Electrical conduction in potassium boro-vanadate iron glass

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The conduction mechanism of $xK_2O:(100-x-y)(1+n)V_2O_5:B_2O_3:yFe_2O_3$ where $x = 0.5, 10, 15, 20$, $y = 5, 7.5, 10, 12.5$ and $15$ and $n = 0.2$ to 1 in step of 0.2 had been explained on the basis of Mott's theory. The dc conductivity of the present glass system was measured in the temperature range 315-435 K for all the different glass compositions. The decrease of conductivity and increase in activation energy had been observed with the increase of Fe$_2$O$_3$ concentration. Estimated small polaron radius is found to be smaller than the atomic site spacing (V-V spacing) and greater than the radius of iron on which the electron is localized. The present glass system shows a semiconducting adiabatic hopping due to a small polaron.

Keywords: Electrical conductivity, Polaron, Activation energy

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1 Introduction

While small polaron hopping theory has been extensively applied to account for the electrical properties of a wide range of transition metal oxide glasses', the best agreement between experimental work and theory has been found for vanadate glasses such as $K_2O:V_2O_5:B_2O_3:Fe_2O_3$. Semiconducting oxide glasses based on $V_2O_5$ were first reported by Denton et al. in 1954.

The electrical properties of semiconducting oxide glasses containing transition metal oxide such as $V_2O_5$-$P_2O_5$, $V_2O_5$-$TeO_3$, $V_2O_5$-$PbO$-$GeO_2$, $TiO_2$-$V_2O_5$-$P_2O_5$, $V_2O_5$-$B_2O_3$, have been reported by several researchers. The electrical conduction in these glasses occurs by electron hopping from an ion of the low valence state ($V^{4+}$) transition metal to an ion of the high valence state ($V^{5+}$). The thermal activation energy for conduction appears to be the dominating factor, which controls the conductivity. In many cases, the pre-exponential factor also has a great influence on the conductivity. Some of the glass systems $V_2O_5$-$P_2O_5$, $Fe_2O_3$-$P_2O_5$, MoO$_3$-$P_2O_5$, TiO$_2$- $P_2O_5$, and $V_2O_5$-$B_2O_3$-$BaO$, in which electron overlap integral between the sites is of significance and the hopping of a small polaron exhibits a non-adiabatic character, while $V_2O_5$-$P_2O_5$ and $WO_3$-$P_2O_5$ glasses follow the adiabatic approximations.

The present study of conduction mechanism has been made on $K_2O$-$V_2O_5$-$B_2O_3$-$Fe_2O_3$ glass system. Fe$_2$O$_3$ has been added as Mössbauer probes. In the present paper, the electrical properties of $xK_2O:(100-x-y)(1+n)V_2O_5:B_2O_3:yFe_2O_3$ glass system have been undertaken in the temperature range 315-435 K and attempt has been made to elucidate the contribution of $V_2O_5$ and Fe$_2$O$_3$ to the conduction process in the glasses.

The dc conductivity of transition metal oxide glass has been expressed by Austin and Mott using the relation

$$\sigma = [v_o e^2c(1-c)/kTR]\exp(-2\alpha R)\exp(-W/kT) \quad (1)$$

where $v_o$ is the optical phonon frequency ($\approx 10^{13}$ Hz), $e$ the electronic charge, $c$ the mole fraction of the site occupied by electron, $R$ the average hopping distance, $\alpha$ is the electron wave function decay constant such that $\exp(-2\alpha R)$ represents electron overlap integral and hence probability of tunneling, $W$ is the activation energy and $T$ is the temperature, where

$$W=W_D + (1/2) W_D \text{ for } T > \theta_D/2$$

$$W_D \quad T < \theta_D/4 \quad (2)$$

where $W_D$ is the polaron hopping energy and $W_D$ is the disordered energy.
The polaron hopping energy $W_H$ is given by

$$W_H = \left( \frac{e^2}{4\epsilon_0} \right) \left[ \frac{1}{\nu_p} - \frac{1}{R} \right] \text{ ... (3)}$$

where $\epsilon_p = (1/\epsilon_a - 1/\epsilon_0)^{-1}$ and $\epsilon_a$ and $\epsilon_0$ are static and high frequency dielectric constants for the glass respectively. $\nu_p$ is the polaron radius\(^1\) which is given by

$$\nu_p = (1/2)(\pi/6N)^{1/3} \text{ ... (4)}$$

where $N$ is the number of sites per unit volume.

