

DC electrical properties and non-adiabatic small polaron hopping in V_2O_5 -CdO-ZnO glass nanocomposites

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Semiconducting transition metal oxide (TMO) doped glass nanocomposites $xV_2O_5-(1-x)$ (0.05CdO-0.95ZnO), $x=0.3, 0.5, 0.7$ and 0.9 have been prepared by melt quenching method. DC electrical conductivity of as prepared glass nanocomposites is investigated over a wide temperature range. Formation of small polarons has been confirmed from dc electrical conductivity experimental data, whereas conductivity is due to mainly polaron hopping from V^{+4} to V^{+5} valence state in these glassy systems. Temperature dependent conductivity data have been analyzed using the small polaron hopping (SPH) model. Low, high temperature activation energy, optical phonon frequency and Debye's temperature have been determined. Conductivity data have been analyzed in view of Mott's variable range hopping (VRH) models and Greaves VRH models; the density of states at the Fermi level has been evaluated. Various polaron hopping parameters such as polaron radius, polaron binding energy, polaron band width and polaron coupling constant (γ_p) have been estimated. It has been ascertained by these estimated quantities and different approaches that the nature of hopping conduction is non-adiabatic variable range hopping of small polarons. The evaluated values of hopping carrier mobility (μ) and hopping carrier concentration (N_c) are found to depend on composition and temperature.

Keywords: DC conductivity, Activation energy, Density of states, Polaron band width, Electron-phonon coupling constant, Hopping carrier mobility, Hopping carrier concentration

1 Introduction

During last few decades, TMO doped glasses have drawn much attention because of their wide applications in electrochemical, electronic and electro-optical devices^{1,2}. The dc conductivity of TMO doped glasses has been investigated for extensive studies³⁻⁵ because of their alluring semiconducting properties. Vanadate glasses have been extensively studied⁶⁻⁹ more than glasses containing other transition metals^{1,7,10}. The vanadate glasses have great technological applications such as in switching and memory devices⁶. V_2O_5 acts as both network former and modifier. The conduction mechanism in TMO doped glasses has been supposed to be by the small polaron hopping (SPH) model^{11,12} where the excess charge carriers coupled with distortions of nearby ions. Hence, the excess charge carriers become localized and the consequent deformation induced in the surrounding oxygen ions

can be regarded as a pseudo particle called small polaron. Further, the small polarons coupled with lattice ions and later they are linked to phonons. Therefore, small polaron transport in solids is associated with the strength of localization and coupled nature of phonons. The transfer of these small polarons from an occupied site to a neighboring unoccupied site can be thermally activated by a hopping or tunneling process depending on the temperature region considered. A general condition for the semi-conducting behavior is the ability of transition metal ions to coexist in more than one valence state, for instance V^{4+} and V^{5+} in vanadate glassy systems^{1,13}, so that the conduction can take place by transfer of electrons from a low to a high valence state. Polaron formation is an indispensable reason for modeling a temperature dependent conductivity and transport mechanisms of TMO doped glass nanocomposites. It has been suggested by Murawski *et al.*² that the thermal activation energy for conduction happens to be the dominating factor

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which controls the conductivity, but in many cases the pre-exponential factor has a great influence on conductivity too. Different theoretical models such as Mott's variable range hopping (VRH)^{12,14} at temperature below half of Debye's temperature ($\theta_D/2$) and Greaves VRH models¹⁵ at temperature above half of Debye's temperature ($\theta_D/2$) can be implemented to understand temperature dependence of conductivity. In the glassy systems^{16,17} $V_2O_5-Fe_2O_3-TeO_2$ and $V_2O_5-NiO-TeO_2$ electron overlap integral between neighboring sites is of significance and the hopping of small polarons exhibits an adiabatic character. On the other hand, in the systems^{18,19} $V_2O_5-Bi_2O_3-SrTiO_3$ and $V_2O_5-B_2O_3$ hopping is non-adiabatic in nature.

In this paper, we have reported the DC electrical conductivity of $xV_2O_5-(1-x)$ (0.05CdO-0.95ZnO), $x=0.3, 0.5, 0.7$ and 0.90 glass nanocomposites in terms of small polaron hopping (SPH) model. We have determined activation energy, optical phonon frequency and Debye's temperature from temperature dependent dc conductivity data. We have also estimated various polaron hopping parameters, hopping carrier mobility (μ) and hopping carrier concentration (N_C) of the as prepared glass nanocomposites.

2 Experimental Details

We have prepared TMO doped semiconducting glassy samples with composition $xV_2O_5 - (1-x)$ (0.05 CdO - 0.95 ZnO), $x=0.30, 0.50, 0.70$ and 0.90 by conventional melt quenching technique. We have used proper molar ratio of precursors vanadium pentoxide (V_2O_5) (purity 99.9%, Loba Chemie), cadmium oxide (CdO) (purity 99.5%, sigma aldrich) and zinc oxide (ZnO) (purity 99.9%, loba chemie). The precursors in proper amounts are weighed, thoroughly mixed and ground in an agate mortar. The mixture has been transferred into an alumina crucible and then kept in a high temperature muffle furnace and heated up to the temperature range from $770^\circ C$ to $900^\circ C$ depending upon the composition. In order to get the homogeneous glass, the melt has been held at maximum temperature for half an hour and then rapidly poured out onto an aluminium plate held under atmospheric conditions and pressed by another aluminium plate immediately. The average thickness of the glassy samples thus obtained are $\sim 0.28-0.88$ mm. Density (ρ) of the glassy samples has been measured by Archimedes principle using acetone as an immersion liquid. For electrical measurements

both sides of the sample are coated with silver paste to serve as the electrode. The resistance of the silver paste coated samples is measured using Metravi made digital meter at various temperatures and the measurements have been made by two-probe method.

