DC Electrical Transport Properties and Non–adiabatic Small Polaron Hopping conduction in Semiconducting Vanadate Glasses

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Abstract: **Transition metal oxide (TMO) doped semiconducting glass nano–composites xV_2O_5–(1–x) ($0.05MoO_3$–$0.95ZnO$), x= 0.3, 0.5, 0.7, 0.9 and 0.93 have been develop by conventional melt quenching technique. The temperature and compositional dependences of the dc electrical transport properties of as prepared vanadate glasses have been reported. Low and high temperature activation energy, density of states at Fermi level, optical phonon frequency and Debye temperature have been computed. Formation of small polaron has been confirmed from dc electrical conductivity experimental data and conductivity is due to mainly polaron hopping from V^{+4} to V^{+5} valence state in these glassy systems. The Schnakenberg's multiphonon assisted hopping model of small polaron is the best model to interpret the temperature dependence of the activation energy and the conductivity over the entire temperature range of measurement. The various polaron hopping parameters such as polaron radius, polaron band width (J), polaron hopping energy and the value of electron–phonon interaction coefficient (γ_P) have been evaluated. The estimated value of hopping carrier mobility (μ) and hopping carrier concentration (N_C) is found to depend on temperature and V_2O_5 content. According to Holstein, it is confirmed that non–adiabatic small polaron hopping is responsible for the electrical conductivity in presently studied glassy systems.**

Keywords: **DC conductivity, polaron hopping energy, polaron band width, electron–phonon coupling constant, hopping carrier mobility, hopping carrier concentration.**

I. INTRODUCTION

The semiconducting glass nano–composites doped with transition metal oxides (TMO) have drawn much attention for last few decades because of their possible applications in electrochemical, electronic and electro-optical devices [1–4]. DC conductivity of TMO doped glasses have been studied extensively [5–10] because of their interesting semiconducting properties and for their many technological applications. Investigations on the temperature dependence of the conductivity are very much crucial in understanding the charge transport mechanisms in TMO doped glasses. In TMO doped glasses the charge carriers are localized, so the conduction can be well interpreted by the small-polaron hopping (SPH) model [11,12]. In the polaron model, a conduction electron localizes at a site in the system and causes a lattice distortion which stabilizes the localized electron [11,12]. Due to thermal motion, this electron migrates from site to site, via a hopping mechanism. If there is a sufficiently strong electron–phonon interaction in these structures, small polarons are formed. As transition metal ions, have more than one valance states, for instance V^{4+} and V^{5+} in vanadate glassy system [13,14] and Mo^{+6} and Mo^{+7} in molybdate glassy system [15], the electrical conduction occurs by thermally activated SPH between low to a high valance state at temperature higher than half of Debye temperature (θ_D). In the theory of SPH, there are two possible natures: - adiabatic and non–adiabatic. To calculate the SPH parameters, it is necessary to determine the nature of the SPH. Emin and Holstein [16] has been given detailed theory for the adiabatic approach. In the adiabatic approach the carrier motion is much faster than that of the lattice. In the adiabatic case, polarons are thermally activated over the potential barrier and there is a high probability of jumping to the next site. In the nonadiabatic regime, the carrier is no longer able to follow rapid fluctuations of the underlying lattice and its probability of hopping is quite small compared to the first case. The effect of the second transition metal oxide on the conductivity of the glasses containing two kinds of transition metal ions, e.g. V_2O_5–NiO–TeO_2 [7], V_2O_5–Fe_2O_3–TeO_2 [17] and V_2O_5–MnO–TeO_2 [18] systems, has been reported. In the glassy systems, V_2O_5–Fe_2O_3–TeO_2 [17] and V_2O_5–NiO–TeO_2 [7], between adjacent sites the electron overlap integral is of significance and the hopping of small polarons exhibits an adiabatic character. On the other hand, in the systems, V_20_5–Bi_2O_3–$SrTiO_3$ [19] and V_20_5–B_2O_3 [20] polaron hopping is

