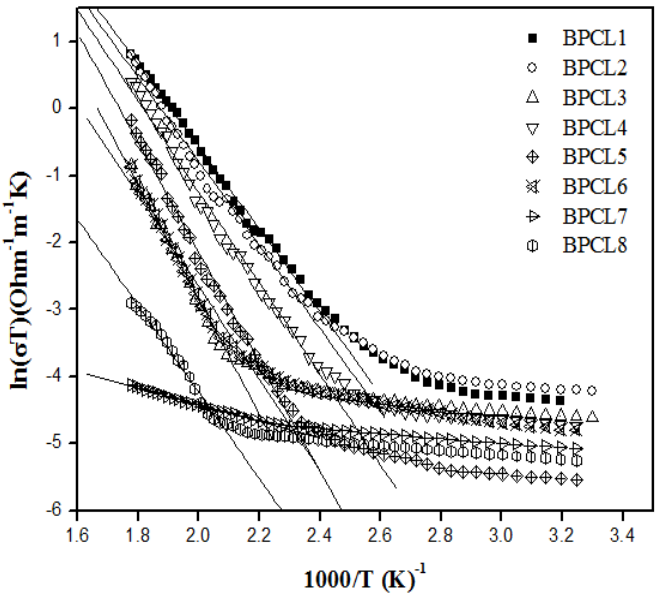

Figure-3
Plots of ln (σT) vs (1/T) for BPCL glasses. Solid lines shown are linear fits as per Mott's (SPH) model for T above T_D.

Where, W is the activation energy and σ_0 the pre-exponential factor given as,

$$\sigma_0 = \upsilon_0 N e^2 R^2 C\left(1-C\right)\exp\left(\frac{-2\alpha R}{K_B}\right) \qquad (3)$$

Where, $\upsilon_0 = \theta_D\left(K_B/h\right)$ is the optical phonon frequency and k_B the Boltzmann constant. The plots of ln(σT) versus (1/T) as per Mott SPH model[15] were sketched and shown in Figure-3. The curves are observed to be linear at high temperature i.e., for $T>T_D$, where T_D is the temperature below which data deviates from Mott's SPH model fit. The linear lines were fit to the data for $T>T_D$. From the slope of the best fit linear lines, W, was determined and tabulated in table-2. As per reference[12], the Debye's temperature, θ_D and T_D are related through $\theta_D = 2T_D$. The best fit linear lines gave correlation coefficients, r^2 in the range 0.999 to 0.998.

Table-2
Polaron hopping parameters for BPCL glasses

Mole fractions of CoO	W ± 0.002 (eV)	σ (475K) (□$^{-1}$m^{-1})	W_H ±0.01 (eV)	ε_P ± 0.02	r_p ± 0.02 (nm)	J ± 0.02 (eV)
0.05	0.502	3.378 x 10^{-3}	0.300	2.81	1.77	0.007
0.10	0.549	3.117 x 10^{-3}	0.328	2.31	1.97	0.006
0.15	0.572	2.817 x 10^{-3}	0.341	2.40	1.82	0.007
0.20	0.674	2.213 x 10^{-3}	0.402	2.06	1.80	0.007
0.25	0.702	1.088 x 10^{-3}	0.419	1.96	1.82	0.007
0.30	0.741	1.088 x 10^{-3}	0.442	2.05	1.65	0.009
0.40	0.711	1.782 x 10^{-3}	0.424	2.21	1.59	0.009
0.50	0.502	1.854 x 10^{-3}	0.300	2.75	1.81	0.007

The W values obtained for the present glasses are in the range of 0.502 eV to 0.741 eV and they agree with those reported for Li_2O doped vanadotellurite glasses[10]. The variations of W and σ (at 475K) with CoO content are shown in figure-4. Conductivity decreased with CoO content up to 0.30 mole fraction and increased for higher amounts of CoO. Activation energy increased up to 0.30 mole fractions of CoO and decreased for further increase in CoO content. The decrease of conductivity and increase of activation energy up to 0.30 mole fractions of CoO and, their reverse behavior for higher amounts of CoO may be due to change over of conduction mechanism from predominant ionic to electronic regimes occurring at around 0.30 mole fractions of CoO. That means that ionic conduction was predominant up to 0.30 mole fractions of CoO and polaronic conduction was predominant for x > 0.30. Since there is mixed conduction i.e., polaronic and ionic one cannot easily relate mean spacing between the TMI's, R to conductivity variation with CoO content (table-1).