3 Results and Discussion

DC electrical conductivity spectra of prepared glassy nanocomposites as a function of reciprocal temperature is shown in Fig. 1(a). All glassy samples exhibit a smooth variation of the conductivity. In Fig. 1(a) it can be seen clearly, the temperature dependent dc conductivity data show typical polaronic type^{20, 21} behavior with different activation energies depending on the temperature region. It is also ascertained from Fig. 1(a) that dc conductivity for all the glass compositions increases with increasing temperature, indicating typical semiconducting behavior. It is also found in Fig. 1(a) that dc electrical conductivity increases with

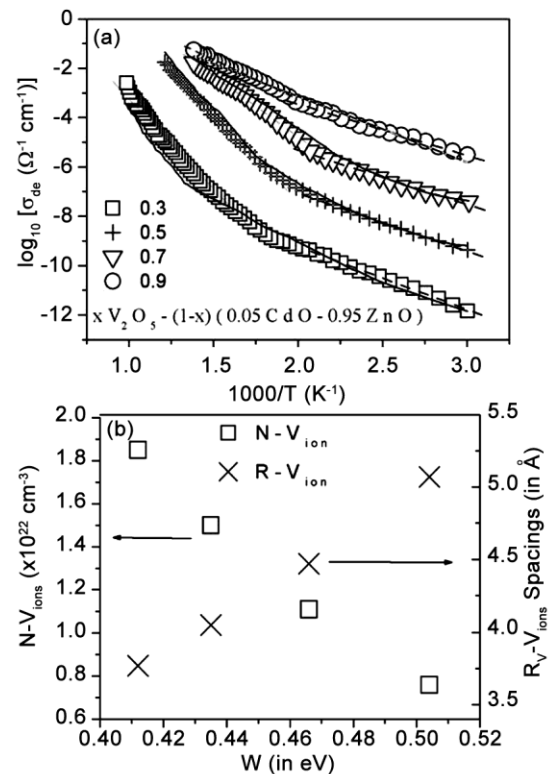


Fig. 1 – (a) The reciprocal temperature dependence of DC electrical conductivity for glass nanocomposites $xV_2O_5-(1-x)$ (0.05CdO-0.95ZnO), $x = 0.30, 0.50, 0.70$ and 0.90 . The 3-point segment lines are best linear fit data and solid lines are best fit of Schnakenberg model (Eq. 5) and (b) effect of mean V-ion site spacing (R_V) and concentration of V-ions (N_{V-ions}) on activation energy (E_A) for all the studied glass nanocomposites.

increasing V₂O₅ concentration in these as prepared glassy samples. We can separate the distinct regions where the slope gets changed and however, in high and low temperature region, the activation energy (E_A) has been computed from the slope of the plot as shown in Fig. 1(a) by 3–point segment lines and the values are listed in Table 1. From Table 1, it is ascertained that the activation energy shows negative correlation with dc conductivity which is consistent with small polaron hopping theory. Based on the evaluated activation energy (E_A) values, hopping transport over energy barrier is the only essential movement in the dc conduction process of the glass nanocomposites under study with the charge carriers thermally activated.

Mott²¹ theoretically investigated most favorable hopping conduction in TMO doped glasses in terms of phonon-assisted hopping of small polarons between localized states and obtained the following expression for dc conductivity for the nearest neighbor hopping in the non-adiabatic regime at high temperature (T > θ_D/2) is expressed^{11,21} by:

$$\sigma_{dc} = [(v_0 N e^2 R_V^2) / K_B T] [C (1 - C)] [\exp (-2\alpha R_V)] [\exp (-E_A / K_B T)] \dots (1)$$

and pre-exponential factor σ₀ of Eq. 1 in non-adiabatic regime can be expressed as:

$$\sigma_0 = [(v_0 N e^2 R_V^2) / K_B] [C (1 - C)] [\exp (-2\alpha R_V)] \dots (2)$$

where, v₀ is the longitudinal optical phonon frequency, R_V is the distance between two neighboring V-ions, α is the inverse localization length that is assumed to describe the localized states at each transition metal ion site or tunneling factor (the ratio of wave function decay), C is the fraction of sites occupied by an electron or polaron, N is the transition metal ion density, e is the electronic charge, K_B is the Boltzmann constant and E_A is the activation energy for hopping conduction. As the behavior of the dc conductivity data show the presence of two regions (as shown in Fig. 1(a)), one at relatively low

temperature, while the other appears at high temperature. The change in these two regions is almost linear and these two linear lines intersect at definite temperature (T_X) differ from one sample to another. According to Hirashima²²:

$$T_X = \theta_D / 2 \dots (3)$$

where, θ_D is the characteristic Debye temperature which characterizes the vibrational spectrum of a poly crystalline material, that defined¹⁴ by:

$$h \nu_0 = K_B \theta_D \dots (4)$$

where, h is Planck’s constant, ν₀ is the optical phonon frequency and K_B is Boltzmann constant. The obtained θ_D and ν₀ values are tabulated in Table 1. The polaron transport in solids is closely related to a certain type of phonon mode with specific phonon energy. These phonons are actually longitudinal optically (LO) active phonons with the frequency range of 10¹³–10¹⁴ Hz. With increasing value of θ_D, the optical phonon frequency increases so, the vibrational amplitude of the glass network also increases.

