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1993 J. Phys.: Condens. Matter 5 8749

(http://iopscience.iop.org/0953-8984/5/46/012)

J. Phys.: Condens. Matter 5 (1993) 8749–8754. Printed in the UK

Adiabatic hopping conduction in vanadium bismuth tellurite glasses

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Received 13 May 1993

Abstract. The electrical conductivity of semiconducting vanadium tellurite glasses containing bismuth oxide is reported in the temperature range 80–450 K. The experimental results are interpreted in terms of polaron-hopping theories. The results suggest that the addition of bismuth oxide to the 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 agreed that the electrical conduction occurs by the hopping of small polarons between two states of the TM ions of different valences [8, 9]. However, controversy exists 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 in the conduction process 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 vanadium tellurite glass.

The objective of the present work is to study the electrical properties of ternary vanadate glasses containing TeO_2 and Bi_2O_3 as glass formers. It has been observed that the experimental data can be interpreted in terms of polaron-hopping theory and that the addition of Bi_2O_3 to the binary vanadium tellurite glasses changes the nature of hopping from non-adiabatic to adiabatic.

2. Experimental procedure

Glassy samples were prepared from reagent-grade V_2O_5, TeO_2 and Bi_2O_3. The appropriate mixtures of these chemicals (table 1) were melted in alumina crucibles at temperatures between 1173 and 1373 K depending on the compositions, for 2 h in an air atmosphere. The melt was quenched by pouring on a brass plate and pressing by another brass plate.

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0953-8984/93/468749+06$07.50

The glassy nature of the samples was confirmed by x-ray diffraction, scanning electron microscopy, differential thermal analysis and infrared spectroscopy. The concentration N of total vanadium ions and the concentration $[V^{4+}]$ of reduced vanadium ions were estimated from 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 using a Keithley 617 programmable electrometer. Before the measurements the 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 80–450 K with a stability of ±0.5 K.

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

Glass composition (mol%)			Density	N	$[V^{4+}]$		R
V_2O_5	TeO_2	Bi_2O_3	(g cm^{-3})	(cm^{-3})	(cm^{-3})	C	(Å)
40	50	10	3.35	1.02×10^{22}	5.00×10^{20}	0.049	4.61
30	50	20	3.46	0.92×10^{22}	5.21×10^{20}	0.056	4.77
20	50	30	3.52	0.83×10^{22}	5.63×10^{21}	0.068	4.93

3. Results and discussion

Figure 1 shows the logarithmic DC conductivity σ of various glass compositions as a function of reciprocal temperature. It is observed from the figure that the conductivity decreases with decrease in V_2O_5 content in the glass compositions and shows an activated behaviour above about 220 K; below this temperature the conductivity exhibits a non-linear characteristic, indicating a temperature-dependent activation energy which decreases with decreasing temperature. In the following, these results are interpreted in terms of 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 the 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

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

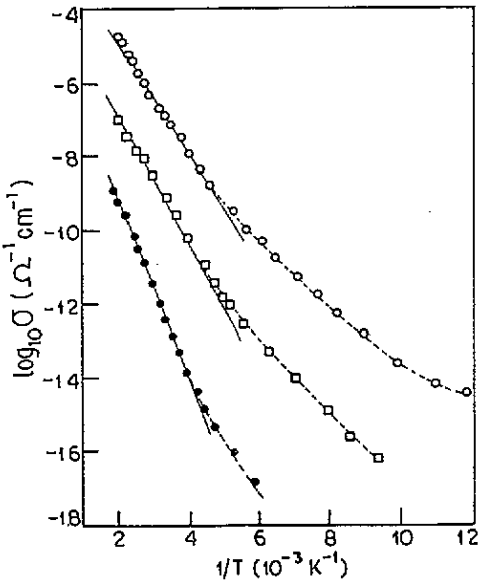

Figure 1. The DC conductivity as a function of reciprocal temperature for three sample compositions: ○, 40 mol% V_2O_5; □, 30 mol% V_2O_5; ●, 20 mol% V_2O_5; ——, fits to equation (1) predicted by the Mott model; - - - -, curves drawn through the data.

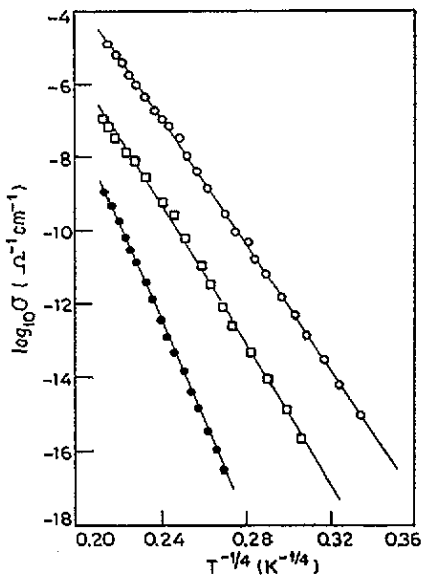

Figure 2. The DC conductivity as a function of $T^{-1/4}$ for the same sample compositions as in figure 1: ——, fits to the variable-range hopping model (equation (5)).

