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Hopping transport in vanadium tellurite glasses containing antimony oxide

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Abstract. The electrical DC conductivity of the semiconducting vanadium tellurite glasses containing Sb_2O_3 is reported in the temperature range 80–500 K. The experimental results are interpreted in terms of polaron-hopping theories. At high temperatures, Mott's phonon-assisted nearest-neighbour hopping is consistent with the data, while at lower temperatures, the variable-range hopping mechanism is dominant. Schnakenberg's hopping model is found to be consistent with the data over the entire temperature range. The results suggest that the addition of Sb_2O_3 to binary vanadium tellurite glasses changes the nature of the hopping mechanism from non-adiabatic to adiabatic.

1. Introduction

Amorphous transition metal (TM) oxides [1], TM oxide gels [2] and oxide glasses containing TM ions [3–7] are of great interest because of their semiconducting properties which arise from the presence of TM ions in multivalent states. It is generally established that electrical conduction occurs by the hopping of small polarons between two different valent states of the TM ions [8, 9]. However, there exists controversy over the exact mechanism of conduction in different temperature regions [3–7]. Binary vanadate glasses with different glass formers such as P_2O_5 and TeO_2 have been studied extensively [3–6]. The contribution of the glass-forming oxides other than the TM oxides to the conduction processes have also been the subject of much controversy [5, 6, 10]. Ioffe *et al* [10] have regarded the glass-forming oxides as non-interacting solvents in the conduction process, while Flynn *et al* [5] have pointed out that the glass-forming oxides might affect the activation energy of the hopping conduction in the vanadium tellurite glasses.

The objective of the present paper is to study the electrical properties of the ternary vanadate glasses containing TeO_2 and Sb_2O_3 as glass formers. It has been observed that the experimental data are interpreted in terms of the polaron-hopping theory and that the addition of Sb_2O_3 to the binary vanadium tellurite glasses changes the nature of hopping from non-adiabatic to adiabatic.

2. Experimental procedure

Glass samples (table 1) were prepared from reagent-grade V_2O_5, TeO_2 and Sb_2O_3. Mixtures of these chemicals were melted in alumina crucibles at a temperature of 1000 °C for 2 h in air. The melts were then quenched by pouring them onto a brass plate and pressing by another

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brass plate. The glassy nature of the samples was confirmed by x-ray diffraction, scanning electron microscopy, differential thermal analysis and IR spectroscopy. The concentration N of total vanadium ions and the concentration $[V^{4+}]$ of reduced vanadium ions were estimated from the glass compositions and magnetic measurements, respectively. The density of the samples was determined by Archimedes' principle. The average intersite separation R was obtained from the glass composition and density. The various physical parameters of the prepared glasses are shown in table 1. For electrical measurements, gold electrodes were deposited on both surfaces of the samples. The conductivity of the samples was measured with a Keithley 617 programmable electrometer. Before measurements, ohmic behaviour 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 80–500 K with a stability of ±0.5 K.

Table 1. Glass compositions, concentrations of total and reduced vanadium ions, their ratios, and average intersite separations for vanadate glass samples.

Glass compositions (mol%)			Density	N	$[V^{4+}]$		R
V_2O_5	TeO_2	Sb_2O_3	(g cm^{-3})	(10^{22} cm^{-3})	(10^{20} cm^{-3})	C	(Å)
40	50	10	3.19	1.13	5.99	0.053	4.46
30	50	20	3.25	0.98	6.17	0.063	4.67
20	50	30	3.38	0.87	6.26	0.072	4.86

3. Results and discussion

The logarithmic DC conductivities σ of various glass compositions are shown in figure 1 as a function of inverse temperature. It is observed that the conductivity increases with increase in the V_2O_5 content in the glass compositions and shows an activated behaviour above about 200 K. However, below 200 K the conductivity exhibits a non-linear characteristic, indicating a temperature-dependent activation energy which decreases with decrease in the temperature. In the following these results are interpreted in terms of the existing theories of polaron-hopping conductivity [8, 9, 11–17].

