IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Multiphonon assisted hopping in strontium vanadate semiconducting glasses

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1999 J. Phys.: Condens. Matter 11 1529

(http://iopscience.iop.org/0953-8984/11/6/017)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 171.66.16.214
The article was downloaded on 15/05/2010 at 06:59

Please note that terms and conditions apply.

J. Phys.: Condens. Matter **11** (1999) 1529–1536. Printed in the UK PII: S0953-8984(99)98639-3

Multiphonon assisted hopping in strontium vanadate semiconducting glasses

Somaditya Sen and A Ghosh†

Solid State Physics Department, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, India

Received 23 October 1998

Abstract. The temperature and compositional dependence of the electrical conductivity of semiconducting strontium vanadate glasses have been reported in the temperature range 80–500 K. It has been observed that the multiphonon assisted hopping model of small polarons in the nonadiabatic regime, which considers the strong interaction of electrons with both the optical and acoustical phonons, can interpret the temperature dependence of the conductivity data of these glasses over the entire temperature range of measurement. The parameters obtained from the fits of the experimental data to this model appear reasonable and are consistent with the glass composition. Mott's optical phonon assisted hopping model at high temperatures yields smaller values of the localization length. However, Mott's variable range hopping model can predict the low temperature data. Schnakenberg's model provided higher values of the hopping energy than the activation energy obtained at the highest temperature range.

1. Introduction

Semiconducting properties of the transition metal (TM) oxide glasses formed with traditional glass network formers such as P_2O_5, GeO_2 etc have been studied extensively [1–7]. However, glasses formed with TM oxides as unique glass network formers [9] have not been studied so far. It has been generally accepted that the electrical conduction in the TM oxide glasses occurs by the hopping of small polarons between two different valency states of the TM ions [1, 2, 5]. It has been alternatively suggested [3] that the electrical transport in the TM oxide glasses can be described by the multiphonon hopping of localized electrons with a weak electron–phonon interaction. There exists also a controversy over the nature of hopping mechanism in different temperature and composition regions [8, 9]. Recently, we have studied the glass formation and structure of strontium vanadate glasses [10]. The reason for interest in these glasses is that single phase amorphous materials with random structure can be obtained for a wide composition range, in which the TM oxide V_2O_5 acts as a unique network former. In the present work we have studied the composition dependence of the electrical properties of the strontium vanadate glasses in a wide composition and temperature range. It has been observed that the multiphonon assisted hopping of electrons with strong interaction with optical as well as acoustical phonons is the dominant transport mechanism in the strontium vanadate glasses in sharp contrast to the results observed for the vanadate glasses formed with traditional network formers [1, 11].

† Author to whom all correspondence should be addressed.

0953-8984/99/061529+08$19.50 © 1999 IOP Publishing Ltd

2. Experiment

Glass samples of compositions $(100-x)$ SrO–x V_2O_5 (table 1) were prepared from the reagent grade chemicals $SrCO_3$and V_2O_5 for $x = 50$–90 (mol%). The appropriate mixtures of these chemicals in 10 g batches were melted for 1 hour in air in alumina crucibles in an electrical furnace at temperatures in the range 850–1050 °C depending on composition. The melts were then quenched either by pressing between two brass plates or by pouring onto a twin roller revolving in opposite directions. The samples were annealed at a temperature which is 50 °C below the glass transition temperature, T_g (table 1) determined by DTA. The amorphous nature of the samples was confirmed from x-ray diffraction and electron microscopic studies [10]. The concentrations of the total (N) and reduced vanadium ions ($[V^{4+}]$) were determined from the glass composition and magnetic susceptibility measurements (Parc model 155) respectively. The average intersite separation (R) between vanadium ions was estimated from the glass composition and density. The various physical parameters obtained from different glass compositions are displayed in table 1.

Table 1. Density, total and reduced vanadium ion concentrations, average intersite separation and glass transition temperatures of different compositions of $(100-x)$ SrO–x V_2O_5 glasses.

Composition x (mol%)	Density (g cm^{-3})	N (10^{22} cm^{-3})	$[V^{4+}]$ (10^{20} cm^{-3})	R (Å)	T_g (°C) (±5)
90	3.03	1.84	10.67	3.78	250
80	3.19	1.76	10.91	3.85	270
70	3.33	1.64	8.04	3.94	270
60	3.44	1.48	5.18	4.07	295
50	3.47	1.27	4.57	4.29	305

For electrical measurements, gold electrodes were deposited on both surfaces of the polished samples by vacuum evaporation. The gold coated samples were heat treated at 150 °C for the stabilization of the electrodes. Measurements of the dc conductivity of the samples were carried out in a Keithley electrometer (model 617). Before measurement the absence of barrier layers at the contacts was confirmed from the linear I–V characteristics. The dc conductivity was also obtained from the extrapolation of the frequency dependent ac conductivity measured using a Quad-Tech RLC meter (model 7600) in a wide frequency range of 10 Hz–2 MHz. The dc conductivity measured by both these methods agreed perfectly well. Measurements below room temperature were taken by placing the sample cells in a cryogenic unit. Measurements were made in the temperature range 80–500 K.