x (mol %)	Density ρ (gm/cm^3)	Low T Activation Energy W_1 (eV)	High T Activation Energy W_2 (eV)	$N_{V\text{-ions}}$ (x 10^{22} cm^{-3})	R (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^{22} eV^{-1} cm^{-3})
0.3	3.872	0.58	1.03	0.76	5.06	2.04	1.86	893	0.316
0.5	3.416	0.56	0.93	1.13	4.45	1.79	1.93	929	0.476
0.7	3.295	0.52	0.81	1.52	4.03	1.62	1.99	957	0.692
0.9	3.158	0.46	0.77	1.88	3.75	1.51	2.03	976	0.969
0.93	3.108	0.35	0.66	1.91	3.73	1.50	2.06	990	1.303

Table I: Density (ρ), Low T & High T Activation energy (W), Concentration of V ion ($N_{V\text{-ions}}$), Mean V_{ion} spacing (R), Polaron radius (R_p), Optical Phonon Frequency(ν_0), Debye temperature (θ_D) and Density of state at Fermi Level [N (E_F)] for glass nano-composites xV_2O_5–(1–x) (0.05 MoO_3–0.95 ZnO), x= 0.3, 0.5, 0.7, 0.9 and 0.93.

non-adiabatic in nature where small polaron cannot follow the rapid fluctuations of underlying lattice, thus, hopping of polarons are quite slower compare to adiabatic regime.

Through this paper, we report temperature dependent dc electrical conductivity of TMO doped semiconducting glass nanocomposites xV_2O_5–(1–x) (0.05MoO_3–0.95ZnO), x= 0.3, 0.5, 0.7, 0.9 and 0.93. The objective of this work is to study the dc electrical conductivity in the light of small polaron hopping conduction. The measured conductivity data are also analyzed to estimate various polaron hopping parameters, hopping carrier mobility (μ) and hopping carrier concentration (N_C) of the as prepared glass nanocomposites formed with second TMO such as MoO_3.

II. EXPERIMENTAL

TMO doped semiconducting glassy samples xV_2O_5 – (1–x) (0.05 MoO_3 – 0.95 ZnO), x = 0.30, 0.50, 0.70, 0.90 and 0.93 have been prepared by melt quenching method. The appropriate amount of oxide materials, V_2O_5 (purity 99.9%, Loba Chemie), MoO_3 (purity 99.5%, Sigma Aldrich) and ZnO (purity 99.9%, Loba Chemie) have been properly weighed and mixed according to stoichiometry of the composition. After that the mixtures are preheated in an alumina crucible and then melted in an electric muffle furnace in the temperature range from 820 0C to 970 0C depending upon the composition. It is realized that as the content of V_2O_5 increases the melting temperature of the glass composition decreases. The melts have been equilibrated for

30 minutes to have better fluidity of the melt and then quenched between two aluminum plates. Thus, glassy plates of thickness ~ 0.5–0.8 mm have been obtained. Density (ρ) of the samples have 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 provide the electrode. The resistance of the silver paste coated samples are measured using Metravi made digital meter at various temperatures and the measurements have been made by the two-probe method.

III. RESULT & DISCUSSION

Fig. 1(a) shows dc conductivity for the as prepared glass compositions as a function of reciprocal temperature. All glass compositions show a smooth variation of conductivity