Mott [8] has investigated a conduction model in TM oxide glasses in terms of phonon-assisted hopping of small polarons between localized states. In this model, the DC conductivity for nearest-neighbour hopping in the non-adiabatic regime at high temperatures ($T > \frac{1}{2}\Theta_D$) *is given by*

$$\sigma = \nu_0[e^2C(1-C)/kTR]\exp(-2\alpha R)\exp(-W/kT) \tag{1}$$

where ν_0 is the longitudinal optical phonon frequency, R is the average site separation, α is the inverse localization length of the s-like wavefunction 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 [9] have shown that

$$W = \begin{cases} W_H + \frac{1}{2}W_D \\ W_D \end{cases} \qquad \text{for} \begin{cases} T > \frac{1}{2}\Theta_D \\ T < \frac{1}{4}\Theta_D \end{cases} \tag{2}$$

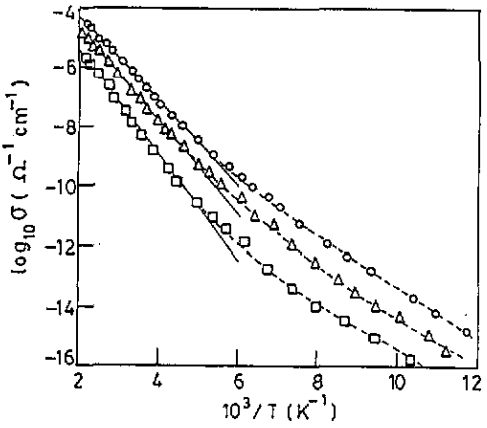

Figure 1. The DC conductivities as a function of reciprocal temperature for three sample compositions: ○, 40 mol% V_2O_5; △, 30 mol% V_2O_5; □, 20 mol% V_2O_5; ——, fits to equation (1) predicted by Mott's model; ----, curves drawn through the data.

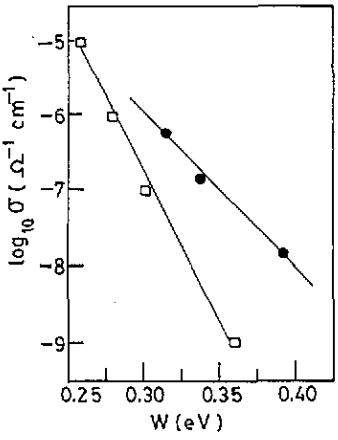

Figure 2. Plots of log σ versus W at 300 K for the present glasses (●). The estimated temperature from the slope is 280 K. For comparison the data (□) for binary vanadium tellurite glasses [5] are also shown (the estimated temperature from the slope is 82 K).

where W_H is the polaron-hopping energy, W_D is the disorder energy and Θ_D, defined by $h\nu_0 = k\Theta_D$, is the characteristic Debye temperature. In the adiabatic limit the overlap integral $J \simeq \exp(-2\alpha R)$ reduces to unity.

The DC conductivity data presented in figure 1 in the high-temperature region ($T >$ 200 K) can be interpreted in terms of this model. Equation (1), which was predicted for the hopping of small polarons, is fitted in figure 1 to the experimental data at high temperatures, using ν_0, α and W as variable parameters. The best fits are observed above 200 K for the values of the parameters shown in table 2. The values of ν_0 obtained from the fitting are of the order of 10^{13} s^{-1} and differ little for different glass compositions. These values of ν_0 are consistent with the estimate of ν_0 from infrared studies [18]. The values of α obtained from the fitting are also reasonable for localized states [12] and increase with increase in the Sb_2O_3 content in the glass compositions, thus indicating stronger localization in the glass composition containing a lower Sb_2O_3 content.

Table 2. Parameters obtained from the fitting of high-temperature data to the Mott model.