For polaron to be small, the polaron radius $\nu_p$ should be smaller than the atomic site\(^1\) spacing $R$. For a non-adiabatic hopping process, $J<\hbar\omega_0$, where $J$ is the electron transfer integral and for adiabatic hopping, $J>\hbar\omega_0$. This approximation\(^12\) is given by:

$$J > \left[ 2kTW_H / \pi \right]^{1/2} \left[ h\nu_\pi / \pi \right]^{1/2} \text{ adiabatic} \text{ ... (5)}$$

$$J < \left[ 2kTW_H / \pi \right]^{1/2} \left[ h\nu_\pi / \pi \right]^{1/2} \text{ Non-adiabatic} \text{ ... (5)}$$

$J$ can be estimated from the difference of mean value of hopping energy and experimental activation energy $W$.

2 Experimental Details

Weighed amounts of analytical grade chemicals $\text{V}_2\text{O}_5$, $\text{H}_3\text{BO}_3$, $\text{K}_2\text{CO}_3$ and $\text{Fe}_2\text{O}_3$ were well mixed and melted in porcelain crucible at temperature of 1000°C and maintained at this temperature for 4 hr. These melts were then quenched onto a clean copper plate at room temperature and subsequently pressed by another plate to provide faster quenching rate. The X-ray diffraction analysis showed that quenched samples were amorphous. The electrical measurements were made by usual technique of two-probe method. Silver paste was painted on the polished rectangular surface of the samples. With the painted silver paste, good ohmic contacts were found. The constant voltage source along with pico-ammeter was used to measure the conductivity at different temperatures.

3 Results and Discussion

The results of the conductivity measurements as a function of temperature in the range 315-435 K for all different compositions are shown in Fig. 1. The general behaviour of curves is similar to that reported for $\text{V}_2\text{O}_5$-$\text{P}_2\text{O}_5$ (Ref. 2, 5) glasses, $\text{V}_2\text{O}_5$-$\text{TeO}_2$ (Ref. 13) and $\text{WO}_3$-$\text{P}_2\text{O}_5$ (Ref. 14). The log $\sigma$ at any given composition increases linearly with $10^3/T$ temperature. According to Arrhenius equation\(^8\),

$$\sigma = \sigma_0 \exp(-W/kT) \text{ ... (6)}$$

It has been observed from Fig. 1 that the conductivity decreases linearly at 373 K for $\text{Fe}_2\text{O}_3 = 5$ to 15 mole %. The variation of conductivity is observed in all glasses from $10^{-6}$ to $10^{-8}$ $\Omega^{-1}\text{cm}^{-1}$ and log $\sigma$ versus $10^3/T$ is linear, which shows the semiconducting behaviour of the present glass series. The $n$-type of semiconducting nature of these glasses has been confirmed by Seebeck measurements.\(^13\) Moni and Sakata\(^16\) reported $\text{V}_2\text{O}_5$-$\text{Sb}_2\text{O}_3$-$\text{TeO}_2$ and $\text{V}_2\text{O}_5$-$\text{Bi}_2\text{O}_3$-$\text{TeO}_2$ glasses as $n$-type semiconductors. For polaron to be small, the polaron radius should be greater than the radius of iron on which the electron is localized but less than the distance $R$ separating two sites\(^16\). As it is evident for the present glass system (Table I), the value of polaron radius 1.738 to 1.820 Å which is less than $R$ (4.31-4.52 Å), which satisfies the condition for small polaron hopping. Similar types of results were also reported for
The reported any given of (Ref. 13) that the activity is (a constant of proportionality between heat of transfer and the kinetic energy of electron), is much less than unity i.e. $\alpha'<<1$, which lies in the range 0.0232-0.0695 and supports the conduction for small polaron hopping.

