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Electrical Conduction in V_2O_5 Doped Borophosphate Glasses

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ABSTRACT

Borophosphate glasses of composition, $(B_2O_3)_{0.2}$ $(P_2O_5)_{0.8-x}$ $(V_2O_5)_x$ with x = 0.35, 0.40, 0.45, 0.50, 0.55 and 0.60 were synthesized. Room temperature density and the conductivity for the temperature range from 300 K to 650 K were measured. Density decreased up to 0.45 mole fractions of V_2O_5, increased for 0.5 mole fractions and decreased thereafter. By employing Mott's SPH (Small Polaron Hopping) model, activation energy for conduction has been determined. Activation energy decreased with increasing V_2O_5 content up to 0.55 mole fractions and increased for further amounts of V_2O_5. Conductivity behaved in the opposite fashion to that of activation energy with V_2O_5 concentration. Increase in conductivity for V_2O_5 up to 0.55 mole fractions and decrease for higher concentrations may be attributed to mixed glass former (MGFE) effect occurring around 0.55 mole fractions of V_2O_5. Conductivity data that was not in agreement with Mott's SPH model has been considered in the light of variable range hopping models of Mott and Greaves. Density of states at Fermi level from both the model fits have been determined and compared. Various polaron hopping related parameters were estimated. For the first time MGFE has been observed in V_2O_5 doped borophosphate glasses of present compositions.

1. Introduction

The semiconducting properties of Transition Metal Ions (TMI) doped oxide glasses were known for long period [1]. Transition metal ions possess different valence states and the electrons transfer from their low valance state to high valance state [2]. For example, vanadium exists in V^{4+} and V^{5+} states and in the vanadium oxide doped glasses, the conduction is due to hopping of electron from V^{4+} to V^{5+} sites. TMI doped borate glasses measured interesting physical properties [3, 4]. There are many articles reporting electrical studies in TMI doped borate, phosphate etc., and glasses. For instance, ionic conductivity was found to be dominant over the electronic conductivity up to certain range of composition in [5]. The ionic conductivity was found to be influenced by the compositional variation of BO_4 and BO_3 units in the 0.2 CdI_2 – 0.8 (0.50Ag_2O – 0.50 (xB_2O_3 – (1-x) P_2O_5)) system [6]. Ionic conductivity of 42.5Li_2O – (57.5-x)B_2O_3 – xP_2O_5 glasses was studied and it was found to be in the range from 9 x 10^{-4} to 3.02 x 10^{-5} $(\Omega m)^{-1}$ [7]. Ionic conductivity has been studied for the glasses, 0.45 Li_2O–0.55 (1-y) P_2O_5–yB_2O_3] and maximum conductivity has been reported for molar ratio of Li to the total glass former to be 0.5 [8]. This was attributed to the structural evolution going on in the glasses with increasing B_2O_3 content. In 0.35 Na_2O–0.65 [xB_2O_3–(1-x) P_2O_5] glasses, ionic conductivity was found to be maximum and activation energy minimum for x = 0.4 and this was recognized to be the mixed glass former effect (MGFE) [9]. Conductivity was found to increase with increasing CuO content in 20Na_2O – 20ZnO –25B_2O_3 – (35-x) P_2O_5 – xCuO glasses [10]. To our knowledge, conductivity studies in V_2O_5 doped borophosphate glasses have not been reported so for by others.

In view of the fact that borophosphate glasses are known to be chemically more durable than pure phosphate and borate glasses and have got attractive applications, it was proposed to study density and conductivity as a function of temperature in borophosphate glasses doped with V_2O_5 of compositions, $(B_2O_3)_{0.2}$ $(P_2O_5)_{0.8-x}$ $(V_2O_5)_x$ with x = 0.35, 0.40, 0.45, 0.50, 0.55 and 0.60 labeled as BPV1, BPV2, BPV3, BPV4, BPV5 and BPV6 respectively. These glasses have not been explored previously for the properties mentioned in this communication.

2. Experimental Methods

Glasses, $(B_2O_3)_{0.2}$ $(P_2O_5)_{0.8-x}$ $(V_2O_5)_x$, (x = 0.35, 0.40, 0.45, 0.50, and 0.60) were prepared by melt quenching technique using analytical grade H_3BO_3, $NH_4H_2PO_4$ and V_2O_5. The chemicals were mixed up in the desired quantities and thoroughly ground in pestle and mortar and mixtures. They were taken in silica crucibles and melted in a molybdenum make electrical furnace at 1400 K. Melt was maintained at this temperature for an hour and obtain transparent liquid. The melt was then quenched to room temperature by pouring onto stainless steel plate and covering it with another such plate. The glass pieces so formed were annealed at 400 K for 12 hours to remove thermal strains. Non-crystalline nature of the glasses was established by XRD studies. It may be noted that glasses containing V_2O_5 in mole fractions less than 0.35 got degraded within couple of weeks and therefore, were not considered for studies reported here.