3. Results and discussion

The temperature dependence of the electrical conductivity for all glass compositions listed in table 1 is shown in figure 1 as a function of T^{-1}. First, it is observed in the figure that the conductivity is nonactivated over the entire temperature range of measurements and that the activation energy decreases with the decrease in temperature. Secondly, it is clear in the figure that the conductivity decreases while the activation energy increases with the vanadium oxide content in the glass compositions.

Earlier, the dc conductivity data of the TM oxide glasses [1, 2, 4–6] at high temperature were interpreted in terms of Mott's model [11] of optical phonon-assisted hopping between nearest neighbours, while Mott's variable range hopping model [12] was used to explain the

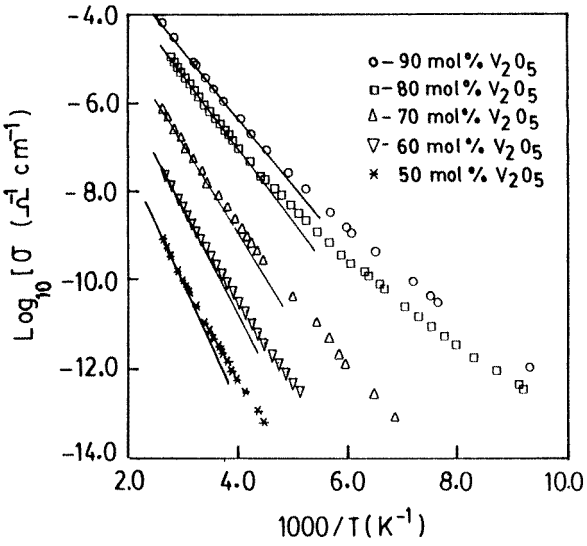

Figure 1. Temperature dependence of the dc conductivity as a function of T^{-1} for different compositions (shown) of the strontium vanadate glasses. The solid lines are the best fits to equations (1).

low temperature conductivity data. In the Mott model [11] the optical phonon assisted hopping of small polarons is considered. At high temperatures the dc conductivity in this model for the nearest neighbour hopping is given by

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

where ν_0 is the optical phonon frequency, C is the fraction of reduced vanadium ions and is thus $[V^{4+}]/N$, α^{-1} is the localization length for the wavefunction, R is the average hopping distance, k is the Boltzmann constant, e is the electronic charge and W is the activation energy for hopping conduction.

The activation energy for the hopping conduction is given by [12]

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

where W_H is the hopping energy, W_D is the energy difference between two adjacent sites i.e. disorder energy and θ_D is the Debye temperature. As far as our data are concerned we observed in figure 1 an approximate linearity in the $\log(\sigma)$ versus $10^3/T$ plot predicted by Mott's model [11], in a limited high temperature range. We obtained the activation energy W and the localization length α^{-1} from the best fits of the Mott's phonon assisted hopping model [11] (equation (1)) to the experimental data at the highest temperatures (the solid lines in figure 1) using the values of the parameters given in table 1. These values of W and α^{-1} are shown in table 2. It may be observed that although the values of W are consistent with those for other vanadate glasses [1], the values of α^{-1} appear unreasonably lower than those ($\approx$10 Å) for other glasses [13].

In the framework of Mott's model, the nature of the hopping mechanism in the high temperature range, where an activated behaviour of the conductivity was observed, can be ascertained from the plot of logarithmic conductivity versus activation energy at an arbitrary

Table 2. Parameters obtained from Mott's optical phonon assisted hopping and variable range hopping models for different compositions of $(100 - x)$ SrO–x V_2O_5 glasses.

