Transport properties of semiconducting ternary vanadate glasses

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Measurements are reported for the electrical dc conductivity of the semiconducting vanadium tellurite glasses containing P$_2$O$_5$, Sb$_2$O$_3$, or Bi$_2$O$_3$ in the temperature range 80–450 K. The experimental data have been analyzed in the light of existing theoretical models. It has been observed that the general behavior of the electrical conductivity is similar for all glass compositions. The high temperature conductivity data are consistent with Mott’s models of phonon-assisted polaronic hopping in the nonadiabatic regime, while at low temperatures variable range hopping is valid. The small polaron hopping model of Schnakenberg is the best model to interpret the temperature dependence of the activation energy and the conductivity in the entire temperature range. The percolation model applied to the polaron hopping regime is also found to be consistent with the temperature dependence of the conductivity data at high and low temperatures. The various parameters obtained by fitting these models to the experimental data are found to depend on glass forming oxides other than the vanadium oxide.

I. INTRODUCTION

Electrical conduction in transition metal (TM) oxide glasses occurs by the hopping of small polarons between two different valence states of the TM ions. However, there exists controversy over the exact nature of conduction mechanism in different composition and temperature ranges. Binary vanadate glasses with different glass formers like P$_2$O$_5$, TeO$_2$, etc., have been studied extensively. The activation energy for the hopping conduction in these glasses is observed to depend on temperature. The contribution of the glass forming oxides other than the TM oxides in the conduction processes have been also the subject of much controversy. Ioffe et al. have regarded the glass forming oxides as noninteracting solvents in the conduction process which is considered to depend on the TM ions only, while Flynn et al. have pointed out that the glass forming oxides might affect the activation energy for the hopping conduction in the vanadium tellurite glass. The objective of the present work is to study the electrical properties of the tellurium vanadate glasses containing either of P$_2$O$_5$, Sb$_2$O$_3$, and Bi$_2$O$_3$. In order to observe the effect of glass forming oxides, the amount of vanadium oxide is kept fixed in all the glass compositions.

II. THEORETICAL BACKGROUND

Many theories have been proposed in the literature to account for the dc conduction processes in amorphous semiconductors. The predictions of these theories need to be examined briefly to compare them with the experimental data.

Mott has proposed a model for conduction processes in TM oxide glasses. In this model, the conduction process is considered in terms of phonon assisted hopping of small polarons between localized states. The dc conductivity in the Mott model for the nearest neighbor hopping in the nonadiabatic regime at high temperatures ($T>\theta_D/2$) is given by

$$\sigma = \nu_0 \left[ e^2 C (1 - C) / kT \right] \exp (-2 \alpha R) \exp (-W/kT),$$

where $\nu_0$ is the longitudinal optical phonon frequency, $R$ is the average site separation, $\alpha$ is inverse localization length of the $s$-like wave function assumed to describe the localized state at each site, $C$ is the fraction of sites occupied by an electron (or polaron) and therefore is the ratio of the TM ion concentration in the low valence state to the total TM ion concentration, and $W$ is the activation energy for the hopping conduction.

Assuming a strong electron–phonon interaction, Austin and Mott have shown that the activation energy $W$ is the result of polaron formation of binding energy $W_p$ and an energy difference $W_D$ which might exist between the initial and final sites due to variation in the local arrangements of ions

$$W = \begin{cases} W_H + W_D/2 & \text{for } T > \theta_D/2 \\ W_D & \text{for } T < \theta_D/4 \end{cases}$$

where $W_p(=W_p/2)$ is the polaron hopping energy and $\theta_D$, defined by $\hbar \nu_0 = k \theta_D$, is the characteristic Debye temperature. In the adiabatic limit the tunneling term $\exp (-2 \alpha R)$ reduces to unity. An estimate of polaron hopping energy is also given by Austin and Mott

$$W_H = e^2 / 4 \epsilon_p r_p,$$

where $r_p$ is the polaron radius and $\epsilon_p$ is the effective dielectric constant given by

$$\epsilon_p^{-1} = \epsilon_a^{-1} - \epsilon_0^{-1},$$

where $\epsilon_0$ and $\epsilon_a$ are static and high frequency dielectric constants, respectively.