Room temperature density, D, of the glasses was measured by following Archimedes principle using a Citizen make single pan balance having precession of 0.0001 mg. The toluene (density = 0.8966 g/cc) was used as an immersion liquid. The uncertainty on the measured density was estimated to be ±0.002 g/cc.

Samples of thickness 2 to 3 mm and cross sectional areas ranging from 30 to 80 mm^2 were chosen for measurement of dc conductivity. The silver paint was applied on two major surfaces of samples. Resistivity, ρ, in the temperature 300 to 650 K was measured using two probe method in a Danbridge make high resistance bridge (DB502). Wayne Kerr make electrical furnace fitted with chromel-alumel thermocouple has been used for heating and temperature sensing respectively. Conductivity, σ, was determined as σ = (1/ρ), where resistivity, ρ (=RA/l) with R being resistance, A cross sectional area and l thickness of the glass. Uncertainty in temperature measurement was about ±1K and that of conductivity was estimated to be within 2%.

3. Results and Discussion

3.1 Density

The room temperature density, D, of the present glasses was found to be in the range from 0.222 gcm^{-3} to 1.776 gcm^{-3} (Table 1). Density decreased with increase in V_2O_5 up to 0.45 mole fractions and, increased for 0.5 mole fractions and decreased for higher amounts of V_2O_5 (Fig. 1). No monotonous increase or decrease in D with V_2O_5 is observed. The molar volume, V_m, has been determined using density with the help of the

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relation, V_m = M/D, where M is the molecular weight, MW of the glasses which is given as M = (0.2) MW (B_2O_3) + (0.8-x) MW (P_2O_5) + x MW (V_2O_5) [11]. The V_m values obtained were found to be in the range from 104.043 cm^3/mol to 843.263 cm^3/mol. The variations of D and V_m with V_2O_5 are shown in Fig. 1. It can be noted that as expected, D and V_m behave in the opposite fashion to one another.

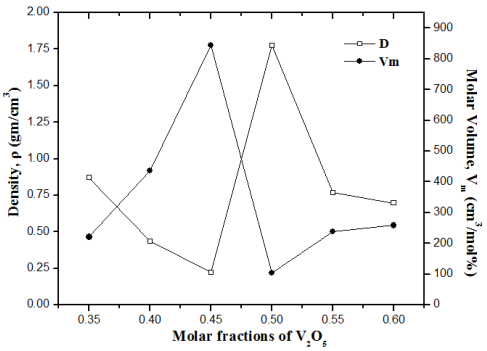


Fig. 1 The plots of density, D, and molar volume, V_m, as a function of mole fractions of V_2O_5 for BPV glasses (Solid lines drawn are the guides to the eye)

The transition metal ion density, N, polaron hopping distance, R were estimated using the relations given in [11, 12] and mentioned in Table 1. The N and R values obtained are in the same order of magnitude reported for other series of borophosphate glasses [12].

Table 1 Physical properties of the glasses

Glass	Mole fractions of V_2O_5	N ±0.01 (x$10^{21}$$cm^3$)	R ±0.01 (nm)
BPV1	0.35	2.016	0.792
BPV2	0.40	1.152	0.954
BPV3	0.45	0.662	0.115
BPV4	0.50	5.880	0.554
BPV5	0.55	2.794	0.710
BPV6	0.60	2.765	0.712

3.2 DC Conductivity

In the studied temperature range, measured σ for the present glasses is found to lie in the range from 10^{-3} $\Omega^{-1}m^{-1}$ to 10^{-5} $\Omega^{-1}m^{-1}$. The temperature response of conductivity (Fig. 2) revealed semiconducting nature of the glasses (Fig. 2). As per the conductivity equation given by Mott's small polaron hopping theory [13], ln(σT) versus (1/T) plots were made and shown in Fig. 2. The curves appeared linear for temperatures above Debye's temperature, T_D. The nature of curves is similar to that reported for Mo and Cu ions doped borophosphate glasses [12, 14], molybdenum [15, 16], cobalt [17] and vanadium [18] doped phosphate and vanadium-borate glasses [19]. The least square lines were fit to the data for temperature above T_D. Here, T_D is the temperature at which conductivity data deviates from the Mott's (SPH) model fit line. The best fits gave the correlation coefficients values near unity and the slopes were used to calculate the activation energy, E_{dc} (Table 2). The E_D values so determined were in the range from 0.521 eV to 0.719 eV and they agree with literature values reported for borophosphate, phosphate and borate glasses doped with different TMIs [17-20].