Composition x (mol%)	W (eV)	α^{-1} (Å)	$N(E_F)$ (eV^{-1} cm^{-3})
90	0.31	0.35	2.83×10^{18}
80	0.34	0.35	2.78×10^{18}
70	0.41	0.35	1.31×10^{18}
60	0.44	0.33	1.00×10^{18}
50	0.47	0.32	8.69×10^{17}

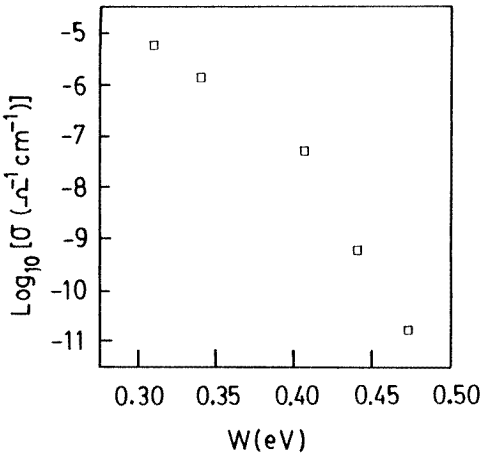

Figure 2. A plot of $\log_{10}\sigma$ versus W for different glass compositions at a temperature of 300 K.

experimental temperature in this range. It has been suggested [1, 2] that the hopping would be in the adiabatic regime if the temperature estimated from such a plot were close to the experimental temperature. Otherwise, the hopping would be in the nonadiabatic regime. In this way, the hopping of small polarons was inferred to be in the adiabatic regime for the TM oxide glasses formed with transitional glass formers [1, 2, 4, 6]. A plot of $\log_{10}\sigma$ at 300 K versus W is shown in figure 2 for different compositions of the present strontium vanadate glasses. It is evident from the figure that the plot is not linear and thus an estimation of temperature and hence the determination of the nature of the hopping mechanism is not possible from the plot in contrast to traditional vanadate and other TM oxide glasses [1, 2, 4].

At lower temperatures, Mott and Davis [13] have shown that hops may occur preferentially beyond nearest neighbours. The conductivity for the so-called variable range hopping mechanism is given by

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right] \tag{3}$$

where σ_0 and T_0 are constants, and T_0 is given by

$$T_0 = 16\alpha^3/kN(E_F) \tag{4}$$

where $N(E_F)$ is the density of states at the Fermi level. We have shown in figure 3 the dc conductivity as a function of $T^{-1/4}$ which indicates a linearity in a considerable temperature

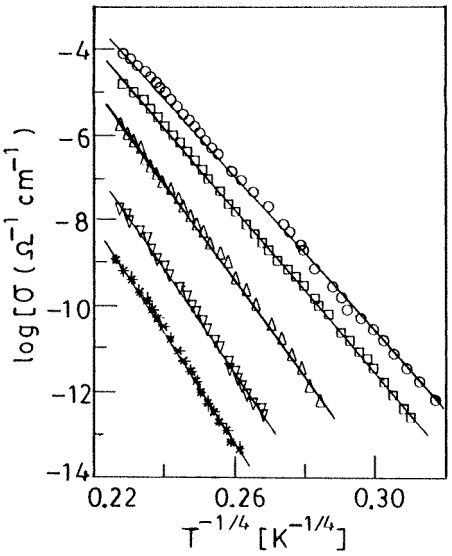

Figure 3. A plot of $\log_{10}\sigma$ versus $T^{-1/4}$ for different glass compositions as shown in figure 1. The solid lines are the best fits to equation (4).

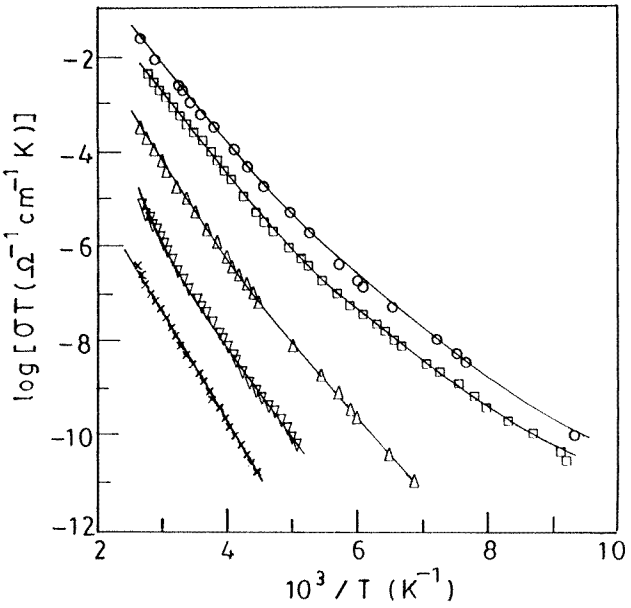

Figure 4. Best fits (solid curves) of the Schnakenberg model (equation (5)) to the experimental data for the different glass compositions as shown in figure 1.

range. Equation (3) was fitted to the data in figure 3. Assuming a reasonable value of $\alpha^{-1} \approx 10$ Å, values of $N(E_F)$ were calculated from equation (4). These values, shown in table 2, are comparable with the values obtained for the vanadate glasses formed with traditional network formers [6, 13] and the other semiconducting glasses [13].