Schnakenberg²³ has proposed a polaron hopping model, where polaron disordered energy, W_D ≠ 0, where the optical multiphonon hopping process determines high temperature dc conductivity, while the acoustical single phonon assisted hopping process is responsible for low temperature dc conductivity. According to Schnakenberg’s model the temperature dependent dc conductivity is given by the relation:

$$\sigma = T^{-1} [\sinh (h\nu_0 / K_B T)]^{1/2} \exp [(-4W_H / h\nu_0) \tanh (h\nu_0 / 4K_B T)] \exp (W_D / K_B T) \dots (5)$$

It may be noted that Eq. 5 predicts a temperature dependent hopping energy which increases with an increase in temperature in consistence with the data presented in Fig. 1(a). In Fig. 1(a), the dc conductivity has been fitted to the theoretical values given by this model Eq. 5 and the solid lines in Fig. 1(a) shows the best fit data of Schnakenberg model. In the fitting

Table 1 – Density (ρ), low T & high T activation energy (E_A), concentration of V ion (N_{V-ions}), mean V_{ion} spacing (R_V), polaron radius (R_p), optical phonon frequency(ν₀), Debye temperature (θ_D) and density of state at Fermi level (N(E_F)) for glass nanocomposites xV₂O₅ – (1–x) (0.05 CdO–0.95 ZnO), where x = 0.30, 0.50, 0.70 and 0.90.

X (mol %)	Density ρ (gm/cm ³)	Low T activation energy E _A ^{LT} (eV)	High T activation energy E _A ^{HT} (eV)	N _{v-ions} (x 10 ²² cm ⁻³)	R _v (Mean V _{ion} spacing) (in Å)	R _p (Polaron radius) (in Å)	ν ₀ (optical phonon frequency) (10 ¹³ S ⁻¹)	θ _D (Debye temperature) (K)	N (E _F) (x 10 ²¹ eV ⁻¹ cm ⁻³)
0.3	3.852	0.50	1.44	0.76	5.07	2.05	1.93	927	3.75
0.5	3.380	0.46	1.39	1.11	4.47	1.80	1.97	946	5.66
0.7	3.248	0.43	0.97	1.51	4.05	1.63	2.01	966	8.34
0.9	3.118	0.41	0.63	1.85	3.77	1.52	2.05	986	11.3

process, optical phonon frequency (ν_0), polaron hopping energy (W_H) and disordered energy (W_D) are used as variable parameters. The best fits of the data have been obtained and the values of those parameters are shown in Table 2. It may be noted that the values of ν_0 are higher than the values obtained from dc electrical conductivity. It is observed from Schnakenberg model and dc electrical conductivity data that with increasing value of optical phonon frequency (ν_0), polaron hopping energy (W_H), and the conductivity of the presently studied glassy samples also increase.

LO active Phonon assisted hopping of electron accompanies a valence change between V^{4+} and V^{5+} in these glassy systems. In hopping process, the distance between two neighboring V-ions (R_V) affects activation energy for conduction and thus, dc electrical conductivity. The activation energies of conduction show a strong dependence on the mean V-ion spacing (R_V) for presently studied glassy systems. In order to confirm the relation between activation energy (E_A) and mean V-ion spacing (R_V) in the present studied glass compositions, the V-ion density ($N_{V\text{-ions}}$) has been calculated²⁴ using the following formula:

$$N_{V\text{-ions}} = 2 * (d * Wt V_2O_5 / Mw V_2O_5) N_A \quad \dots (6)$$

where, d is the density, $Wt V_2O_5$ is the weight percentage of V_2O_5 , $Mw V_2O_5$ is the molecular weight of V_2O_5 and N_A is Avogadro's number. The calculated values are enlisted in Table 1. The mean spacing (R_V) between any two V-ions also calculated²⁴ from the relationship:

$$R_V = (1 / N_{V\text{-ions}})^{1/3} \quad \dots (7)$$

The variation of activation energy (E_A) with mean V-ion Spacing (R_V) and with V-ion density ($N_{V\text{-ions}}$) for the presently studied glassy systems is shown in Fig. 1(b). It is ascertained from Fig. 1(b) that the activation energy decreases as the mean spacing

between two V-ions (R_V) decreases which makes dc conductivity of present glassy systems to increase. It is also observed from Fig. 1(b) that as the V-ion density ($N_{V\text{-ions}}$) increases, mean V-ion spacing (R_V) decreases which makes dc conductivity of the present glassy systems to increase due to formation of more non-bridging oxygen in the glassy matrix. Similar, results are found for other glassy systems^{4,17}. The above-mentioned results for the glassy systems under study indicate the confirmation of the dependence of the activation energy on the mean spacing between two V-ions (R_V) suggesting small polaron hopping between V-ions. Using the mean V-ions spacing (R_V) calculated from Eq. 7, the polaron radius R_p is calculated according to the following relation²⁵ and the calculated values of R_p are tabulated in Table 1:

$$R_p = (\pi/6)^{1/3} * (R_V / 2) \quad \dots (8)$$

It is ascertained from Table 1 that as the dc conductivity of the as prepared glassy systems increases, radii of polaron decreases. The density of state at the Fermi level can be estimated²⁶ from the following expression:

$$N(E_F) = 3 / (4\pi R_V^3 E_A) \quad \dots (9)$$

The results for the present glasses are listed in Table 1. The values of $N(E_F)$ are reasonable for localized states. It is ascertained from Table 1 that as the conductivity increases the value of density of state at Fermi level $N(E_F)$ also increases, this kind of behaviour is expected.

