Electrical Conduction in V_{2}O_{5} Doped Borophosphate Glasses


Department of Physics, Gulbarga University, Gulbarga – 585 106, Karnataka, India.

**ABSTRACT**

Borophosphate glasses of composition, \((\text{Bi}_{2} \text{O}_{3})_{0.42} (\text{P}_{2} \text{O}_{5})_{0.58}(\text{V}_{2} \text{O}_{5}), x = 0.35, 0.40, 0.45, 0.50, 0.55\) 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 \(\text{V}_{2} \text{O}_{5}\) increased for 0.5 mole fractions and decreased thereafter. By employing Mott’s SPH model, activation energy for conduction has been determined. Activation energy decreased with increasing \(\text{V}_{2} \text{O}_{5}\) content up to 0.55 mole fractions and increased for further amounts of \(\text{V}_{2} \text{O}_{5}\). Conductivity behaved in the opposite fashion to that of activation energy with \(\text{V}_{2} \text{O}_{5}\) concentration. Increase in conductivity for \(\text{V}_{2} \text{O}_{5}\) 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 \(\text{V}_{2} \text{O}_{5}\). 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 Gravaees. 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 \(\text{V}_{2} \text{O}_{5}\) doped borophosphate glasses of present compositions.

1. Introduction

The semiconducting properties of \(\text{Transition Metal Ions (TMI)} \) 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 \(\text{V}^{4+}\) and \(\text{V}^{5+}\) states and in the vanadium oxide doped glasses, the conduction is due to hopping of electron from \(\text{V}^{4+}\) to \(\text{V}^{5+}\) 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 \(\text{BO}_{3}\) and \(\text{BO}_{4}\) units in the \(\text{CdI}_{2} - 0.8 (0.5 \text{Kg} \text{d}_{2} - 0.50 \text{ (x} \text{BO}_{3} - (1-x) \text{Bo}_{4}) \text{P}_{2} \text{O}_{5}) \text{system} [6]\). Ionic conductivity of \(42.5 \text{Li}_{2} \text{O} - (85.75-\text{xBi}_{2} \text{O}_{3} - x \text{P}_{2} \text{O}_{5}) \text{glasses was studied and it was found to be in the range from 9 x 10^{–4} to 3.02 x 10^{–4} (\text{hm})^{–1} [7]. Ionic conductivity has been studied for the glasses,} 0.45 \text{Li}_{2} \text{O} - 0.55 (1-x) \text{P}_{2} \text{O}_{5} - \text{y} \text{BO}_{3} \text{J 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 \(\text{BO}_{3}\) content. In 0.35 \text{Na}_{2} \text{O} - 0.65 [x(\text{BO}_{3} -(1-x) - \text{P}_{2} \text{O}_{5}) \text{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 20\text{Na}_{2} \text{O} - 40\text{ZnO} - 25\text{BO}_{3} - (35-x) \text{P}_{2} \text{O}_{5} - x \text{CuO} \text{glasses [10]. To our knowledge, conductivity studies in \(\text{V}_{2} \text{O}_{5}\) doped borophosphate glasses have not been reported so far 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 \(\text{V}_{2} \text{O}_{5}\) of compositions, \((\text{Bi}_{2} \text{O}_{3})_{x} (\text{P}_{2} \text{O}_{5})_{y} (\text{V}_{2} \text{O}_{5}), \text{with} \ x = 0.35, 0.40, 0.45, 0.50, 0.55 \text{ and 0.60} \text{ labeled as BPV1, BPV2, BPV3, BPV4, BPV5 and BPV6 respectively. These glasses have not been explored for the properties mentioned in this communication.} \)

2. Experimental Methods

Glasses, \((\text{Bi}_{2} \text{O}_{3})_{x} (\text{P}_{2} \text{O}_{5})_{y} (\text{V}_{2} \text{O}_{5}), \ (x = 0.35, 0.40, 0.45, 0.50, \text{ and 0.60}) \) were prepared by melt quenching technique using analytical grade \(\text{H}_{2} \text{BO}_{3}, \text{ NH}_{4} \text{H}_{2} \text{PO}_{4}, \text{and} \text{V}_{2} \text{O}_{5}\). The chemicals were mixed up in the desired quantities and thoroughly ground in pestle and mortar and mixtures. They were taken in silica crucible 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 \(\text{V}_{2} \text{O}_{5}\) in mole fractions less than 0.35 got degraged within couple of weeks and therefore, were not considered for studies reported here.

Room temperature density, \(\text{D}, \) of the glasses was measured by following Archimedes principle using a Citizen make single pan balance having precession of 0.0001 g. The tolue (density = 0.8966 g/cc) was used as an immersion liquid. The uncertainty on the measured density was estimated to be 0.0002 g/cc.