A polaron hopping model, where $W_D \neq 0$, has been considered by Schnakenberg [14]. In this model, the optical multiphonon hopping process determines the dc conductivity at high temperatures, while at low temperatures the conductivity is determined by the acoustical single phonon assisted hopping process. The temperature dependence of the dc conductivity in this model is given by

$$\sigma = \frac{A}{T}[\sinh(h\nu_0/kT)]^{1/2} \exp[-(4W_H/h\nu_0)\tanh(h\nu_0/4kT)] \exp(-W_D/kT). \tag{5}$$

It may be noted that equation (5) predicts a temperature dependent hopping energy which decreases with an increase of temperature in consistence with the data presented in figure 1. In figure 4, the dc conductivity has been fitted to the theoretical values given by the model (equation (5)). In the fitting process ν_0, W_H and W_D were used as variable parameters. The best fits of the data have been obtained for the values of the parameters shown in table 3. It may be noted that the values of ν_0 are close to the values obtained from infrared spectra [10]. However, this model yields high values of W_H than the values of the activation energy estimated at higher temperatures (table 2).

Table 3. Parameters obtained from the fits of the experimental data to the Schnakenberg model for different compositions of $(100 - x)$ SrO–x V_2O_5 glasses.

Composition x (mol%)	W_H (eV)	W_D (eV)	ν_0 (s^{-1})
90	0.33	0.11	1.08×10^{13}
80	0.36	0.12	1.23×10^{13}
70	0.40	0.14	1.10×10^{13}
60	0.49	0.15	1.31×10^{13}
50	0.49	0.30	1.60×10^{13}

Emin and coworkers [15, 16] have proposed a most general small polaron hopping model in which they have considered the strong interaction of electrons with the optical as well as acoustical phonons. The dc conductivity for this multiphonon assisted hopping model of small polarons is given by

$$\sigma = \frac{Ne^2R^2}{6kT}\left(\frac{J}{\hbar}\right)^2\left[\frac{\pi\hbar^2}{2(E_c^{op}+E_c^{ac})kT}\right]^{1/2}\exp\left[\frac{-W_D^2}{8(E_c^{op}+E_c^{ac})kT}-\frac{W_D}{kT}\right] \times \exp\left[-\frac{(E_A^{op}+E_A^{ac})}{kT}\right] \tag{6}$$

where J and W_D are the transfer integral and energy difference between adjacent sites, $\hbar = h/2\pi$, N is the carrier density, R is the hopping distance, E_c^{op} E_c^{ac}, E_A^{op} and E_A^{ac} are defined as

$$\begin{aligned}
E_c^{op} &= \frac{\hbar^2}{4kT}\frac{1}{N_p}\sum_q\left(\frac{2E_b^{op}}{\hbar\omega_{q,0}}\right)\text{cosech}\left(\frac{\hbar\omega_{q,0}}{2kT}\right)\omega_{q,0}^2 \\
E_c^{ac} &= \frac{\hbar^2}{4kT}\frac{1}{N_p}\sum_q\left(\frac{2E_b^{ac}}{\hbar\omega_{q,a}}\right)\text{cosech}\left(\frac{\hbar\omega_{q,a}}{2kT}\right)\omega_{q,a}^2 \\
E_A^{op} &= kT\left(\frac{2E_b^{op}}{\hbar\omega_0}\right)\tanh\left(\frac{\hbar\omega_0}{2kT}\right) \\
E_A^{ac} &= kT\frac{1}{N_p}\sum_q\left(\frac{2E_b^{ac}}{\hbar\omega_{q,a}}\right)\tanh\left(\frac{\hbar\omega_{q,a}}{2kT}\right)
\end{aligned} \tag{7}$$

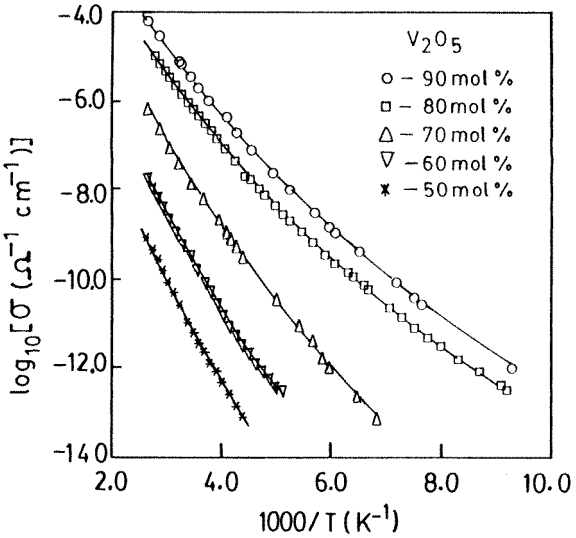

Figure 5. Best fits (solid curves) of the Emin model (equation (6)) to the experimental data for different glass compositions shown in the figure.