V_2O_5 content (mol%)	W (eV)	ν_0 (10^{13} s^{-1})	α ($Å^{-1}$)	r_p (Å)	
				From equation (3)	From equation (4)
40	0.31	0.98	0.69	1.81	1.89
30	0.34	1.01	0.72	1.87	1.91
20	0.39	1.10	0.75	1.93	1.97

An estimate of the polaron radius r_p may be obtained experimentally within the framework of the model of Austin and Mott [9] from the relation

$$W_H = e^2/4\epsilon_p r_p \qquad (3)$$

where r_p is the polaron radius and ϵ_p is the effective dielectric constant given by $\epsilon_p^{-1} = \epsilon_\alpha^{-1} - \epsilon_0^{-1}$, where ϵ_0 and ϵ_α are the static and high-frequency dielectric constants, respectively,

which were estimated from the Cole–Cole plot of the complex dielectric constant [18]. On the assumption that $W \simeq W_H$ and $W_H \gg J$, the calculated values of r_p are included in table 2. It has been shown theoretically by Bogomolov *et al* [19] that for a non-dispersive system of frequency ν_0 the polaron radius is given by

$$r_p = (\tfrac{1}{6}\pi)^{1/3}(\tfrac{1}{2}R) \tag{4}$$

where R is the average intersite separation. Equation (4) is obviously oversimplified for a complex system, but the infrared spectra of the present glass compositions [18] suggest that this approximation is reasonably valid for these glass systems. The values of the polaron radius calculated from equation (4) using the values of R from table 1 are shown in table 2. It may be noted from table 2 that the experimental and theoretical values of r_p are comparable.

It has been proposed in the literature [3, 6] that the nature of hopping at high temperatures can be determined by estimating the temperature from the slope of the log σ versus W plot at a fixed experimental temperature. It has been shown [3, 6] that the estimated temperature is close to the experimental temperature if hopping occurs in the adiabatic regime; otherwise hopping is non-adiabatic. Such a plot is shown in figure 2 at an experimental temperature of 300 K. The estimated temperature is close to 300 K. Thus the hopping occurs in the adiabatic regime in these glasses in contrast with the non-adiabatic hopping observed in binary vanadium tellurite glasses containing a similar vanadium oxide content [5].

At lower temperatures where the disorder energy plays a dominant role, Mott has proposed that hops may occur beyond nearest neighbours. The conductivity for the so-called variable-range hopping conductivity is given by [11, 12]

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}] \tag{5a}$$

where T_0 is given by

$$T_0 = 19.44\alpha^3/kN(E_F) \tag{5b}$$

where $N(E_F)$ is the density of states at the Fermi level.

Plots of logarithmic conductivity versus $T^{-1/4}$ are shown in figure 3 for the present glass compositions. It is clear from the figure that the plots are linear over a considerable temperature range, consistent with equation (5). Experimental points are fitted in figure 3 to equation (5*a*) by the least-squares fitting procedure. The values of σ_0 and T_0 obtained by the best fit are shown in table 3. Using the previous estimate of the localization lengths the values of $N(E_F)$ are estimated from the values of T_0 and are shown in table 3. The values of $N(E_F)$ decrease with decrease in the vanadium ion content in the glass compositions.

Table 3. Parameters obtained by fitting the experimental data to the variable-range hopping.

V_2O_5 content (mol%)	σ_0 (10^{15} Ω^{-1} cm^{-1})	T_0 (10^6 K)	$N(E_F)$ (10^{21} eV^{-1} cm^{-3})
40	3.65	2.46	1.08
30	5.75	2.85	1.05
20	1.41	3.57	0.95

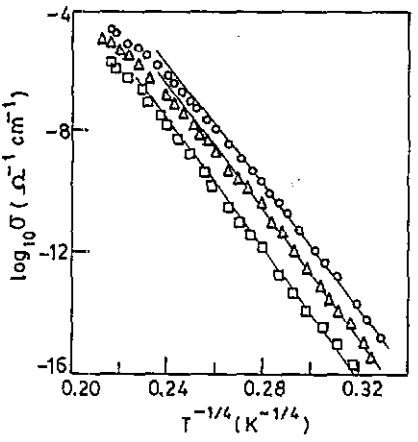

Figure 3. The DC conductivities shown as a function of $T^{-1/4}$ for the same sample compositions as in figure 1: ——, fits to the variable-range hopping model (equation (5)).