At lower temperatures ($T<\theta_D/4$), where polaron binding energy is small and the disorder energy (i.e., $W_D$) plays a dominant role in the conduction mechanism, Mott has pro-
posed that hop may occur preferentially beyond nearest neighbors. The conductivity for the so-called variable range hopping is predicted to be

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

(5)

where $A$ and $B$ are constants and $B$ is given by

$$B = 2.1(\alpha^3/kN(E_F))^{1/4},$$

(6)

where $N(E_F)$ is the density of states at the Fermi level. Thus the variable range hopping model predicts a $T^{-1/4}$ dependence of the logarithmic conductivity at low temperatures. Similar temperature dependence of the conductivity at low temperatures has been also obtained by Ambegaokar and co-workers on the basis of percolation model.

Holstein and co-workers have investigated a generalized polaron hopping model assuming $W_p = 0$, covering both the adiabatic and nonadiabatic hopping processes. On the basis of molecular crystal model the dc conductivity has been deduced as

$$\sigma = (3e^2N^2J^2/2kT)(\pi/kTW_H)^{1/2}\exp(-W_H/kT)$$

(7)

for nonadiabatic hopping, while for adiabatic hopping it has been shown that

$$\sigma = (8\pi Ne^2R^2\nu_0/3kT)\exp(-(W_H-J)/kT),$$

(8)

where $N$ is the site concentration and $J$ is the polaron bandwidth related to electron wave function overlap on adjacent sites. The condition for the nature of hopping has been also proposed in this model and is expressed by

$$J > (kTW_H/\pi)^{1/4}(h\nu_0/\pi)^{1/2}$$

for adiabatic hopping

$$J < (kTW_H/\pi)^{1/4}(h\nu_0/\pi)^{1/2}$$

for nonadiabatic hopping

(9)

with the condition for the existence of a small polaron being $J \leq W_H/3$.

A more general polaron hopping model, where $W_p \neq 0$, has been considered by Schnakenberg. In this model, optical multiphonon process determines the dc conductivity at high temperatures, while at low temperatures charge carrier transport is an acoustical one phonon-assisted hopping process. The temperature dependence of the dc conductivity in the Schnakenberg model has the form

$$\sigma \sim T^{-1}[\sinh(h\nu_0/kT)]^{1/2}$$

$$\times \exp[-(4W_H/h\nu_0)\tanh(h\nu_0/4kT)]\exp(-W_p/kT).$$

(10a)

It may be noted that Eq. (10a) predicts a temperature dependent hopping energy given by

$$W'_H = W_H \tanh(h\nu_0/4kT)/(h\nu_0/4kT)$$

(10b)

which indicates a decrease of activation energy with decrease of temperature.

Killias has proposed a polaron model in which the variation of activation energy with temperature is considered to be due to thermally activated hopping in a system which has a distribution of hopping distances. Assuming a Gaussian distribution of hopping distances centered around a median value $R_0$, Killias has obtained the following expression for the dc conductivity:

$$\sigma = A \exp[ -W(R_0)/kT - (a/2\beta kT)^2 ]$$

$$\times \left[ 1 - \frac{1}{2} \text{erfc}(\beta R_0 - a/2\beta kT) \right]$$

(11)

where $A$ is a constant, $a = dW/dR$, and $\beta^{-1}$ is proportional to the width of the Gaussian distribution. Equation (11) predicts a nonlinear variation of the dc conductivity which may be described most conveniently by a temperature dependent activation energy given by

$$W(T) = W_0 (1 - \theta R/T)$$

(12a)

where $W_0$ and $\theta R$ are constants and $\theta R$ is given by

$$\theta R = a^2/4\beta kW_0.$$  

(12b)

Recently, Trigeris and Friedman have applied percolation theory to the small polaron hopping regime and evaluated the conductivity in disordered systems. Considering correlation due to the energy of common site in a percolation cluster they have obtained,

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}].$$

(13a)

where the constant $T_0$ has different forms at high and low temperatures

$$T_0 = \begin{cases} 
12.5\alpha^3/kN_0 & \text{for high temperatures} \\
17.8\alpha^3/kN_0 & \text{for low temperatures}
\end{cases}$$

(13b)

where $N_0$ is the density of states assumed constant. It might be noted that Eq. (13) is similar to the prediction of Mott’s variable range hopping model [Eqs. (5) and (6)] with different values of $T_0$.