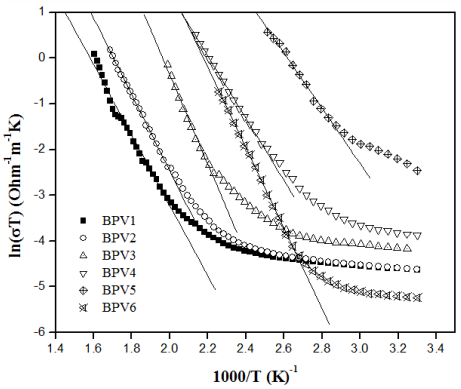


Fig. 2 Plots of ln(σT) versus (1/T) for BPV glasses as per Mott's (SPH) model (Solid lines are the least square linear fits in the high temperature region).

The variation of E_D and σ (at 473 K) with molar concentration of V_2O_5 is depicted in Fig. 3. Conductivity increased with increase of V_2O_5 up to 0.55 mole fractions and decreased thereafter. Activation energy behaved opposite to that of conductivity with increase of V_2O_5. These variations in σ and E_{dc} with increase in V_2O_5 may be due to mixed glass former effect (MGFE) occurring in these glasses at around 0.55 mole fractions of V_2O_5. Similar observation was made in Na_2O doped borophosphate glasses [9].

Austin and Mott considered strong electron- polaron interaction and derived an expression for activation energy for conduction to be [14],

$$W = W_H + W_D/2 \quad T > \theta_D/2 \qquad (1)$$
$$\cong W_D \quad T < \theta_D/4$$

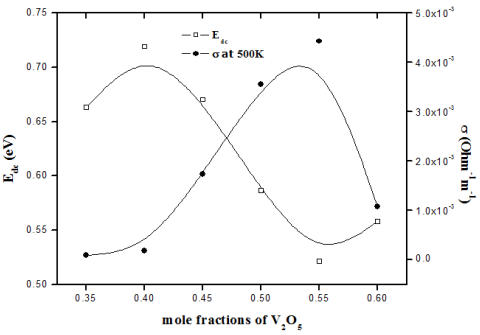


Fig. 3 Variation of conductivity, σ, at 473 K and activation energy, E_{dc}, with mole fractions of V_2O_5 (Solid lines are the guides to the eye).

Where, W_H and W_D are polaron hopping energy and disorder energy arising from the energy of the neighbors between two hopping sites respectively.

The value of W_H is calculated using an equation [21],

$$W_H = \frac{W_P}{2} = \left(\frac{e^2}{4\varepsilon_p}\right)\left(r_p^{-1} - R^{-1}\right) \qquad (2)$$

Where, W_P is the polaron binding energy and ε_p the effective dielectric constant which is determined using the relation, $\varepsilon_p = e^2/4Wr_p$ [22] and the small polaron radius, $r_p = (1/2)(\pi/6N)^{1/3}$ [11]. The estimated values of ε_p and r_p, are listed in Table 2 and they are comparable with the literature values for similar kind of glasses [17, 18].

In SPH model, the polaron bandwidth, J, that contains information about the overlap of wave functions of adjacent sites given for adiabatic and non-adiabatic cases as [21],

$$J > \left(\frac{2KTW_H}{\pi}\right)^{1/4} \times \left(\frac{h\upsilon_0}{\pi}\right)^{1/2} \quad \text{for adiabatic SPH}$$
$$J < \left(\frac{2KTW_H}{\pi}\right)^{1/4} \times \left(\frac{h\upsilon_0}{\pi}\right)^{1/2} \quad \text{for non-adiabatic SPH} \qquad (3)$$

The polaron band width has been calculated with the help of a relation, $J = J_0 \exp(-\alpha R)$, with $J_0 = W_{H\min}/4$ [23] and are listed in Table 2. The value of α was taken from the literature quoted for TMI doped glasses to be 20 nm^{-1} [21]. From Table 2, it is clear that the Polaron bandwidth, *J* for the present glasses satisfy the condition for non-adiabatic conduction given in Eqn. (3) and Holstein's condition i.e., $J < W_H/4$ [12].

Table 2 Polaron hopping parameters for BPV series.

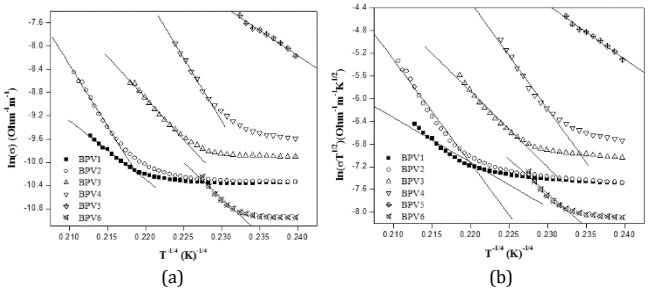
Glass	Mole Fraction	W ±0.002 (eV)	W_H ±0.001 (eV)	ε_p ±0.02	r_p ±0.04 (nm)	J x10^{-5} ±0.001 (eV)
BPV1	0.35	0.663	0.396	1.18	31.9	0.0523
BPV2	0.40	0.719	0.429	0.91	38.4	0.0483
BPV3	0.45	0.670	0.400	0.81	46.3	0.0438
BPV4	0.50	0.586	0.350	1.91	22.3	0.0589
BPV5	0.55	0.521	0.311	1.68	28.6	0.0545
BPV6	0.60	0.558	0.333	1.56	28.7	0.0544