According to Mott and Davis²⁶, the hopping of charge carriers is described by the nearest-neighbor hopping. On the other hand, at sufficiently low temperatures ($T < \theta_D/2$), hopping may preferentially occur beyond the nearest neighbors by variable range hopping (VRH) process. At temperatures below $\theta_D/2$, Mott proposed a variable range hopping model. The mathematical expression of variable range hopping conductivity²⁷ is given by:

Table 2 – DC conductivity ($\log \sigma_{dc}$) at 373 K, the value of $N(E_{FM})$ using Mott's model (Eq. 11), $N(E_{FG})$ using Greaves model (Eq. 14) and parameters obtained by fitting the conductivity data to the Schnakenberg polaron hopping model (Eq. 5) for glass nanocomposites $xV_2O_5-(1-x)$ (0.05 CdO-0.95 ZnO), where $x=0.3, 0.5, 0.7$ and 0.90 .

X (mol %)	Log σ_{dc} ($\Omega^{-1} cm^{-1}$) at 373 K	$N(E_{FM})$ ($\times 10^{28}$)	$N(E_{FG})$ ($\times 10^{28}$)	R_{hop} (nm) (at 400 K)	W_{hop} (μeV) (at 400 K)	ν_0 (Phonon frequency) ($\times 10^{13} S^{-1}$)	W_H (Hopping energy) (eV)	W_D (Disorder Energy) (eV)
		Mott model ($eV^{-1} cm^{-3}$)	Greaves model ($eV^{-1} cm^{-3}$)					
0.3	-10.98	2.54	0.32	7.72	28.4	2.76	0.77	0.026
0.5	-8.74	3.58	0.42	7.03	25.9	6.38	0.80	0.022
0.7	-6.77	4.77	0.58	6.50	23.9	9.35	0.82	0.065
0.9	-4.78	6.21	3.01	5.67	20.9	15.3	0.85	0.084

$$\sigma_{dc} = B \exp [-A / T^{1/4}] \quad \dots (10)$$

$$\text{where, } A = 4 [2\alpha^3 / 9\pi K_B N(E_{FM})]^{1/4} \quad \dots (11)$$

$$\text{and } B = [e^2 / 2(8\pi)^{1/2}] v_0 [N(E_{FM}) / \alpha K_B T]^{1/2} \quad \dots (12)$$

Here, $N(E_{FM})$ is the density of states of charge carriers at the Fermi level using Mott model. In Fig. 2(a), dc conductivity at low temperature is plotted against $T^{-1/4}$. The experimental data are fitted to Eq. 10 in Fig. 2(a). Using the value of $\alpha^{-1} = 10 \text{ \AA}$ for localized states²⁶ using the slope (as shown in Fig. 2(a) by solid lines) obtained from this linear relation the value of $N(E_{FM})$ has been estimated from Eq. 11 and values are presented in Table 2. The value of $N(E_{FM})$ is found to increase with x , which justifies dc conductivity data. These values appear higher than those for the other vanadate glasses^{28,29}. These results suggest that increasing content of V_2O_5 must be playing an important role in the conduction process.

The temperature dependence of dc conductivity at high temperatures ($T > \theta_D/2$), cannot be met using Mott's model. However, Greaves³⁰ predicts a temperature dependent variable range hopping which is dominant in this region. His derived mathematical

expression of variable range hopping conductivity is given by:

$$\sigma_{dc} T^{1/2} = A \exp [-B / T^{1/4}] \quad \dots (13)$$

where, A and B are constants and B is given by: $B = 2.1 [\alpha^3 / K_B N(E_{FG})]^{1/4} \dots (14)$

The plot of $\log(\sigma T^{1/2})$ against $T^{-0.25}$ is shown in Fig. 2(b). It may be noted in Fig. 2(b) that Greaves model yields good fits to the data. Using the value of $\alpha^{-1} = 10 \text{ \AA}$ for localized states²⁶, using the slope (as shown by solid lines in Fig. 2(b)) obtained from this linear relation the value of $N(E_{FG})$ has been estimated from Eq. 14 and values are tabulated in Table 2. The value of $N(E_{FG})$ is also found to increase with x , which once again confirms dc conductivity data. It should be noted from Table 2 that the values of $N(E_{FM})$ and $N(E_{FG})$ that are obtained from two models are close to each other though they are operative in different temperature ranges. It is obvious that at high temperature due to thermal agitation the LO active phonon assisted polaron hopping occurs and probable collision between phonon and nanoclusters takes place inside the glassy samples under investigation. Due to collision, a part of energy may loss, which keeps the values of $N(E_{FM})$ and $N(E_{FG})$ close to each other.