### III. EXPERIMENTAL PROCEDURE

Glassy samples were prepared from reagent grade $V_2O_5$, $TeO_2$, $(NH_4)_2HPO_4$, $Sb_2O_3$, and $Bi_2O_3$. The appropriate mixtures of these chemicals (Table I) were melted in alumina crucibles at 1173 K for 2 h in air atmosphere. The melt was quenched by pouring on a brass plate and pressing by another brass plate. The glassy nature of the samples was confirmed by x-ray diffraction, scanning electron microscopy.
differential thermal analysis and IR spectroscopy. The concentrations of total (N) and reduced (V\(^{4+}\)) vanadium ions were estimated from glass compositions and magnetic measurements, respectively. The density of the samples was determined by Archimedes’ principle. The average interisite separation (R) was obtained from glass composition and density. The various physical parameters of the prepared glasses are shown in Table I. For electrical measurements gold electrodes were deposited on both surfaces of the samples. The conductivity of the samples was measured using a Keithley 617 programmable electrometer. Before measurements Ohmic behavior at the contacts was ascertained from the linearity of the I–V characteristics. An evacuable chamber was employed as a sample cell and was inserted in a cryostat for low temperature measurements. Measurements were made in the temperature range 80–450 K with a stability of ±0.5 K.

**IV. RESULTS AND DISCUSSION**

The logarithmic dc conductivity \(\sigma\) of various glass compositions is shown in Fig. 1 as a function of reciprocal temperature. It is observed from the figure that for all glass compositions the dc conductivity shows an activated behavior above about 200 K and below this temperature the conductivity exhibits a nonlinear characteristic, indicating a temperature dependent activation energy, which decreases with the decrease in temperature. It is also observed that at all temperatures the conductivity of the glass composition containing \(P_2O_5\) is higher and that of the glass composition containing \(Bi_2O_3\) is lower than that of the composition containing \(Sb_2O_3\). It might be noted that the conductivity of the \(P_2O_5\) containing glass is higher and that of the \(Sb_2O_3\) containing glass in contrast with the conductivity. The values of \(\nu_0\) obtained from the fitting are reasonable and differ for different glass compositions. These values of \(\nu_0\) are consistent with the estimate of \(\nu_0\) from infrared studies. The values of \(\alpha\) obtained from the fitting are also reasonable for localized states and indicate strong localization in all glass compositions.

An estimate of the polaron radius \(r_p\) may be obtained experimentally within the framework of the Mott model\(^2\) from Eq. (3), assuming \(W = W_H\) and \(W_H \gg J\). The calculated values are included in Table III. The values of \(\epsilon_p\) used in the calculation were estimated from Eq. (4), where \(\epsilon_p\) and \(\epsilon_{\alpha}\) were obtained from Cole–Cole plot of the complex dielectric constants. It has been shown theoretically by Bogomolov and co-workers\(^6\) that for the case of nondispersive system of frequency \(\nu_0\) the polaron radius is given by

\[
r_p = (\pi/6)^{1/3}(R/2),
\]

where \(R\) is the average interisite separation. Equation (14) is obviously oversimplified for a complex system, but the infrared spectra of the present glass compositions\(^5\) suggest that this approximation is valid for these glass systems fairly well. The values of the polaron radius calculated from Eq. (14) using the values of \(R\) from Table I are shown in Table III. It may be noted from Table III that the experimental and theoretical values of \(r_p\) are comparable.

**TABLE III. Effective dielectric constants and polaron radii calculated from Eqs. (3) and (14).**

<table>
<thead>
<tr>
<th>Samples</th>
<th>(\epsilon_p)</th>
<th>(r_p (\AA)) (\text{Calculated from Eq. (3)})</th>
<th>(r_p (\AA)) (\text{Calculated from Eq. (14)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP</td>
<td>6.82</td>
<td>1.70</td>
<td>1.65</td>
</tr>
<tr>
<td>GS</td>
<td>6.34</td>
<td>1.79</td>
<td>1.72</td>
</tr>
<tr>
<td>GB</td>
<td>5.71</td>
<td>1.86</td>
<td>1.80</td>
</tr>
</tbody>
</table>

\(^4\text{From Cole–Cole plot of the complex dielectric constants (Ref. 15).}\)