For temperatures below T_D, ln(σT) versus (1/T) plots show nonlinearity which indicates the temperature-dependent activation energy. For this, Mott proposed variable range VRH) hopping of polarons to be the

conduction mechanism [19]. An expression for conductivity due to Mott's VRH model has been derived to be,

$$\sigma = A\exp(B/T^{-1/4})$$

where, $A = 4\left[2\alpha^3/9\pi kN(E_F)\right]^{1/4}$ and $B = \left[e^2/2(8\pi)^{1/2}\right]\rho_0\left[N(E_F)/\alpha kT\right]^{1/2}$



(a) (b)

Fig. 4 Plots of (a) ln(σ) versus ($T^{-1/4}$) as per Mott's VRH model and (b) ln($\sigma T^{1/2}$) versus ($T^{-1/4}$) as per Greaves's VRH model (Solid lines are the linear fits to the data).

Using the data pertaining to temperature below T_D, the graphs of ln(σ) versus ($T^{-1/4}$) were plotted as shown in Fig. 4. The data appeared linear down to certain temperature and hence linear lines were fit and constants A and B were extracted. From constant B, $N(E_F)$ values were estimated [19]. The $N(E_F)$ values thus obtained were in the range from 10^{25} to 10^{28} $eV^{-1}m^{-1}$ (Table 3). These are comparable with TMO doped glasses [24, 25]. The data below T_D has also been viewed in terms of Greaves VRH model [25]. According to this model, conductivity has to vary with temperature as [22], $\sigma T^{1/2} = A\exp(-B/T^{1/4})$, Where A and B are constants. The plots of ln($\sigma T^{1/2}$) versus ($T^{-1/4}$) were sketched and shown in Fig. 5. Again, data appeared linear down to certain temperature. So, linear lines were fit and coefficients A and B were extracted. The constant B and $N(E_F)$ were connected as per, $B = 2.1\left[\alpha^3/k_B N(E_F)\right]^{1/4}$.

Using B in this relation, $N(E_F)$ values were determined and tabulated in Table 3. These $N(E_F)$ values are greater than that obtained Mott's VRH model fit.

Table 3 Density of states, $N(E_F)$, due to Mott's and Greave's VRH models for BPV Glasses.

Mole fractions of V_2O_5	[a]$N(E_F)^*$ ($eV^{-1}m^{-3}$)	[b]$N(E_F)^{**}$ ($eV^{-1}m^{-3}$)
0.35	$1.81x10^{25}$	$1.19x10^{28}$
0.40	$1.54x10^{25}$	$5.08x10^{28}$
0.45	$4.15x10^{28}$	$2.73x10^{27}$
0.50	$1.68x10^{26}$	$7.12x10^{26}$
0.55	$1.76x10^{25}$	$5.68x10^{25}$
0.60	$1.53x10^{28}$	$1.10x10^{28}$

[a]$N(E_F)$ due to Mott's VRH model, [b]$N(E_F)$ due to Greave's VRH model

For inspection, both Mott's and Greaves VRH model fits appear good. However, $N(E_F)$ values from Mott's VRH fit are closer to the literature values than Greaves. That is why. Mott's VRH model may be considered to be suitable to understand conductivity data below T_D for the present glasses.

4. Conclusion

V_2O_5 doped borophosphate glasses have been prepared and studied for room temperature density and, dc conductivity in the temperature range from 300 K to 650 K. The density decreased with increasing mole fractions of V_2O_5 up to 0.45, increased for 0.5 and decreased for further concentrations of V_2O_5. Conductivity increased up to 0.55 mole fractions of V_2O_5 and decreased thereafter. Activation energy derived from the Mott's (SPH) model fits to the data behaved in the opposite fashion to that of conductivity. This particular way of variation of conductivity and activation energy with V_2O_5 content revealed mixed glass former effect occurring in the present glasses around 0.55 mole fractions of V_2O_5. VRH models have been applied to analyze the data deviated from the Mott's (SPH) model and the density of states Fermi level were determined. The density of states obtained from Mott's VRH model are nearer to the reported values for other semiconducting glasses Therefore, Mott's VRH model may be considered to be suitable for describing low temperature conductivity of the present glasses.

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