Sayer and Mansingh noted that a plot of log $\sigma$ versus activation energy $W$ at a certain temperature allows one to distinguish between adiabatic and non-adiabatic hopping and judge the relative importance of the two experimental terms. The calculated temperature, $T_c$, estimated from the slope of such a plot will be close to $T$ if $\exp(-2\alpha R)$ term in

$$E(1)$$

does not contribute to the conductivity and will be different from $T$ if $E(1)$ is more appropriate i.e., $\exp(-2\alpha R)$ term contributes to the conductivity. Fig. 2 shows the plot of log $\sigma$ versus $W$ at three different temperatures. The temperature $T_c$ estimated from the slope of each line for all glasses is close to $T$ and $\alpha R$ term remains almost constant irrespective of composition, means hopping can be ascribed as adiabatic and tunneling term $\alpha$ in $E(1)$ does not contribute to the conductivity.

Holstein suggested that the hopping process is controlled by the activation energy and is given by $E(5)$. The values of $W_f$ lie in the range 0.313 - 0.343 eV (Table 1). The values of right hand side of $E(5)$ were calculated for an optical phonon frequency of $\approx 10^{13}$ Hz. These values lie in the range 0.0123-0.0126 eV. These values, which are less than the values of $J$, lie between 0.083-0.179 eV (Table 1) and satisfy the condition for adiabatic hopping. Hirashima et al. also reported adiabatic hopping in PbO-PbO-P$_2$O_5 glasses.

The dependence of conductivity on Fe$_2$O$_3$ amounts was discussed by many researchers. The electrical transport properties on the glass system (Fe$_2$O$_3$)$_x$(V$_2$O$_5$)$_{1-x}$ was investigated where the sample exhibited a thermally activated hopping conduction. The electrical conduction mechanism of the system Fe$_2$O$_3$-V$_2$O$_5$ was reported by Kurina and Ediseova and Burzo. They also showed that the introduction of Fe$_2$O$_3$ causes a decrease in conductivity. In the present glass system, an attempt has been made to study the effect of Fe$_2$O$_3$ on conductivity and activation energy.

### Table 1 — Electrical conductivity data

<table>
<thead>
<tr>
<th>Mole % Fe$_2$O$_3$</th>
<th>$W$ (eV)</th>
<th>$W_f$ (eV)</th>
<th>$\nu$ (Å)</th>
<th>$\alpha'$</th>
<th>V-V spacing ($\frac{R}{\pi}$)</th>
<th>$J$</th>
<th>$\frac{2KW_f}{\pi}$</th>
<th>$\frac{\nu_h}{\nu}$</th>
<th>$\sigma_{100}$</th>
<th>$\Omega^{-1} \text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.410</td>
<td>0.343</td>
<td>1.738</td>
<td>0.0232</td>
<td>4.31</td>
<td>0.083</td>
<td>0.0126</td>
<td>2.40 x 10$^6$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>0.431</td>
<td>0.334</td>
<td>1.746</td>
<td>0.0397</td>
<td>4.33</td>
<td>0.104</td>
<td>0.0125</td>
<td>8.59 x 10$^7$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.455</td>
<td>0.327</td>
<td>1.760</td>
<td>0.0463</td>
<td>4.37</td>
<td>0.128</td>
<td>0.0124</td>
<td>5.13 x 10$^7$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.5</td>
<td>0.496</td>
<td>0.319</td>
<td>1.788</td>
<td>0.0579</td>
<td>4.44</td>
<td>0.169</td>
<td>0.0124</td>
<td>2.00 x 10$^7$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.506</td>
<td>0.313</td>
<td>1.802</td>
<td>0.0695</td>
<td>4.52</td>
<td>0.179</td>
<td>0.0123</td>
<td>7.94 x 10$^8$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\nu_h$ is the highest phonon frequency (1501 cm$^{-1}$) and $\nu_{ps}$ is the optical phonon frequency (1738 cm$^{-1}$).
Table 1 shows the decrease of the conductivity with Fe$_2$O$_3$ amount. The increase of Fe$_2$O$_3$ amount in the glasses leads to the formation of Fe$^{3+}$-Fe$^{3+}$ associates, which coexist, with V$^{4+}$-Fe$^{3+}$ associates. All researchers pointed out the formation of mixed clusters of V$^{4+}$ and Fe$^{3+}$ ions and discussed their effect on the electrical conductivity of glasses.