Using the value of $N(E_{FM})$, the hopping parameters, the temperature-dependent hopping distance R_{hop} and average hopping energy²⁶ W_{hop} are given as:

$$R_{hop} = [9 / (8\pi N(E_{FM}) \alpha K_B T)]^{(1/4)} \quad \dots (15)$$

$$\text{and } W_{hop} = [3 / 4\pi R_{hop}^3 N(E_{FM})] \quad \dots (16)$$

The values of R_{hop} and W_{hop} are obtained at 400 K for all the glass nanocomposites and values are tabulated in Table 2. In the VRH model, dc conduction takes place in such a way that the thermally activated charge carriers rather execute distant hops to find out a potential localized state of close energy within the range of $[R_{hop}, N(E_{FM})]$ so that a minimum energy separation between the interactive localized states is achieved. The VRH requirements $R_{hop} \alpha \geq 1$ and $W_{hop} > K_B T$, necessary for the validity of Mott's VRH model, are satisfied. Figure 3 shows the variation of R_{hop} and W_{hop} as a function of V_2O_5 concentration, it is found that with increasing V_2O_5 content the value of R_{hop} and W_{hop} decreases, while dc conductivity increases.

It is well known that the typical feature of SPH is either associated with adiabatic or non-adiabatic mechanism in which a clear insight into the interaction of lattice distortion coupled with small

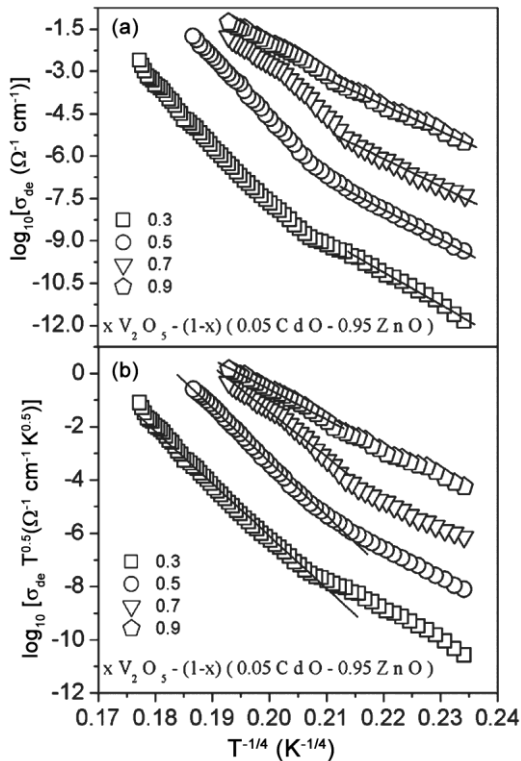


Fig. 2 – (a) Variation of dc conductivity as a function of $T^{-0.25}$ (Mott model), solid lines indicate the best fitted straight line fit and (b) variation of $\sigma_{dc} T^{1/2}$ as a function of $T^{-0.25}$ (graves model), solid lines indicate the best fitted straight line fit.

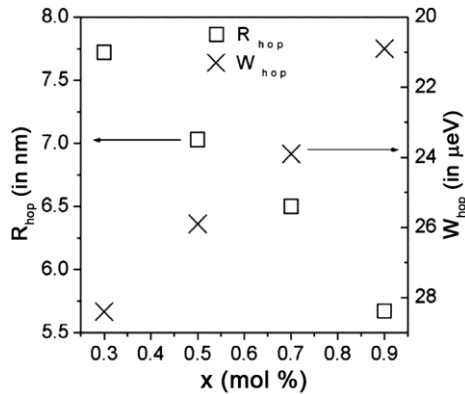


Fig. 3 – The temperature–dependent hopping distance, R_{hop} and average hopping energy W_{hop} of all the glass nanocomposites.

polaron motion is highlighted. Assuming a strong electron-phonon interaction, Austin and Mott³¹ showed that the activation energy for the jump of polarons between nearest neighbors is defined by the relation:

$$E_A = W_H + W_D / 2 \text{ for } T > \theta_D / 2 \quad \dots (17)$$

$$= W_D \text{ for } T < \theta_D / 4 \quad \dots (18)$$

where, θ_D is Debye temperature, W_H is the polaron hopping energy or polaron forming energy which is equal to $W_P/2$, W_P is polaron binding energy and W_D is disorder energy arising from the energy difference between two neighboring sites due to variation in the local arrangement of ions. Mott suggested that in the dominant process, activation energy decreases due to interaction between polarons and optical phonons. If Eq. 1 is totally dependent on V_2O_5 concentration, it is said to be in non-adiabatic regime and if it is independent of V_2O_5 content, it is said to be in adiabatic regime. In the case of adiabatic hopping, the tunneling term $\exp(-2\alpha R)$ in Eq. 1 reduces to unity and the conductivity^{1,27} is given by:

$$\sigma_{dc} = [(v_0 N e^2 R_V^2) / K_B T] [C (1 - C)] [\exp(-E_A / K_B T)] \quad \dots (19)$$

If Eq. 19 is independent of V_2O_5 concentration, then it indicates the adiabatic nature of hopping conduction^{32–34}. If it is found that the tunneling factor in Eq. 1, $\exp(-2\alpha R_V)$, is neither constant nor equal to one for different compositions of the glassy systems, as evidenced by the fact that σ_0 varies with composition, indicating thereby non-adiabatic nature of hopping conduction³⁵. The term of pre-exponential factor (σ_0) has been evaluated using the experimental values, namely the intercept of $\log \sigma_{dc}$ versus $(1000/T)$ plot at $(1000/T) = 0$ ¹. Figure 4(a) shows the

