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Hopping conduction in calcium vanadate semiconducting glasses

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Abstract. The temperature and compositional dependences of the electrical conductivity of semiconducting calcium 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. On the other hand, Mott's nearest neighbour hopping model at high temperatures yields smaller values of the localization length. Moreover, Mott's variable range hopping model is consistent with the low temperature data.

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 exclusively [1–8]. However, glasses formed with TM oxides as unique glass network formers [9] have not been studied so extensively [9, 10]. Generally, the electrical conduction in the TM oxide glasses occurs by the hopping of small polarons between two different valence states of the TM ions [1, 2, 5]. However, there exists a controversy over the nature of hopping mechanisms in different temperature and composition regions [8, 9]. The effect of glass forming oxides on the hopping conduction is not also fully resolved. Some authors [7] have shown that the activation energy of hopping conduction is affected by glass forming oxides. Recently, we have studied the glass formation and structure of alkaline earth vanadate glasses [11]. 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 V_2O_5 acts as a unique glass network former. In the present work we have studied electrical properties of the calcium vanadate glasses in wide composition and temperature ranges. It has been observed that the multiphonon assisted hopping of small polarons with strong interaction with optical as well as acoustical phonons is the dominant transport mechanism in the calcium vanadate glasses in sharp contrast to the results observed for the vanadate glasses formed with traditional network formers [1, 2].

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2. Experiment

Glass samples of compositions $(100 - x)\text{CaO} - x\text{V}_2\text{O}_5$ (table 1) were prepared from reagent grade CaCO_3 and V_2O_5 for $x = 50$ – 90 mol%. The appropriate mixtures of these chemicals in 10 g batches were melted in air in alumina crucibles in an electrical furnace at temperatures in the range 700 – 850 °C depending on composition. The melts were then quenched either by pressing between two brass plates or by pouring onto twin rollers 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 from DTA. X-ray diffraction and electron microscopic studies confirmed the amorphous nature of the samples [11]. The concentrations of the total (N) and reduced vanadium ions ($[\text{V}^{4+}]$) were determined from the glass composition and magnetic susceptibility measurements (Parc model 155) respectively. The average inter-site separation (R) between vanadium ions was estimated from the glass composition and density. The various physical parameters obtained for different glass compositions are displayed in table 1. It may be noted in table 1 that the reduced vanadium ion concentrations did not vary systematically with composition. This is due to the fact that redox reaction in the melts occurred for different duration of time, because the melts of different compositions were kept for different durations of time for homogenization at the melting temperatures.

Table 1. Density, total and reduced vanadium ion concentrations, average inter-site separation and glass transition temperatures of different compositions of $(100 - x)\text{CaO} - x\text{V}_2\text{O}_5$ glasses.

| Composition x (mol%) | Density (g cm^{-3}) | N (10^{22} cm^{-3}) | $[\text{V}^{4+}]$ (10^{20} cm^{-3}) | R (Å) | T_g (°C) |
|---------------------------|-----------------------------------|--------------------------------------|--|------------|---------------|
| 90 | 2.94 | 1.88 | 7.83 | 3.76 | 225 |
| 80 | 2.96 | 1.82 | 11.40 | 3.80 | 265 |
| 70 | 3.00 | 1.75 | 8.19 | 3.85 | 270 |
| 60 | 3.03 | 1.66 | 9.54 | 3.92 | 285 |
| 50 | 3.08 | 1.50 | 4.10 | 4.05 | 370 |

Gold electrodes were deposited on both surfaces of the polished samples by vacuum evaporation for electrical measurements. 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 (mode 617). Before measurement the absence of barrier layers at the contacts were 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 to 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 – 300 K with a stability of ± 0.5 K.

3. Results and discussion

The electrical conductivity for different glass samples listed in table 1 is shown in figure 1 as a function of T^{-1} . First, we observe in the figure that the activation energy decreases with the decrease in temperature. However, above about 250 K, the activation energy may be assumed constant. The high temperature activation energies were calculated at the highest temperature range and are shown in table 1. The composition dependence of the conductivity at 373 K and the activation energy calculated at high temperatures is shown in figure 2. It is also observed

in the figure that the conductivity decreases while the activation energy increases with the decrease of vanadium oxide content in the glass compositions.