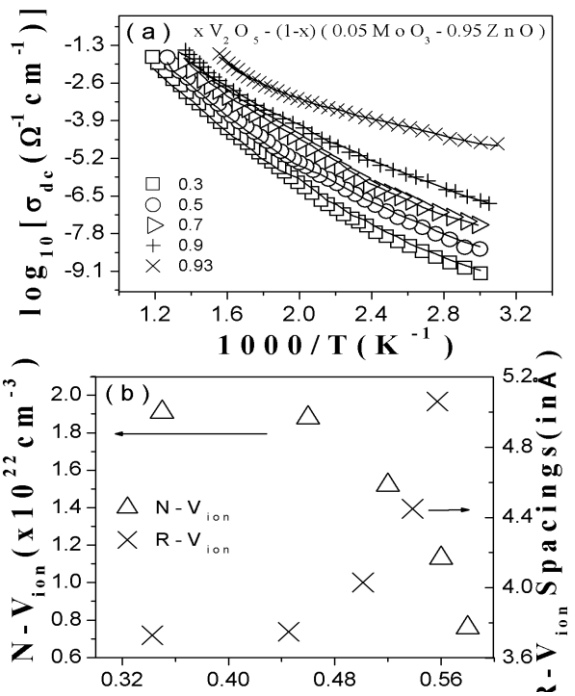

Fig. 1 (a) The reciprocal temperature dependence of D.C electrical conductivity for glass nanocomposites xV_2O_5–(1–x) (0.05MoO_3–0.95ZnO), x= 0.3, 0.5, 0.7, 0.9 and 0.93. The solid lines are best fit data of Schnakenberg model (Eq. 7); (b) Effect of mean V-ion site spacing (R) and concentration of V-ions (N V-ion) on activation energy (W) for all the studied glass nanocomposites.

with reciprocal temperature, which indicates temperature dependent activation energy which is the characteristic of small polaron hopping conduction [12,21,22]. It is also realized that the dc conductivity for all the glass compositions increases with increasing temperature, showing semiconducting behavior. However, in the high and low temperature region, the activation energy is found to be different and the value of activation energy have been computed from the slope of the graph and the values are listed in Table I. From Table I, it is ascertained that the activation energy shows negative correlation with dc conductivity, which is very much consistent with small polaron hopping theory. The dc electrical conductivity also increases with increasing V_2O_5 concentration in these as prepared glassy samples. It is also observed that the plot of log σ_{dc} against

1000/T is non-linear in nature, this is because of process involving several similar activation energies, conduction by polarons or variable range hopping of carriers [1]. During the conduction process, phonon–assisted hopping of electrons accompanies a valence change between V^{4+} and V^{5+} in these glassy systems. In hopping mechanism, mean V-ion site spacing (R) affects activation energy for conduction and thus, dc electrical conductivity. The activation energy of conduction is dependent on the mean V-ion spacing (R) for present glassy systems. In order to confirm the relation between activation energy (W) and mean V-ion spacing (R) in the present studied glass compositions, at first, the V-ion density ($N_{V\text{-ions}}$) has been calculated using the following formula [23]

$$N_{V-ions} = 2 * \left(\frac{d * Wt\ V_2O_5}{MW\ V_2O_5} \right) N_A \quad (1)$$

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 obtained values are enlisted in Table I. The mean spacing between any two V-ions (R) also calculated [23] from the relationship

$$R = \left(\frac{1}{N_{V-ions}} \right)^{\frac{1}{3}} \quad (2)$$

The variation of activation energy (W) with mean V-ion Spacing (R) and with V-ion density ($N_{V\text{-ions}}$) for the present glassy systems is shown in Fig. 1(b). It is ascertained from Fig. 1(b) that the activation energy decreases as mean V-ion spacing (R) 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) decreases which makes dc conductivity of the present glassy systems to increase due to formation of more non–bridging oxygens (NBOs) which can be described in light of structural analysis reported elsewhere [24]. Similar results are found for other glassy systems also [7, 9] The above-mentioned results for the present glassy systems directly indicate the confirmation of the dependence of the activation energy on mean V-ion site spacing (R), suggesting small polaron hopping between V-ions. Using the mean V-ion spacing (R), calculated from Eq. 2, the polaron radius (Rp) can be calculated according to the following relation [25] and the calculated values of R_P are tabulated in Table I.

$$R_P = \left(\frac{\pi}{6} \right)^{\frac{1}{3}} \left(\frac{R}{2} \right) \quad (3)$$

It is observed from Table I that smaller the radii of polaron higher the dc conductivity of the glassy systems. The density of states at Fermi level [N (E_F)] can be estimated from the following expression [26]

$$N(E_F) = \frac{3}{(4\pi R^3 W)} \quad (4)$$

The results for the present glasses are listed in Table I. The values of N (E_F) are reasonable for localized states. It is noticeable from Table I that as the conductivity increases the value N (E_F) also increases, this kind behavior is as expected.