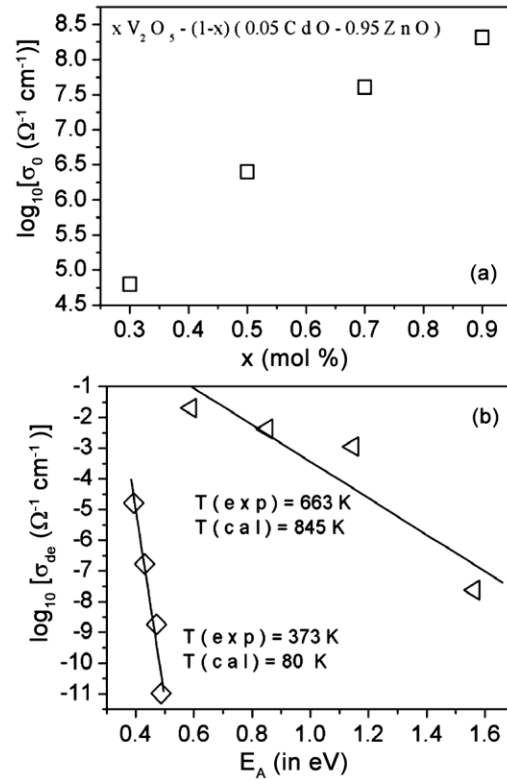


Fig. 4 – (a) Effect of V_2O_5 concentration on pre-exponential factor, σ_0 for different compositions of $xV_2O_5-(1-x)$ (0.05CdO–0.95ZnO), $x=0.30, 0.50, 0.70$ and 0.90 glass nanocomposites and (b) the dc conductivity at experimental temperatures (T) 373 K and 663 K versus the activation energy for all the glass nanocomposites. Symbols represent experimental data and solid lines represent the linear fit.

variation pre-exponential factor (σ_0) on V_2O_5 concentration. As previously discussed, we can conclude that the conduction is due to non-adiabatic small polaron hopping. It has been suggested that the hopping process should be of adiabatic type if the calculated temperature from the slope of $\log \sigma_{dc}$ vs E_A (activation energy) plots is close to experimental temperature, otherwise, the hopping would be of nonadiabatic type^{36,37}. Figure 4(b) shows plots of $\log \sigma_{dc}$ with E_A at two different experimental temperatures 373 K and 663 K. The corresponding values of calculated temperatures from slopes $(-1/2.303 \cdot K_B T)$ of these plots are found to be 80 K and 845 K, respectively, which are very much different from experimental temperatures. Therefore, the validity of the non-adiabatic polaron hopping conduction mechanism for the present studied glassy systems is justified. On the other hand, we can evaluate approximately the value of the tunneling factor, α , as the ratio of the wave function decay. According to

Eq. 2, α can be calculated from the slope of $\log \sigma_0$ with R_V (mean spacing between V_{ions}) plot¹, the result of such calculation is shown in Fig. 5(a), the value of slope is (-2α) . The obtained value of α is $1.361 \times 10^8 \text{ cm}^{-1}$, which is in the order of that for some other semiconducting glassy systems^{1,35}. Figure 5(b) show the plot of the mean site distance of V_{ion} (R_V) with different concentrations of V_2O_5 . The mean site

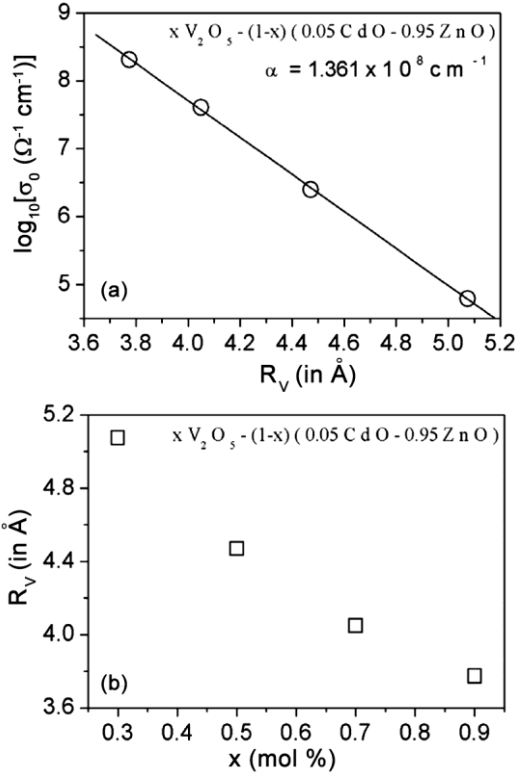


Fig. 5 – (a) Relationship between $\log \sigma_0$ and mean V-ion site spacing (R_V) for different compositions of $xV_2O_5-(1-x)$ (0.05CdO–0.95ZnO), $x= 0.30, 0.50, 0.70$ and 0.90 glass nanocomposites. Solid line represents linear fit data, the slope of these line is (-2α) and (b) relationship between mean V-ion site spacing (R_V) and V_2O_5 concentration (mol %) dependence of $xV_2O_5-(1-x)$ (0.05CdO–0.95ZnO), $x = 0.30, 0.50, 0.70$ and 0.90 glassy systems.

distance of V_{ion} (R_V) is found to decrease with increasing V_2O_5 content. Assuming that the conductivity is due to polaron hopping from V^{+4} to V^{+5} valence state, then with the decrease of average V_{ion} site separation (R_V) and the increase of dc conductivity is clearly expected and satisfied.