Changeover of conduction mechanism from electronic to ionic or vice-versa has been previously reported for zincovandophosphate glasses[18], Sodium vanadophosphate glasses[9], lithium-vanado tellurite glasses[10] and silver vanadotellurite glasses[19].

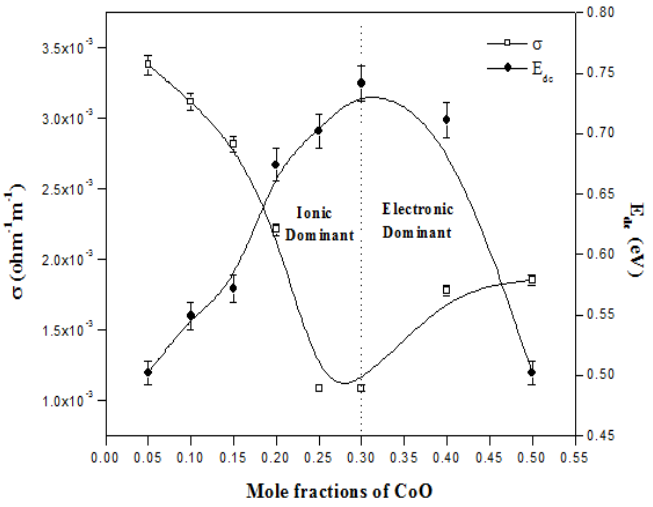

Figure-4
Variation Conductivity, σ, at 573K and high temperature activation energy, E_a, with mole fractions of CoO for all glasses. Solid lines are guides to the eye.

The data below T_D has been analyzed using variable range hopping models due to Mott and Greaves. Conductivity expression as per Mott's VRH model is given as[13],

$$\sigma = B \exp\left(-\frac{A}{T^{\frac{1}{4}}}\right) \quad (4)$$

Where, $A = 4\left[\frac{2\alpha^3}{9\pi k_B N(E_F)}\right]^{\frac{1}{4}}$ and $B = \left[\frac{e^2}{2(8\pi)^{\frac{1}{2}}}\right] v_0 \left[\frac{N(E_F)}{\alpha k_B T}\right]^{\frac{1}{2}}$

and $N(E_F)$ is the density of states at the Fermi level. Greaves VRH model gives conductivity as[17],

$$\sigma T^{\frac{1}{2}} = A \exp\left(-\frac{B}{T^{\frac{1}{4}}}\right) \quad (5)$$

Where, A and B are constants and $B = 2.1\left[\frac{a^3}{k_B N(E_F)}\right]^{\frac{1}{4}}$.

Plots of ln(σ) vs $T^{-1/4}$ as per Mott's VRH expression given in equation-4 were made. A typical plot for BPCL4 is shown in figure-5. A line was fit in the temperature region where appeared linear and the slope and intercepts were extracted. Using the slope and intercept, $N(E_F)$ value due to Mott's VRH has been determined. Similar analysis was performed on the data of the remaining glasses and $N(E_F)$ values were determined and are tabulated in table-3.

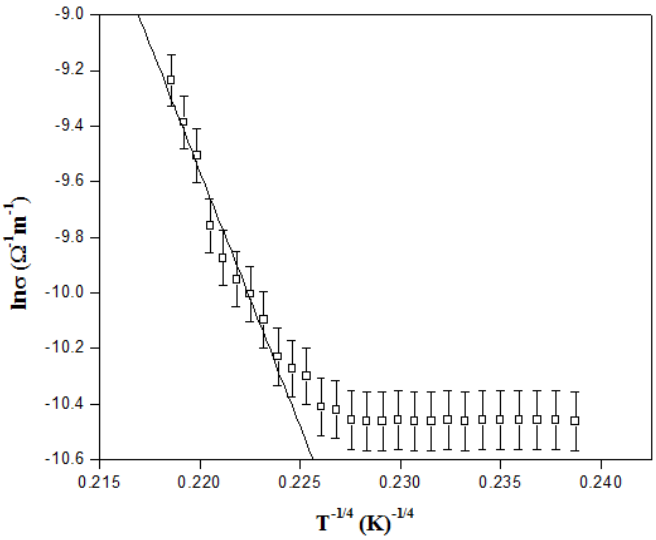

Figure-5
A plot of ln (σ) vs (T)$^{-1/4}$ for BPCL4 glass as per Mott's (VRH) model for T below T_D. Solid line is a linear fit.