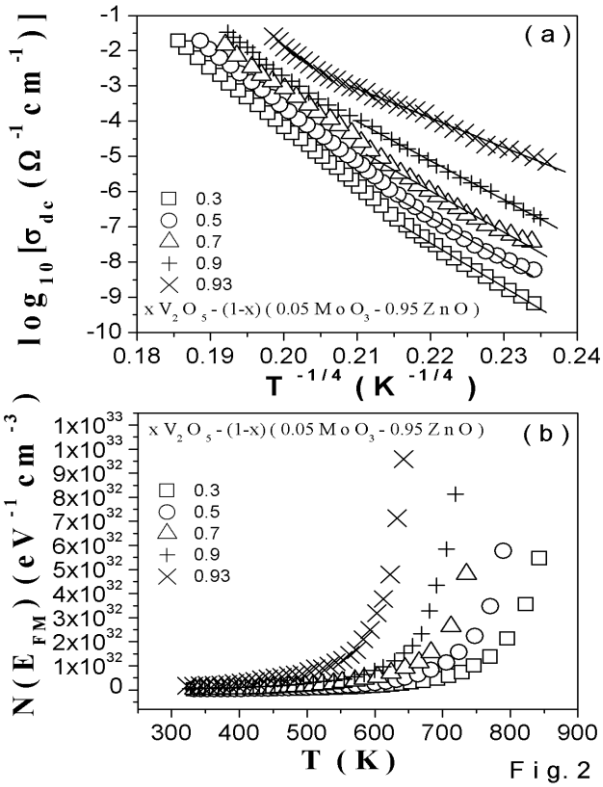

Fig. 2 (a) Variation of dc conductivity at low temperatures as a function of $T^{-0.25}$ (Mott model), Solid lines are calculated by using the least squares technique; (b) The variation of density of states at Fermi level ($N(E_{FM})$) of Mott's model as a function of temperature.

The dc conductivity of the glassy systems under study (Fig. 1a) shows the presence of two regions in relation, the change in these two regions is almost linear and these two straight lines intersect at definite temperature (T_X) differ from one sample to another. It is presumed that at such definite temperature there may be some structural changes happened

and vanadium may be playing a different role. According to Hirashima [27]

$$T_X = \frac{\theta_D}{2} \quad (5)$$

Where θ_D is the characteristic Debye temperature that defined by [27]

$$h\nu_0 = K_B \theta_D \quad (6)$$

Where h is Planck's constant, ν_0 is the optical phonon frequency and K_B is Boltzmann constant. The obtained θ_D and ν_0 values are tabulated in Table. 1. It can be observed that with increasing conductivity optical phonon frequency (ν_0) increases, that means structural vibration also increases.

Schnakenberg [28] has proposed a polaron hopping model, where W_D (disordered energy) ≠ 0, in which dc conductivity

at high temperatures is due to the optical multiphonon hopping, 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 the relation

$$\sigma = T^{-1}[\sinh\left(\frac{h\nu_0}{K_B T}\right)]^{0.5} \exp[\left(\frac{-4W_H}{h\nu_0}\right)\tanh\left(\frac{h\nu_0}{4K_B T}\right)]\exp\left(\frac{W_D}{K_B T}\right) \quad (7)$$