Alternatively, the nature of hopping mechanism may be determined by a small polaron hopping model suggested by Holstein³⁸. According to this model, the condition for the nature of hopping can be expressed using the following inequalities:

$$J > J^* \text{ adiabatic} \quad \dots (20)$$

$$J < J^* \text{ non-adiabatic} \quad \dots (21)$$

$$\text{where, } J^* = [(2 K_B T W_H / \pi)^{1/4}] [(hv_0 / \pi)^{1/2}] \quad \dots (22)$$

Here, J is the polaron bandwidth or transfer integral related to electron wave function overlap on the adjacent sites and W_H is polaron hopping energy. The values of W_H is obtained from the Eq. 17 taking the value of W_D from Schnakenberg model and J can be obtained^{36,37} the following relation:

$$J = [0.67 * hv_0] / [(T / \theta_D)^{1/2}] \quad \dots (23)$$

The values of J, J^* and W_H are listed in Table 3. According to Mott and Davis²⁶ at low temperatures, the polaron hopping energy W_H^* is given as:

$$W_H^* = W_H [\tanh (hv_0 / 4 K_B T)] / [(hv_0 / 4 K_B T)] \quad \dots (24)$$

Perusal of data listed in Table 3, reveals that the inequality Eq. 21 ($J < J^*$, non-adiabatic) is valid in the present studied glassy samples which in turn support our assertion that polaronic conduction in the present studied glassy systems is non-adiabatic in nature. Another supportive approach to the assertion of non-adiabatic polaron hopping conduction can be accomplished by estimating the dimensionless small polaron coupling constant. The small polaron coupling constant (γ_P), a measure of electron-phonon interaction^{38,39} is given by:

Table 3 – Polaron hopping parameters of $xV_2O_5-(1-x)$ (0.05 CdO–0.95 ZnO) where $x = 0.30, 0.50, 0.70$ and 0.90 glass nanocomposites at 373 K and comparing those data with $50V_2O_5-20Bi_2O_3-30ZnO$ glass and VN–PbO–TeO₂ glass.

Glass composition (x)	Parameters					
	W_H (eV)	J^*	J	W_H^* (eV)	γ_P	m_P / m^*
0.3	0.491	0.0505	0.0426	0.490	12.3	4.2×10^5
0.5	0.454	0.0500	0.0432	0.453	11.1	1.2×10^5
0.7	0.402	0.0490	0.0439	0.401	9.67	7.71×10^4
0.9	0.369	0.0485	0.0442	0.368	8.72	4.5×10^4
$50V_2O_5 - 20Bi_2O_3 - 30ZnO$	0.446	0.046	0.037	0.445	13.8	1.1×10^6
VN – PbO – TeO ₂	0.32	0.034	0.023	0.31	15.3	4.5×10^6

$$\gamma_P = 2 W_H / h\nu_0 \quad \dots (25)$$

The calculated values of γ_P are listed in Table 3 and it is found that the values of γ_P vary from 12.9 to 10.7 for all the glass nanocomposites under study, which indicate a very strong electron–phonon interaction, as $\gamma_P > 4$ indicates a strong electron–phonon interaction³⁷. Thus, it appears reasonable to conclude that a relatively strong coupling exists between electrons and lattice distortions in all the glass nanocomposites; that is, once again ensure the small polaron is essentially formed. However, it is also observed from Table 3 that this electron–phonon interaction decreases with increasing V₂O₅ content in the present studied glass compositions. The ratio of polaron mass (m_p) to rigid lattice effective mass³⁷ (m^*) is obtained by the relation:

$$m_p = [(h^2 / 8\pi^2 J R^2)] \exp(\gamma_P) = m^* \exp(\gamma_P) \quad \dots (26)$$

The evaluated values of m_p / m^* are very large for presently studied glass compositions and tabulated in Table 3. That is, once more time indicates strong electron–phonon interaction in those glassy systems. From Table 3 it is observed that the values of m_p / m^* decreases with increasing V₂O₅ concentration in those as prepared glassy systems. Scrutinizing of data listed in Table 3, it is ascertained that the values of polaron hopping parameters are temperature and composition dependent. We have also included polaron hopping parameters of 50V₂O₅ – 30Bi₂O₃ – 20ZnO³⁷ and VN – PbO – TeO₂⁴⁰ glassy systems for comparison in Table 3.