According to Greave's VRH[4] expression, $\ln(\sigma T^{1/2})$ vs $T^{-1/}$were plotted for all the glasses. A plot made for BPCL4 glass is shown in figure-6. In this plot, it can be seen that data is linear down to only certain temperature. Therefore, a linear line was fit to the data in the region where it appeared linear and, slope and intercepts were extracted. From intercept, B, the $N(E_F)$ value was determined. $N(E_F)$ values obtained for all the present glasses due to Greaves VRH model fit are recorded in Table.3. From $N(E_F)$ values it can be seen that results of neither of the two VRH models are nearer to the reported values for other similar oxide glasses[10,16]. Further, none of the two models covered entire data below T_D. Therefore, these two VRH models

cannot be considered to be adequate to explain conductivity behavior below T_D.

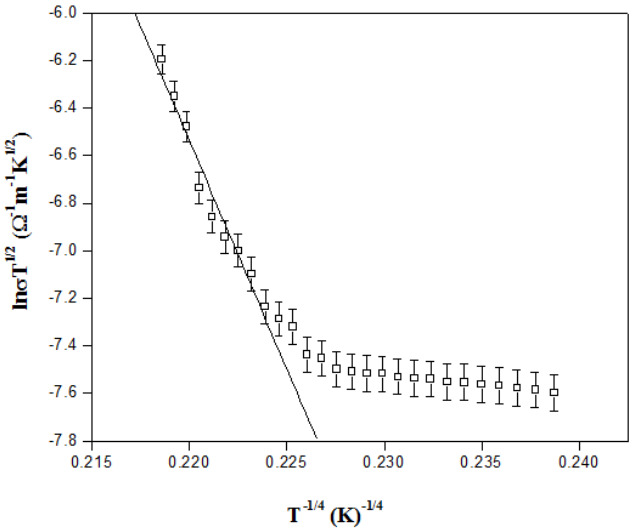

Figure-6
A plot of ln ($\sigma T^{1/2}$) vs $(T)^{-1/4}$ for BPCL4 glass as per Greaves (VRH) model for T below T_D. Solid line is a linear fit

Table-3
Density of states at Fermi level, $N(E_F)$ due to Mott's (VRH) and Greaves (VRH) model fits

Mol. Fractions of CoO	$N(E_F)$ (eV^{-1} m^{-3}) MVRH	$N(E_F)$ (eV^{-1} m^{-3}) GVRH
0.05	1.243×10^{31}	5.311×10^{27}
0.10	5.914×10^{31}	1.044×10^{28}
0.15	6.412×10^{31}	7.059×10^{27}
0.20	7.457×10^{31}	2.691×10^{27}
0.25	3.392×10^{31}	2.363×10^{29}
0.30	0.625×10^{31}	1.791×10^{28}
0.40	-	3.704×10^{28}
0.50	-	1.964×10^{28}

Conclusion

i. CoO and Li_2O doped borophosphate glasses were synthesized and their non-crystallinity was confirmed through x-ray diffraction analysis. ii. The measured variation of room temperature density with CoO concentration indicates that structure and topology of the present glasses is sensitive to CoO content. However, no orderly change in the structure or topology with CoO is evident in the present glasses. iii. Variation of conductivity and activation energy with increasing CoO content reveals a switchover of conduction mechanism from the ionic predominance regime to the electronic regime at about 0.30 mole fraction of CoO. This may be considered as chief result of this article. iv. Density of states at Fermi level obtained from the analysis of the data using Mott and Greaves VRH model gave abnormally higher values. This made to conclude that data below T_D cannot be satisfactorily explained using these two VRH models.

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