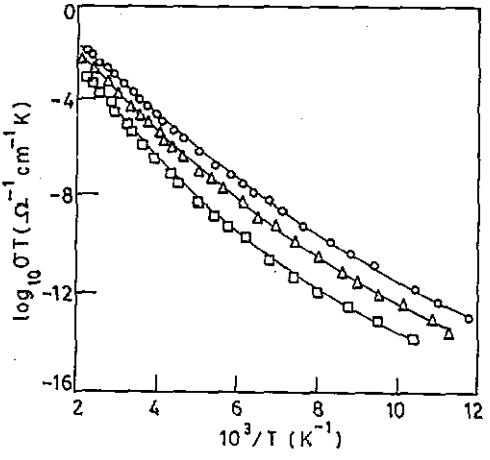

Figure 4. Plots of log (σT) as a function of reciprocal temperature for the same glass compositions as in figure 1: ——, fits to equation (7) predicted by Schnakenberg's model.

Holstein [14], Emin and Holstein [15] and Friedman and Holstein [16] have investigated a generalized polaron-hopping theory on the basis of the molecular crystal model assuming that $W_D = 0$, covering both the adiabatic and the non-adiabatic hopping processes. The temperature dependence of the conductivity (figure 1), similar to the Mott model, is also predicted by the model of Holstein and co-workers [14–16] for the adiabatic hopping limit in the high-temperature region. This model also provides an independent check of the nature of hopping. The condition for the nature of hopping is expressed by [14]

$$J \begin{cases} > \\ < \end{cases} (kTW_H/\pi)^{1/4}(h\nu_0/\pi)^{1/2} \qquad \begin{cases} > & \text{for adiabatic hopping} \\ < & \text{for non-adiabatic hopping} \end{cases} \tag{6}$$

with the condition for the existence of a small polaron being $J \leqslant \frac{1}{3}W_H$. The limiting values of J estimated from the right-hand side of (6) at 300 K, using the values of ν_0 and $W_H \simeq W$ from table 2 are of the order of 0.03 eV for all compositions. An estimate of J can be made from the expression [12] $J \simeq e^3[N(E_F)/\epsilon_0^3]^{1/2}$. Using the value of $N(E_F)$ from table 3, J is estimated to be about 0.06 eV. Thus the hopping in these glasses in the high-temperature region occurs by the adiabatic process. It may be noted that hopping in the binary vanadium tellurite glasses containing less than 50 mol% V_2O_5 was observed to be non-adiabatic in nature [5]. In the present ternary glass compositions, the V_2O_5 content is kept below 50 mol% and thus the addition of Sb_2O_3 to the binary vanadate glasses alters the nature of the hopping mechanism [5].

A more general polaron-hopping model, where $W_D \neq 0$, has been considered by Schnakenberg [17]. In this model, at high temperatures, the optical multiphonon process determines the DC conductivity while, at low temperatures, charge carrier transport is an acoustical phonon-assisted hopping process. The temperature dependence of the DC conductivity in Schnakenberg's model has the form

$$\sigma \sim T^{-1}[\sinh(h\nu_0/kT)]^{1/2}\exp[-(4W_H/h\nu_0)\tanh(h\nu_0/4kT)]\exp(-W_D/kT). \tag{7}$$

It may be noted that equation (7) predicts a temperature-dependent hopping energy which decreases with decrease in the temperature, consistent with the data presented in figure 1.

In figure 4, the experimental points are fitted to equation (7) by the best-fit method. The best fits to the data have been observed for the values of the parameters ν_0, W_H and W_D shown in table 4. It may be noted that the values of ν_0 are close to the values obtained from the infrared data [18]. The values of the hopping energy W_H increase with decrease in the V_2O_5 content in the glasses, similar to the activation energy. The values of W_D are also close to the estimates of W_D from the Miller–Abrahams [20] theory.

Table 4. Parameters obtained by fitting Schnakenberg's model for various glass compositions.

V_2O_5 content (mol%)	ν_D (10^{13} s^{-1})	W_H (eV)	W_D (eV)
40	0.84	0.25	0.13
30	1.04	0.27	0.18
20	1.09	0.34	0.20

4. Conclusions

The DC conductivity of the semiconducting vanadium tellurite glasses containing Sb_2O_3 has been presented in the temperature range 80–500 K. 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 is valid at lower temperatures for all compositions. Schnakenberg's model is consistent with the temperature dependence of the DC conductivity in the measured temperature range. The addition of Sb_2O_3 to the binary vanadium tellurite glasses alters the nature of the hopping mechanism from non-adiabatic to adiabatic.

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