**FIG. 1.** The dc conductivity shown as a function of reciprocal temperature for different sample compositions: \(\bigcirc\), sample containing \(P_2O_5\) (GP); \(\triangle\), sample containing \(Sb_2O_3\) (GS); \(\bullet\), sample containing \(Bi_2O_3\) (GB). The solid lines are fits to Eq. (1) predicted by Mott’s model. The dashed curves are drawn through the data.
At low temperatures, the dc conductivity data can be fitted to Eq. (5) predicted by Mott’s variable range hopping model. A semilogarithmic plot of the conductivity vs \( T^{-1/4} \) is shown in Fig. 2 for the glass compositions. The plot shows two distinct linear regions one above and other below about 130 K. The low temperature data (i.e., below 130 K) are fitted to Eqs. (5) and (6) in Fig. 2 by the least-square fitting procedure. It may be noted in Fig. 2 that the fit is fairly well. The values of \( N(E_F) \) obtained from the best fits are shown in Table IV. In the calculation, previous estimate of \( \alpha \) (Table II) was used. The values of \( N(E_F) \) are reasonable for localized states.\(^9\) However, the data above 130 K, where the multiphonon process is dominant\(^1\)\(^2\) are not fitted to the viable range hopping model. The linear region above 130 K in Fig. 2 is discussed later in the text. In the context of the Mott model it might be observed from Figs. 1 and 2 that the temperature dependence of the activation energy in the intermediate temperature range can not be interpreted by this model.

The temperature dependence of the conductivity, similar to the Mott model, is also predicted by the Holstein model [Eq. (8)] for the nonadiabatic hopping limit in the high temperature region. This model [Eq. (9)] also provides an independent check of the nature of hopping. The limiting values of \( J \) estimated from the right-hand side of Eq. (6) at 300 K, using the values of \( v_0 \) and \( W_H = W \) from Table II, are of the order of 0.031 eV for all compositions. An estimate of \( J \) can be made from the following expression:\(^9\)

\[
 J \approx e^{3} [N(E_F)/\epsilon_p^3]^{1/2}.
\]  

Using previous estimate of \( N(E_F) \) (Table IV), Eq. (15) gives \( J \approx 0.013 \) eV. Thus the hopping in these glasses in the high temperature region occurs by nonadiabatic process.

The Schnakenberg model [Eq. (10)] predicts a temperature dependent activation energy in consistence with the data presented in Fig. 1. In Fig. 3, \( \log_{10}(\sigma T) \) is plotted as a function of reciprocal temperature. The theoretical curves given by the Schnakenberg model [Eq. (10a)] are fitted in Fig. 3 to the experimental data. In the fitting procedure, \( v_0, W_H, \) and \( W_D \) are used as variable parameters. The best fits to the data have been observed for those values of the parameters as shown in Table V. It may be noted that the values of \( v_0 \) are close to the values obtained from the infrared data. As expected the values of the hopping energy \( W_H \) are less than the high temperature activation energy. The values of \( W_D \) are also close to the estimates of \( W_D \) from the Miller–Abrahams theory.\(^17\) It might be noted that the value of \( W_{H} + W_{D}/2 \) (Table V) is approximately equal to \( W \) (Table II) in accordance with the prediction of the Mott model.

Another model, which accounts for the decrease of activation energy with decrease of temperature, is due to Killias.\(^13\) In this model, the temperature dependence of the activation energy arises from the dependence of the activa-

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**TABLE IV. Parameters obtained from Mott’s variable range hopping and percolation models.**

<table>
<thead>
<tr>
<th>Glass samples</th>
<th>( N(E_F) ) (eV(^{-1}) cm(^{-3}))</th>
<th>( N_0 ) (eV(^{-1}) cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP</td>
<td>( 1.7 \times 10^{19} )</td>
<td>( 1.1 \times 10^{19} )</td>
</tr>
<tr>
<td>GS</td>
<td>( 1.5 \times 10^{19} )</td>
<td>( 0.96 \times 10^{19} )</td>
</tr>
<tr>
<td>GB</td>
<td>( 1.4 \times 10^{19} )</td>
<td>( 0.85 \times 10^{19} )</td>
</tr>
</tbody>
</table>

**TABLE V. Parameters obtained by fitting the Schnakenberg model to the experimental data.**

<table>
<thead>
<tr>
<th>Glass samples</th>
<th>( v_0 ) (s(^{-1}))</th>
<th>( W_H ) (eV)</th>
<th>( W_D ) (eV)</th>
<th>( W_H + W_D/2 ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP</td>
<td>( 9.2 \times 10^{12} )</td>
<td>0.25</td>
<td>0.13</td>
<td>0.315</td>
</tr>
<tr>
<td>GS</td>
<td>( 1.0 \times 10^{13} )</td>
<td>0.26</td>
<td>0.15</td>
<td>0.325</td>
</tr>
<tr>
<td>GB</td>
<td>( 1.1 \times 10^{13} )</td>
<td>0.28</td>
<td>0.17</td>
<td>0.365</td>
</tr>
</tbody>
</table>

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**FIG. 2.** The dc conductivity shown as a function of \( T^{-1/4} \) for the same sample compositions as in Fig. 1. The solid lines below 130 K are fits to the variable range hopping model [Eq. (5)] and the solid lines above 130 K are fits to the percolation model of Triberis and Friedman [Eq. (11)].