Samples of thickness 2 to 3 mm and cross sectional areas ranging from 30 to 80 mm² were chosen for measurement of dc conductivity. The silver paint was applied on two major surfaces of samples. Resistivity, \(\rho, \) 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, \(\sigma, \) was determined as \(\sigma = 1/\rho\) where resistivity, \(\rho = (R/\Delta t) \) with \(R \) being resistance, \(\Delta t \) thickness of the glass. Uncertainty in temperature measurement was about ±1 K and that of conductivity was estimated to be within 2%.

3. Results and Discussion

3.1 Density

The room temperature density, \(\text{D}, \) of the present glasses was found to be in the range from 0.222 g/cm³ to 1.776 g/cm³ (Table 1). Density decreased with increase in \(\text{V}_{2} \text{O}_{5}\) up to 0.45 mole fractions and, increased for 0.5 mole fractions and decreased for higher amounts of \(\text{V}_{2} \text{O}_{5}\) (Fig. 1). No monotonous increase or decrease in \(\text{D}\) with \(\text{V}_{2} \text{O}_{5}\) is observed. The molar volume, \(v_{m}\) has been determined using density with the help of the...
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>
<thead>
<tr>
<th>Glass</th>
<th>Mole fractions of V2O5</th>
<th>N (cm⁻²)</th>
<th>R (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPV1</td>
<td>0.35</td>
<td>2.016</td>
<td>0.792</td>
</tr>
<tr>
<td>BPV2</td>
<td>0.40</td>
<td>1.152</td>
<td>0.954</td>
</tr>
<tr>
<td>BPV3</td>
<td>0.45</td>
<td>0.662</td>
<td>0.115</td>
</tr>
<tr>
<td>BPV4</td>
<td>0.50</td>
<td>5.880</td>
<td>0.554</td>
</tr>
<tr>
<td>BPV5</td>
<td>0.55</td>
<td>2.794</td>
<td>0.710</td>
</tr>
<tr>
<td>BPV6</td>
<td>0.60</td>
<td>2.765</td>
<td>0.712</td>
</tr>
</tbody>
</table>

3.2 DC Conductivity

In the studied temperature range, measured α for the present glasses is found to lie in the range from 10⁻¹Ω m⁻¹ to 10⁻²Ω m⁻¹. The temperature response of conductivity [Fig. 2] revealed semiconducting nature of the glasses. 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, T0. 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 T0. Here, T0 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, ε0 (Table 2). The ε0 values so determined were in the range from 0.52 to 0.719 eV and they agree with literature values reported for borophosphate, phosphate and borate glasses doped with different TMIs [17-20].

For temperatures below T0, 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

$$ W = W_0 + W_D/2 $$

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$$ T > \theta_0/2 $$

$$ T < \theta_0/4 $$

$$ W = W_0 $$

$$ T > \theta_0/2 $$

$$ T < \theta_0/4 $$

$$ W = W_0 $$
conduction mechanism [19]. An expression for conductivity due to Mott's VRH model has been derived to be,

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

where, $A = \frac{2e^5}{9\hbar^5 N(E_F)}$ and $B = \left[28\alpha^4 \frac{\pi}{\hbar^2 k_B T}\right]^{1/2}$

Fig. 4 Plots of (a) ln(σ) versus (T^1/4) as per Mott’s VRH model and (b) ln(Tσ) 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^(-3) (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 $[22] \sigma^{-1/4} = A \exp\left(-B/T^{1/4}\right)$, Where A and B are constants. The plots of ln(σT) 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 $B = 2.10^4 / k_B N(E_F)$.

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 Greaves’s VRH models for BPV Glasses

<table>
<thead>
<tr>
<th>Mole fractions of V_2O_5</th>
<th>N(E_F) (eV^-1m^3)</th>
<th>N(E_F)^* (eV^-1m^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>1.81x10^10</td>
<td>3.19x10^10</td>
</tr>
<tr>
<td>0.40</td>
<td>1.54x10^11</td>
<td>5.08x10^10</td>
</tr>
<tr>
<td>0.45</td>
<td>4.15x10^24</td>
<td>2.73x10^27</td>
</tr>
<tr>
<td>0.50</td>
<td>1.60x10^24</td>
<td>7.12x10^26</td>
</tr>
<tr>
<td>0.55</td>
<td>1.76x10^24</td>
<td>5.60x10^25</td>
</tr>
<tr>
<td>0.65</td>
<td>1.52x10^25</td>
<td>1.10x10^28</td>
</tr>
</tbody>
</table>

N(E_F) due to Mott’s VRH model, N(E_F)* due to Greaves’s VRH model

For inspection, both Mott’s and Greaves VRH model fit appears 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 fitted 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 semiconductor glasses Therefore, Mott’s VRH model may be considered to be suitable for describing low temperature conductivity of the present glasses.

References

[9] R. Christensen, G. Olsen, S.W. Martin, Ionic conductivity of mixed glass formed 0.35Na$_2$O + 0.65B$_2$O$_3$ + (1-x)P$_2$O$_5$, J. Glasses, Phys. Chem. B. 117 (2013) 16577–16586.