Schnakenberg model (Eq. 7) predicts a temperature dependent polaron hopping energy which decreases 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. 7) and the solid lines in Fig. 1(a) shows the best fit data of Schnakenberg model. Optical phonon frequency (ν_0), polaron hopping energy (W_H) and disordered energy (W_D) are used as variable parameters in the fitting process. The best fits of the data have

been obtained and the values of those parameters are shown in Table II. It may be noted that the values of ν_0 are much higher than the values obtained from dc electrical conductivity. It is observed from Schnakenberg model and dc electrical conductivity data that optical phonon frequency (ν_0) increases as the conductivity of the glass sample increases. It is also observed that the values of polaron hopping energy (W_H) of the studied glassy samples increases as the conductivity increases.

For temperature below half of the Debye temperature ($\theta_D/2$), Mott [29] proposed a variable range hopping (VRH) model. In the VRH model, a carrier moves by hopping from one localized state to another. Mott VRH occurs when the density of states is finite and the states are localized at the Fermi energy. The mathematical expression of VRH conductivity is given by

$$\sigma_{dc} = A\exp\left[-\left(T_0/T\right)^{0.25}\right] \quad (8)$$

where A and T_0 are constants and T_0 is given by

$$T_0 = \frac{16\,\alpha^3}{k\ N(E_{FM})} \quad (9)$$

Where T_0 is the characteristic temperature coefficient, α^{-1} is the localization length and $N(E_{FM})$ is the density of states at the Fermi level from Mott's VRH model. In Fig. 2(a), dc conductivity is plotted against $T^{-0.25}$. The experimental data are fitted to Eq. 8 in Fig. 2(a). At temperature below $\theta_D/2$, using the value of α^{-1} =10Å for localized states [26] 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. 9 and values are presented in Table II. The value of $N(E_{FM})$ is found to increase with x, which confirms nature of dc conductivity data. Again, Density of states at Fermi level of Mott's model ($N(E_{FM})$) [29] have been estimated using experimental data and have been plotted as a function of temperature which is presented in Fig. 2(b). Fig. 2(b) shows that the value of $N(E_{FM})$ increases with increasing temperature gradually and $N(E_{FM})$ does not increase sharply at any particular temperature. It is also observed that $N(E_{FM})$ is composition dependent too. These results convey the fact that increasing content of V_2O_5 is the most important factor for the conduction process.

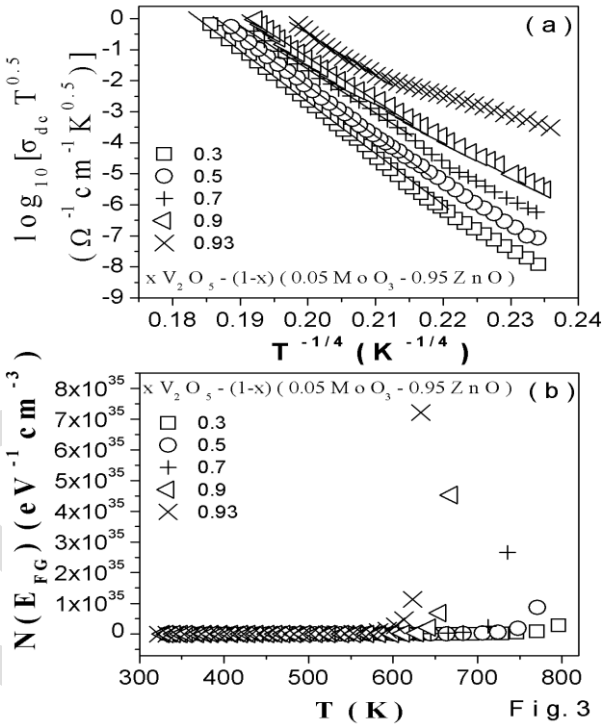

Fig. 3 (a) Variation of $\sigma_{dc}\ T^{1/2}$ at high temperatures as a function of $T^{-0.25}$ (Graves Model), Solid lines are calculated by using the least squares technique; (b) The variation of density of states at Fermi level ($N(E_{FG})$) of Greaves model as a function of temperature.