In the present glass system, it has been observed that an increase of K$_2$O also affects the V-V spacing, which increases from 4.31 to 4.52 Å (Table 1). An increase of Fe$_2$O$_3$ amount leads to decrease the Fe-Fe spacing from 10.997 to 7.523 Å. An incorporation of Fe$^{3+}$ ions into the vanadate skeleton leads to increase of average spacing between vanadium sites with Fe$_2$O$_3$ concentration. The effect of the addition of Fe$_2$O$_3$ in glasses on activation energy and conductivity can also be presumably explained by change in distance between vanadium sites. As average spacing between Fe$^{11+}$ and V$^{4+}$ ions increases, which requires a larger energy for hopping and the mobility of the charge carriers found to decrease from 5.82 x 10$^{-8}$ to 1.96 x 10$^{-9}$ cm$^2$V$^{-1}$S$^{-1}$, which decreases the conductivity of glass system, which lie in the range of 2.40 x 10$^{-6}$ - 7.94 x 10$^{-9}$ Ω$^{-1}$cm$^{-1}$ (Table 1). Fig. 3 shows a plot of log $\sigma$ at 100 °C and activation energy $W$, versus V-V spacing. It is observed that the conductivity at 100 °C decreases and the activation energy increases with V-V spacing. An increase in the activation energy and decrease of conductivity with the decrease of V$_2$O$_5$ amount has been interpreted in terms of increase of the distance $R$, between vanadium sites. To get a clear picture of the effect of Fe$_2$O$_3$ in the glasses, a sample had been prepared with zero amount of Fe$_2$O$_3$ using 5K$_2$O:95[1.2V$_2$O$_5$:B$_2$O$_3$]. The conductivity of glasses without Fe$_2$O$_3$ is 1.89 x 10$^{-7}$ Ω$^{-1}$cm$^{-1}$, which increases by 92%, when 5% of Fe$_2$O$_3$ is added with no amount of K$_2$O in the glass. Thus, incorporation of Fe$_2$O$_3$ in the glass increases the conductivity. The conductivity of the samples containing 5% of K$_2$O, 7.5 moles Fe$_2$O$_3$ and other without Fe$_2$O$_3$ keeping same K$_2$O is compared; it is found that the conductivity is larger for the glass sample with 7.5 mole % of Fe$_2$O$_3$ than that of the sample with zero amount of Fe$_2$O$_3$. It means Fe$^{3+}$ ions participate in conduction process in the present glass system. However, the decrease in Fe-Fe spacing would also be responsible for increasing the conductivity, but at the same time V-V spacing increases in the glass samples which produces the reverse effect. Therefore, the average effect, which has been observed, is the decrease in the conductivity of all the glass samples. This may be due to the fact that (1) an increase between Fe$^{3+}$ and V$^{4+}$ spacing and V$^{4+}$ increases the conductivity; (2) due to the non-existence of Fe$^{2+}$ ions in all glass samples, conduction between Fe$^{2+}$ and Fe$^{3+}$ does not exist; (3) increase in conductivity due to decrease in Fe$^{3+}$-Fe$^{3+}$ spacing is dominated by the effect of decrease in conductivity.

Therefore, it is ascribed that all the glass samples in present glass system show a semiconducting adiabatic hopping due to small polaron. The conductivity of the present glass system is found to decrease with the increase of Fe$_2$O$_3$ concentration.

References

en vanadium of Fe$_2$O$_3$ in with zero Bl03$. The 89x10$^{-7}$Ω$^{-1}$ of Fe$_2$O$_3$ is glass. Thus, 
increases the samples. It is the glass that of the Fe$^{3+}$ ions present glass re spacing by spacing the V spacing induces the effect, which conductivity to the fact spacing and due to the samples, exist; (3) Fe$^{3+}$–Fe$^{3+}$ increase in
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