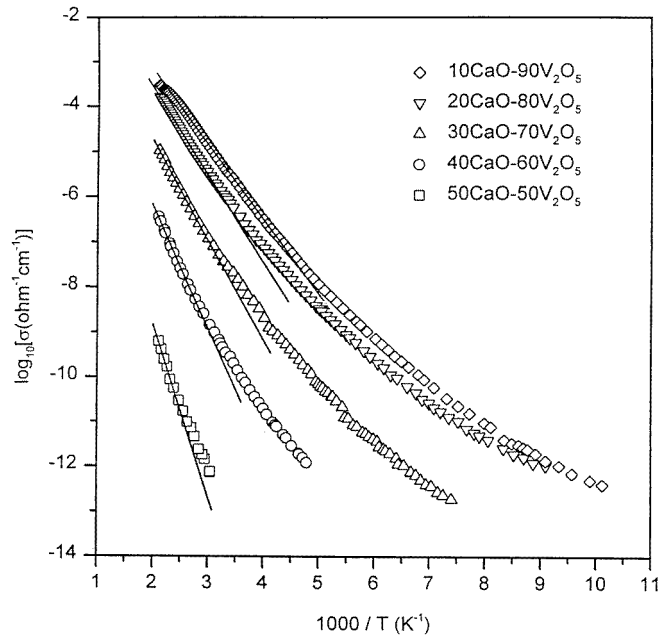


Figure 1. The dc conductivity as a function of T^{-1} for different compositions (shown) of the calcium vanadate glasses. The solid lines are the best fits to equation (1).

The dc conductivity data of the TM oxide glasses [1, 2, 4–6] at high temperatures have been interpreted in terms of Mott's model [12] of optical phonon-assisted hopping between nearest neighbours, while Mott's variable range hopping model [13] was used to explain the low temperature conductivity data. At high temperatures ($>\theta_D/2$) the dc conductivity in this model for the nearest neighbour hopping is given by

$$\sigma = v_0 [e^2 C (1 - C) / k T R] \exp(-2\alpha R) \exp(-W/kT) \quad (1)$$

where v_0 is the optical phonon frequency, C is the fraction of reduced vanadium ion, α^{-1} is the localization length for the wave function, 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 [13],

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

where W_H is the hopping energy and 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 observe in figure 1 an approximate linearity in the $\log \sigma$ versus $10^3/T$ plot predicted by Mott's model [12] in a limited high temperature range. We have fitted Mott's model [12] (equation (1)) to the experimental data in this temperature range (the solid lines in figure 1). Using the values of the parameters given in table 1 we have calculated the values of localization length α^{-1} , which are shown in table 2. It may be observed that the values of α^{-1} appear much lower than those ($\approx 10 \text{ \AA}$) obtained for other glasses [14].

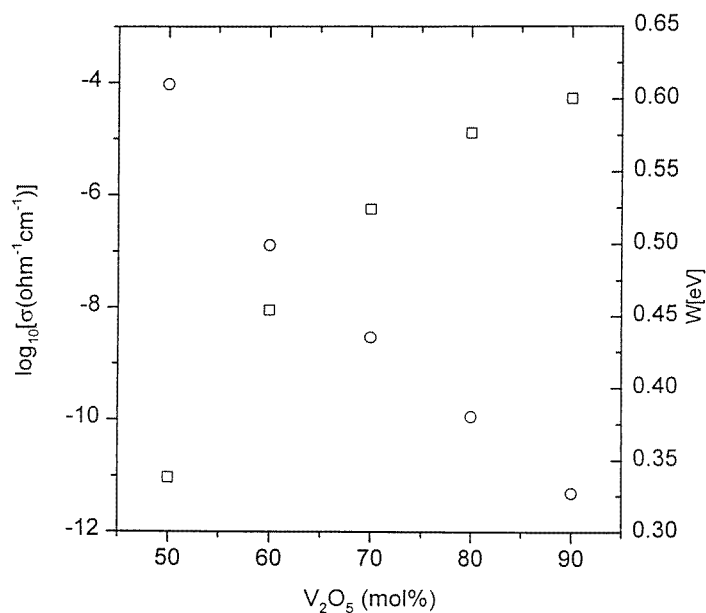


Figure 2. Variation of $\log_{10} \sigma$ (\square) and W (\circ) at a temperature of 373 K with composition.