The temperature dependence of dc conductivity at temperature above half of the Debye temperature ($\theta_D/2$), cannot be met using Mott's model. However, Greaves [30] predicts a temperature dependent VRH which is dominant in this region (temperature above ($\theta_D/2$)). Greaves has been obtained the following expression for the dc conductivity

$$\sigma_{dc}\,T^{1/2} = A'\exp\left[-\left(T_0'/T\right)^{0.25}\right] \quad (10)$$

Where A' and T_0' are constants and T_0' is given by

$$T_0' = \frac{19.4\,\alpha^3}{k\ N(E_{FG})} \quad (11)$$

Where $N(E_{FG})$ is the density of states at the Fermi level from Greaves VRH model. In Fig. 3(a), log ($\sigma\ T^{1/2}$) is plotted against $T^{-0.25}$. It may be noted in Fig. 3(a) that Greaves model yields good fits to the data. At high temperature region, Using the value of α^{-1} =10Å for localized states, using the slope (as shown in Fig. 3(a) by solid lines) obtained from this linear relation the value of $N(E_{FG})$ have been estimated from Eq. 11

x (mol %)	Log σ_{dc} (Ω^{-1} cm^{-1}) At 363K	N(E_{FM}) (x 10^{28} eV^{-1}cm^{-3}) Mott Model	N(E_{FG}) (x 10^{28} eV^{-1}cm^{-3}) Greaves Model	R_{hop} (400K) (nm)	W_{hop} (at 400K) (μ eV)	Greaves Threshold Temperature (T_{HG}) (K)	ν_o (Phonon Frequency) (x10^{13} S^{-1})	W_H (Hopping Energy) (eV)	W_D (Disorder Energy) (eV)
0.3	-8.61	1.64	0.64	7.93	29.2	747	1.21	0.24	0.035
0.5	-7.81	1.96	0.73	7.59	27.9	726	2.21	0.27	0.078
0.7	-7.06	2.08	1.24	7.47	27.5	683	5.84	0.37	0.078
0.9	-5.98	2.64	1.33	7.04	25.9	628	9.84	0.43	0.075
0.93	-4.36	8.29	1.48	5.29	19.5	586	12.9	0.56	0.085

Table II: DC conductivity (log σ_{dc}) at 363K, the value of N(E_{FM}) using Mott's model (Eq. 9), N(E_{FG}) using Greaves model (Eq. 11), hopping distance (R_{hop}), hopping energy (W_{hop}), Greaves Threshold temperature (T_{HG}) and parameters obtained by fitting the conductivity data to the Schnakenberg polaron hopping model (Eq. 7) for glass nanocomposites xV_2O_5–(1–x) (0.05 MoO_3–0.95 ZnO), x= 0.3, 0.5, 0.7, 0.9 and 0.93.

and values are tabulated in Table II. The value of N(E_{FG}) is found to increase with x, which once again confirms dc conductivity data. It should be noted from Table. II 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 range. It is also observed that as the dc conductivity increases the value of density of states at Fermi level N(E_{FM}) and N(E_{FG}) also increases. It is natural that at high temperature the optical phonon assisted polaron hopping takes place and possible collision between phonon and nanoclusters inside the glassy samples may take place which is currently under investigation. Due to collision, a part of energy may loss, which keeps the values of density of states at fermi level close to each other. Once Again, Density of states at Fermi level of Greaves model (N(E_{FG})) [30] has been computed using experimental data and have been plotted as a function of temperature which is presented in Fig. 3(b). From Fig. 3(b), it can be observed that the value of N(E_{FG}) almost constant in low temperature range and increases sharply at a particular temperature represented as Greaves threshold temperature (T_{HG}) and the values of T_{HG} are shown in Table II. It is perceived from Table I and Table II that the value of T_{HG} is higher than half of Debye temperature (θ_D) and value of T_{HG} decreases with increasing V_2O_5 content, while dc conductivity increases.