Table 4. Parameters obtained from the fits of the experimental data to the multiphonon assisted hopping models for different compositions of $(100 - x)$ SrO–x V_2O_5 glasses.

Composition x (mol%)	E_c^{op} (eV)	E_b^{ac} (eV)	J (eV)	W_D (eV)	ν_0 (10^{13} s^{-1})
90	0.46	0.36	0.010	0.07	1.80
80	0.49	0.39	0.010	0.07	1.92
70	0.58	0.48	0.007	0.08	1.90
60	0.71	0.61	0.007	0.08	2.37
50	0.74	0.64	0.005	0.08	2.36

where $\omega_0 = 2\pi\nu_0$ is the mean optical frequency, $\omega_{q,0}$ and $\omega_{q,a}$ are the optical and acoustical phonon frequencies respectively at the wave vectors q and N_p is the number of phonon modes. E_b^{op} and E_b^{ac} are the polaron binding energies related to the optical and acoustical phonons, respectively.

The dc conductivity was calculated from equations (6) and (7) assuming that the acoustic phonon density of states is approximately given by $g(\omega) \propto \omega^2$ and that the optical phonon density of states is constant. The best fits to the experimental data are shown in figure 5 for all the compositions. The values of the parameters E_b^{op}, E_b^{ac}, W_D, J and ν_0 for the best fits are shown in table 4 for all glass compositions. It is observed in figure 5 that the agreement between theory and experiment is very good over the entire temperature range of the measurement. It may be noted that the values of the transfer integral J obtained from the fits are consistent with the small polaron hopping in the nonadiabatic regime [12]. The site energy difference, W_D, does not change with the vanadium oxide content in the glass compositions in agreement with the results obtained from the structural studies of the glasses [10]. The values of the optical phonon frequency, ν_0, are also consistent with those obtained from the infrared spectra [10]. It is also noteworthy that the values of the polaron binding energy increase with the decrease of the vanadium oxide content in the glass compositions in agreement with the values of the activation energy (table 2).

4. Conclusions

Mott's optical phonon assisted hopping model of small polarons provides unreasonably low values of the localization length. However, Mott's variable range hopping model seems valid at lower temperatures. The Schnakenberg model yields high values of the hopping energy. The small polaron hopping model of Emin which considers the strong interaction of electrons with both the optical and acoustical phonons is consistent with the temperature dependence of the dc conductivity in the entire temperature range of measurements. Reasonable values of the transfer integral, disorder energy etc were obtained from the fits of this model to the experimental data.

Acknowledgment

The financial support for this work by the CSIR (India) via grant No 3(772)/95-EMR-II is gratefully acknowledged.

References

[1] Sayer M and Mansingh A 1972 *Phys. Rev.* B **6** 4672
[2] Chung C H, Mackenzie J D and Murawski L 1979 *Rev. Chem. Miner.* **16** 308
[3] Shimakawa K 1989 *Phil. Mag.* B **60** 377
[4] Ghosh A 1989 *J. Phys.: Condens. Matter* **1** 7819
[5] Ghosh A and Chackraborty D 1993 *Phys. Rev.* B **48** 5167
[6] Ghosh A 1990 *Phys. Rev.* B **42** 5665
[7] Ghosh A 1995 *J. Chem Phys.* **102** 1385
[8] Hazra s and Ghosh A 1995 *J. Chem. Phys.* **103** 6270
[9] Murawski L, Chung C H and Mackenzie J D 1979 *J. Non-Cryst. Solids* **32** 91
[10] Sen S and Ghosh A to be published
[11] Mott N F 1968 *J. Non-Cryst. Solids* **1** 1
[12] Austin I G and Mott N F 1969 *Adv. Phys.* **18** 41
[13] Mott N F and Davis E A 1979 *Electronic Processes in Non-Crystalline Materials* 2nd edn (Oxford: Clarendon)
[14] Schnakenberg J 1968 *Phys. Status Solidi* **28** 623
[15] Emin D 1974 *Phys. Rev. Lett.* **32** 303
Emin D 1975 *Adv. Phys.* **24** 305
[16] Gorham-Bergeron E and Emin D 1977 *Phys. Rev.* B **15** 3665