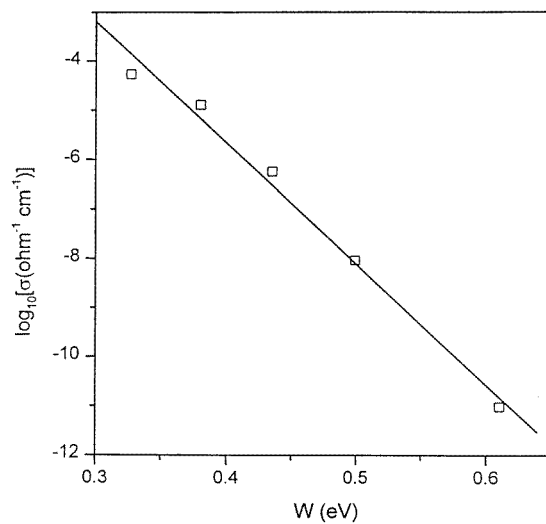


Figure 3. A plot of $\log_{10} \sigma$ versus W at 373 K. The solid line is the least squares straight line fit to the data.

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 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 is close to the experimental temperature. Otherwise, the hopping would be in the nonadiabatic regime. In this way, the

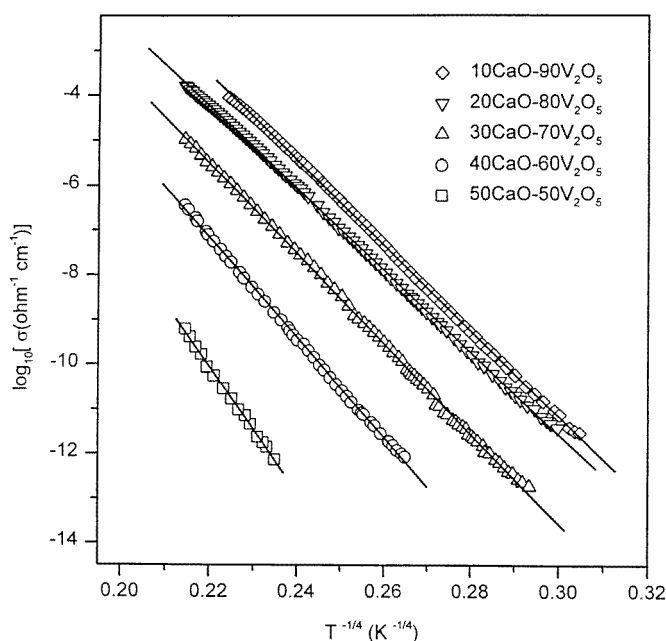


Figure 4. A plot of $\log_{10} \sigma$ versus $T^{-1/4}$ for different glass compositions as shown in figure 1. The solid lines are the best fits to equation (3).

hopping of small polarons was inferred to be in the adiabatic regime for the TM oxide glasses formed with traditional glass formers [1, 2, 4, 6]. A plot of $\log_{10} \sigma$ at 373 K versus W is shown in figure 3 for different compositions of the CaO–V₂O₅ glasses. A least squares straight line fit to the data yields a temperature of 204 K, which is largely different from the experimental temperature. Thus the hopping in the CaO–V₂O₅ glasses can be described by the nonadiabatic process in contrast to traditional vanadate glasses [1, 2, 4].

Table 2. Activation energy calculated at high temperatures, localization length and the density of states at the Fermi level obtained from hopping models for different compositions of (100 – x)CaO– x V₂O₅ glasses.

| Composition x (mol%) | W (at higher temperatures) (eV) | α^{-1} (Å) | $N(E_F)$ (eV ⁻¹ cm ⁻³) |
|---------------------------|--|----------------------|--|
| 90 | 0.33 | 0.28 | 2.75×10^{18} |
| 80 | 0.38 | 0.28 | 3.22×10^{18} |
| 70 | 0.44 | 0.28 | 2.19×10^{18} |
| 60 | 0.50 | 0.28 | 1.46×10^{18} |
| 50 | 0.61 | 0.27 | 5.88×10^{17} |

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

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

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

$$T_0 = 16\alpha^3 / kN(E_F) \quad (4)$$

where $N(E_F)$ is the density of states at the Fermi level. We have shown in figure 4 the dc conductivity as a function of $T^{-1/4}$ which indicates linearity in a considerable temperature range. Equation (3) was fitted to the data in figure 4 and, assuming a reasonable value of $\alpha^{-1} \approx 10 \text{ \AA}$, the 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] and the other semiconducting glasses [14].