**FIG. 3.** Plot of \( \log_{10}(\sigma T) \) as a function of reciprocal temperature for the same glass compositions as in Fig. 1. The solid curves are fits to Eq. (10) predicted by Schnakenberg’s model.
tion energy on hopping distance [Eq. (12)]. Equation (12) indicates that the activation energy is linearly dependent on the inverse temperature. However, the experimental data estimated from Fig. 1 do not show inverse temperature dependence, rather follows Eq. (10) predicted by the Schnakenberg model (Fig. 3).

The percolation model [Eq. (13)] of Triberis and Friedman\(^1\) predicts a \(T^{-1/4}\) dependence of the logarithmic conductivity in the high as well as in the low temperature region. The data presented in Fig. 2 also show linearity in the \(\log_{10} \sigma \) vs \(T^{-1/4}\) plot above and below 130 K in consistence with the percolation model. However, it has been observed earlier in the text that the data below 130 K is consistent with the variable range hopping model of Mott. When the model of Triberis and Friedman is fitted to the data below 130 K, the values of \(N_0\) obtained are close to the values obtained for \(N(E_F)\) from Mott’s model. In Fig. 2 the data above 130 K are fitted to the model of Triberis and Friedman. The values of \(N_0\) obtained from the least-square fitting procedure are shown in Table IV. The values of \(N_0\) are consistent with the values of the density of states at the Fermi level obtained from the Mott’s variable range hopping model.

It is clear from the above discussion that the general behavior of the electrical properties of the vanadium tellurite glasses containing \(P_2O_5\), \(Sb_2O_3\), or \(Bi_2O_3\) is similar. However, there are differences in the values of the conductivity, activation energy and various parameters, namely \(\alpha\), \(\nu_0\), \(r_p\), \(N(E_F)\), etc., obtained by fitting the experimental data to the theoretical models for different glass compositions, although the \(V_2O_5\) content is same for all compositions. The values of \(\alpha\) (Tables II) increase from the glass composition containing \(P_2O_5\) to the composition containing \(Bi_2O_3\), indicating decrease of localization in the same order. The phonon frequency (Tables II and V) is higher in the \(Bi_2O_3\) containing glass and lower in the \(P_2O_5\) containing glass than that in the \(Sb_2O_3\) containing glass. Similar trends have been observed in the values of hopping and disorder energies (Table V) and polaron radius (Table III) in consistence with the high temperature activation energy (Table II) and localization length \((\alpha^{-1})\) respectively. However, opposite trends have been observed in the values of density of states at the Fermi level (Table IV) in the Mott model and constant density of states (Table VI) in the Triberis and Friedman model in consistence with the vanadium ion concentrations (Table I) in the glasses. The glass forming oxides thus contribute significantly to the conduction processes in addition to the vanadium oxide.

V. CONCLUSIONS

The dc conductivity of the semiconducting vanadium tellurite glasses containing \(P_2O_5\), \(Sb_2O_3\), or \(Bi_2O_3\) has been presented in the temperature range 80–450 K. It has been observed that the general behavior of the temperature dependence of the dc conductivity of all glass compositions is similar. However, at all temperatures the conductivity of the glass composition containing \(P_2O_5\) is higher and that of the glass composition containing \(Bi_2O_3\) is lower than that of the composition containing \(Sb_2O_3\). Opposite trends have been observed in the values of activation energy. Analysis of the dc conductivity data shows that at high temperatures the dc conductivity is consistent with the predictions of the phonon-assisted hopping model of Mott, while the variable range hopping model is valid at lower temperatures for all compositions. The Holstein and Friedman model indicates that hopping in these glasses occurs by the nonadiabatic process. The Schnakenberg model is consistent with the temperature dependence of the dc conductivity in the measured temperature range. The Triberis and Friedman model can also interpret the dc data at high as well as at low temperatures. Reasonable values of the various physical parameters, namely, hopping and disorder energies, localization length, phonon frequency, density of states at the Fermi level, etc., have been obtained by fitting the experimental data to these theoretical models. The difference in the values of the conductivity, activation energy and the various other parameters has been attributed to the effect of the glass forming oxides on the conduction processes.

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