Finally, the expression of hopping carrier mobility (μ) for non-adiabatic polaron hopping conduction^{21,26,41} is given as:

$$\mu = [(eR^2J^2) / (h K_B T)] [(\pi / 4 W_H K_B T)^{1/2}] \exp[-W / K_B T] \quad \dots (27)$$

where, hopping carrier mobility (μ) values are calculated for all studied temperature range with the data of W, R, J and W_H given in Table 1 and 3. The values of μ at 373 K and at 703 K are listed in Table 4. The mobility (μ) of present glassy systems is very small, suggesting that electrons or polarons are localized at V-ions^{20,42}. Since, the conduction of localization for conductive electrons or polarons is generally $\mu < 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,⁴³ the hopping mechanism for conduction in this system of glasses are reconfirmed. Figure 6(a) shows the variation of hopping carrier mobility ($\log \mu$) with temperature (T) for the as prepared glassy samples. It is seen that μ increases with increasing content of V₂O₅ and with

increasing temperature, thus, the conductivity also increases. So, it can be concluded that μ of as prepared glassy samples are temperature and composition dependent. The hopping carrier concentration (N_C), is then obtained³⁸ using the well-known formula:

$$\sigma = e N_C \mu \quad \dots (28)$$

The calculated values of N_C at 373 K and 703 K are listed in Table 4. Figure 6(b) shows the variation of hopping carrier concentration ($\log N_C$) with concentration of V₂O₅ (x mol %) for the present

Table 4 – The hopping carrier mobility (μ) and hopping carrier concentration (N_C) of $xV_2O_5-(1-x)$ (0.05 CdO–0.95 ZnO), where x = 0.30, 0.50, 0.70 and 0.90 glass nanocomposites at 373 K.

Glass composition (x)	μ (cm ² V ⁻¹ s ⁻¹)		N_C (cm ⁻³)	
	at 373 K	at 703 K	at 373 K	at 703 K
0.3	1.15x10 ⁻⁵	8.83x10 ⁻³	6.52x10 ¹²	4.21x10 ¹³
0.5	3.12x10 ⁻⁵	9.85x10 ⁻³	5.37x10 ¹⁴	1.08x10 ¹⁸
0.7	7.36x10 ⁻⁵	1.76x10 ⁻²	1.36x10 ¹⁶	3.66x10 ¹⁸
0.9	1.41x10 ⁻⁴	3.12x10 ⁻²	6.41x10 ¹⁷	5.65x10 ¹⁸

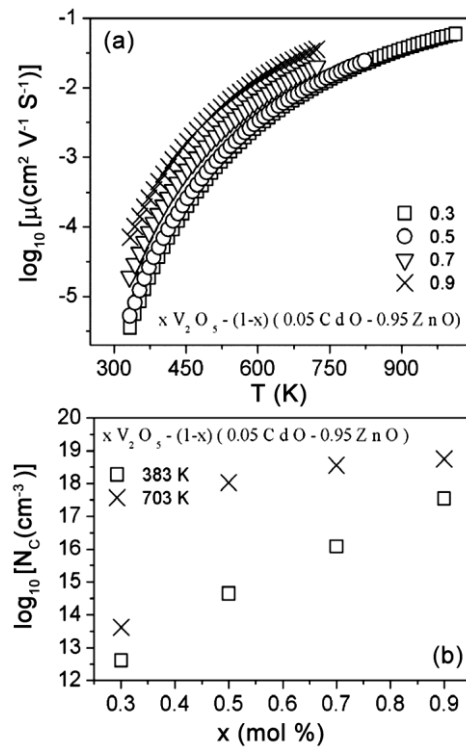


Fig. 6 – (a) The plot of hopping carrier mobility ($\log \mu$) against temperature (T) for different compositions of $xV_2O_5-(1-x)$ (0.05CdO–0.95ZnO), x= 0.30, 0.50, 0.70 and 0.90 glass nanocomposites and (b) effect of V₂O₅ content on hopping carrier concentration ($\log N_C$) at 383 K and 703 K for different compositions of $xV_2O_5-(1-x)$ (0.05CdO–0.95ZnO), x = 0.30, 0.50, 0.70 and 0.90 glass nanocomposites.

studied glassy systems. Figure 6(b) clearly indicates that hopping carrier concentration (N_C) increases with increasing V_2O_5 content and also with increasing temperature. These smaller value of hopping carrier mobility (μ) and higher value of hopping carrier concentration (N_C) have been confirmed that hopping electrons or polarons in the present glassy systems are localized mainly at V_{ion} sites, corresponding to the strong electron–lattice indicating the large γ_p . This also reconfirms the formation of small polarons. From Fig. 6 and Table 4, it is ascertained that hopping carrier mobility (μ) and hopping carrier concentration (N_C) depends on temperature and composition the same as the conductivity of the as prepared glassy systems.

4 Conclusions

The temperature dependence dc conductivity of $xV_2O_5 - (1-x) (0.05 CdO - 0.95 ZnO)$, $x = 0.30, 0.50, 0.70$ and 0.90 semiconducting glass nanocomposites have been studied over wide temperature range. DC conductivity is analyzed in the framework of Mott's model in temperature region below $\theta_D/2$ and Greave's model in temperature region above $\theta_D/2$. Schnakenberg's multi-phonon polaron hopping model is consistent with the temperature dependent activation energy. A strong electron–phonon interaction is found to be dominant in the whole studied temperature region and conduction takes place due to small polaron hopping in non-adiabatic regime, whereas conductivity is due to mainly polaron hopping from V^{+4} to V^{5+} valence state. Reasonable values of the various polaron hopping parameters, namely, polaron hopping energy, disorder energy, optical phonon frequency, the density of states at the Fermi level, polaron band width and electron–phonon coupling constant etc. have been obtained by fitting the experimental data to theoretical models. The dc conductivity (σ_{dc}), hopping carrier mobility (μ) and hopping carrier concentration (N_C) of as prepared glassy systems are temperature and composition dependent.

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