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

The DC conductivity data presented in figure 1 in the high-temperature region ($T >$ 220 K) can be interpreted in terms of this model. Equation (1), predicted for the hopping of small polarons, is fitted in figure 1 to the experimental data at high temperatures, using ν_o, α and W as variable parameters. The best fits are observed above 220 K for the values of the parameters shown in table 2. The values of ν_o obtained from the fitting are of the order of 10^{13} s^{-1} and differ little for different glass compositions. These values of ν_o are consistent with the estimate of ν_o from infrared studies [18]. The values of α obtained from the fitting are also reasonable for localized states [12] and increase with increase in Bi_2O_3 content in the glass compositions, thus indicating stronger localization in the glass composition with a lower Bi_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_o (s^{-1})	α ($Å^{-1}$)	r_p (Å)	
				From equation (3)	From equation (4)
40	0.35	1.9×10^{13}	0.71	1.81	1.89
30	0.39	1.1×10^{13}	0.90	1.87	1.91
20	0.48	1.1×10^{13}	1.09	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

$$W_H = e^2/4\epsilon_p r_p \tag{3}$$

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 $W_H \gg J$, where J is the polaron band width, the calculated values of r_p are included in table 2. It has been shown theoretically by Bogomolov and co-workers [19] that for the case of a non-dispersive system of frequency ν_o 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 holds fairly well 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.

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]

$$\sigma = A\exp(-B/T^{1/4}) \tag{5a}$$

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

$$B = 2.1[\alpha^3/kN(E_F)]^{1/4} \tag{5b}$$

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

A plot of logarithmic conductivity versus $T^{-1/4}$ is shown in figure 2 for the present glass compositions. It is clear from the figure that the plot is linear below about 200 K, consistent with equations (5). Experimental points are fitted in figure 2 to equations (5) by the least-square fitting procedure, using α and $N(E_F)$ as variable parameters. The values of α and $N(E_F)$ obtained by the best fit are shown in table 3. These values are reasonable for localized states [12] and are consistent with the estimates from high-temperature electrical data (table 2). The values of $N(E_F)$ decrease with decrease in vanadium ion content in the glass compositions.

Table 3. Parameters obtained by fitting the experimental data to equations (5) and (7) for variable-range hopping and the Schnakenberg model, respectively.

V_2O_5 content (mol%)	$N(E_F)$ (eV^{-1} cm^{-3})	α ($Å^{-1}$)	ν_o (s^{-1})	W_H (eV)	W_D (eV)
40	7.7×10^{19}	0.81	1.1×10^{13}	0.29	0.13
30	7.7×10^{19}	0.91	1.1×10^{13}	0.34	0.13
20	2.3×10^{19}	1.00	1.0×10^{13}	0.41	0.14

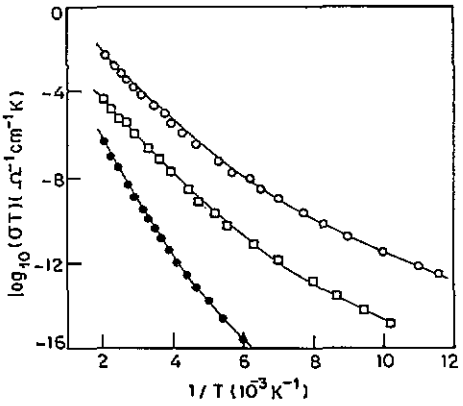

Figure 3. Plot of $\log_{10}(\sigma T)$ as a function of reciprocal temperature for the same glass compositions as in figure 1: ——, fits to equation (7) predicted by the Schnakenberg model.

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]

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

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 0.033 eV for all compositions. An estimate of J can be made from the expression [12] $J \simeq e^3[N(E_F)/\epsilon_p^3]^{1/2}$. Using the value of $N(E_F) \simeq 10^{19}$ eV^{-1} cm^{-3} (table 3), J is estimated to be about 0.065 eV. Thus the hopping in these glasses in the high-temperature region occurs by the adiabatic process. It may be noted that the hopping in the binary vanadium tellurite glasses containing less than 50 mol% V_2O_5 was observed to be non-adiabatic in nature. In the present ternary glass conditions, the V_2O_5 content is kept at less than 50 mol% and thus the addition of Bi_2O_3 to the binary vanadate glasses alters the nature of the hopping mechanism.

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

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

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 3, 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 3. 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 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.

4. Conclusions

The DC conductivity of the semiconducting vanadium tellurite glasses containing Bi_2O_3 has been presented in the temperature range 80–450 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 variable-range hopping is valid at lower temperatures for all compositions. The Schnakenberg model is consistent with the temperature dependence of the DC conductivity in the measured temperature range. The addition of Bi_2O_3 to the binary vanadium tellurite glasses alters the nature of the hopping mechanism from non-adiabatic to adiabatic.

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