The most general small polaron hopping model has been proposed by Emin and coworkers [15, 16] considering 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

$$\sigma = (Ne^2R^2/6kT)(J/\hbar)^2[\pi\hbar^2/2(E_c^{op} + E_c^{ac})kT]^{1/2} \times \exp[-\{W_D^2/8(E_c^{op} + E_c^{ac})kT\} - W_D/kT] \exp[-(E_A^{op} + E_A^{ac})/kT] \quad (5)$$

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

$$\begin{aligned} E_c^{op} &= (\hbar^2/4kT)(1/N_p) \sum_q (2E_b^{op}/\hbar\omega_{q,0}) \operatorname{cosech}(\hbar\omega_{q,0}/2kT) \omega_{q,0}^2 \\ E_c^{ac} &= (\hbar^2/4kT)(1/N_p) \sum_q (2E_b^{ac}/\hbar\omega_{q,a}) \operatorname{cosech}(\hbar\omega_{q,a}/2kT) \omega_{q,0}^2 \\ E_A^{op} &= kT(2E_b^{op}/\hbar\omega_{q,0}) \tanh(\hbar\omega_0/2kT) \\ E_A^{ac} &= kT(1/N_p) \sum_q (2E_b^{ac}/\hbar\omega_{q,a}) \tanh(\hbar\omega_{q,a}/2kT) \end{aligned} \quad (6)$$

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 (5) and (6) 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 glass compositions. The values of the parameters E_b^{op} , E_b^{ac} , W_D and J and ν_0 for the best fits are shown in table 3 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 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 [13]. The site energy difference, W_D , differs slightly from the low temperature activation energies. The values of the optical phonon frequency, ν_0 , are also consistent with those obtained from the infrared spectra [11]. It is also noteworthy that the values of the polaron binding energy increase with decrease of the vanadium oxide content in the glass compositions, consistent with the composition dependence of the high temperature 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

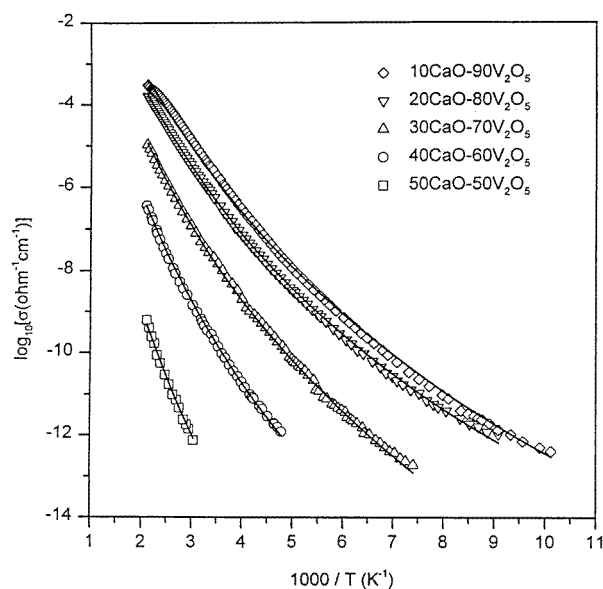


Figure 5. Best fits (solid curves) of the Emin model (equation (5)) to the experimental data for different glass compositions shown in the figure.

Table 3. Parameters obtained from the fits of the experimental data to the multiphonon assisted hopping models for different compositions of $(100 - x)\text{CaO} - x\text{V}_2\text{O}_5$ glasses.

| Composition x (mol%) | E_b^{op} (eV) | E_b^{ac} (eV) | J (eV) | W_D (eV) | ν_0 (10^{13} s^{-1}) |
|---------------------------|--------------------|--------------------|-------------|---------------|---|
| 90 | 0.59 | 0.43 | 0.034 | 0.070 | 2.2 |
| 80 | 0.65 | 0.42 | 0.021 | 0.077 | 2.4 |
| 70 | 0.73 | 0.51 | 0.013 | 0.070 | 2.6 |
| 60 | 0.82 | 0.75 | 0.010 | 0.026 | 3.1 |
| 50 | 0.90 | 0.85 | 0.001 | 0.095 | 3.0 |

valid at lower temperatures. The small polaron hopping model of Emin 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. This model also provides additional evidence for the nature of the hopping mechanism.

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References

- [1] Sayer M and Mansingh A 1972 *Phys. Rev. B* **6** 4629
- [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. Phys. Chem.* **102** 1385
- [8] Murawski L, Chung C H and Mackenzie J D 1979 *J. Non-Cryst. Solids* **32** 91
- [9] Hazra S and Ghosh A 1995 *J. Chem. Phys.* **103** 6270
- [10] Sen S and Ghosh A 1999 *J. Phys.: Condens. Matter* **11** 1529
- [11] Sen S and Ghosh A unpublished
- [12] Mott N F 1968 *J. Non-Cryst. Solids* **1** 1
- [13] Austin I G and Mott N F 1969 *Adv. Phys.* **18** 41
- [14] Mott N F and Davis E A 1979 *Electronic Processes in Non-Crystalline Materials* 2nd edn (Oxford: Clarendon)
- [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