Using the value of N(E_{FM}), the hopping parameters, the temperature–dependent hopping distance R_{hop} and average hopping energy W_{hop} are given as [26]

$$R_{hop} = \left[\frac{9}{8\pi N(E_{FM})\,\alpha\, K_B\, T}\right]^{1/4} \qquad (12)$$

and

$$W_{hop} = \frac{3}{4\,\pi\, R_{hop}^3\, N(E_{FM})} \qquad (13)$$

The values of R_{hop} and W_{hop} are obtained at 400 K for all the glass nanocomposites and are tabulated in Table II. The VRH

requirements $R_{hop}\ \alpha \geq 1$ and $W_{hop} > K_BT$, necessary for the validity of Mott's VRH model, are clearly satisfied. Fig. 4 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.

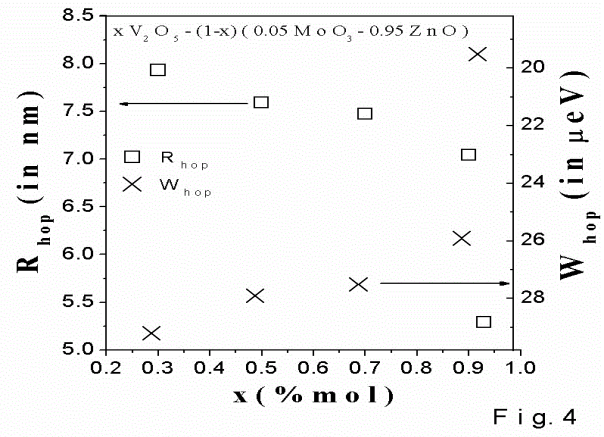

Fig. 4 The temperature–dependent hopping distance, R_{hop} and average hopping energy, W_{hop} of all the glass nano-composites.

Mott [22] theoretically investigated the hopping conduction in TMO doped glasses in terms of phonon–assisted hopping of small polarons between localized states and obtained the following expression for the dc conductivity for the nearest neighbor hopping in the non-adiabatic regime is expressed by [11, 22]

$$\sigma_{dc} = \frac{\nu_0\, N\, e^2 R^2}{K_B\, T}\,[C\,(1-C)]\,[\exp(-2\alpha R)\,]\,[\exp\left(\frac{-W}{K_B\, T}\right)] \qquad (14)$$

and pre-exponential factor σ_0 of Eq. 14 in non-adiabatic regime can be expressed as

$$\sigma_0 = \frac{\nu_0\, N\, e^2 R^2}{K_B}\,[C(1-C)]\exp(-2\alpha R) \qquad (15)$$

Where ν_0 is the longitudinal optical phonon frequency, R is the average inter-site separation, α is the inverse localization length that is assumed to describe the localized states at each transition metal ion site (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 W is the activation energy for hopping conduction. Assuming a strong electron-phonon interaction, Mott and Davis [22] showed that

$$W_H = W_D + \frac{W_D}{2} \quad \text{for } T > \theta_D/2 \qquad (16)$$

$$= W_D \quad \text{for } T < \theta_D/4 \qquad (17)$$

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 localized sites due to variation in the local arrangement of ions. Mott suggested that the dominant process decreasing the activation energy is an

interaction between polarons and optical phonons. If Eq. 14 is totally dependent on V_2O_5 concentration, it is said to be in non-adiabatic regime and if it varies with V_2O_5 content, it is said to be in adiabatic regime. In the case of adiabatic hopping, the tunneling term exp (–2αR) in Eq. 14 reduces to unity and the conductivity is given by [13, 23, 27]

$$\sigma_{dc} = \frac{\nu_0 N e^2 R^2}{K_B T} [C(1-C)] \left[\exp\left(\frac{-W}{K_B T}\right)\right] \quad (18)$$

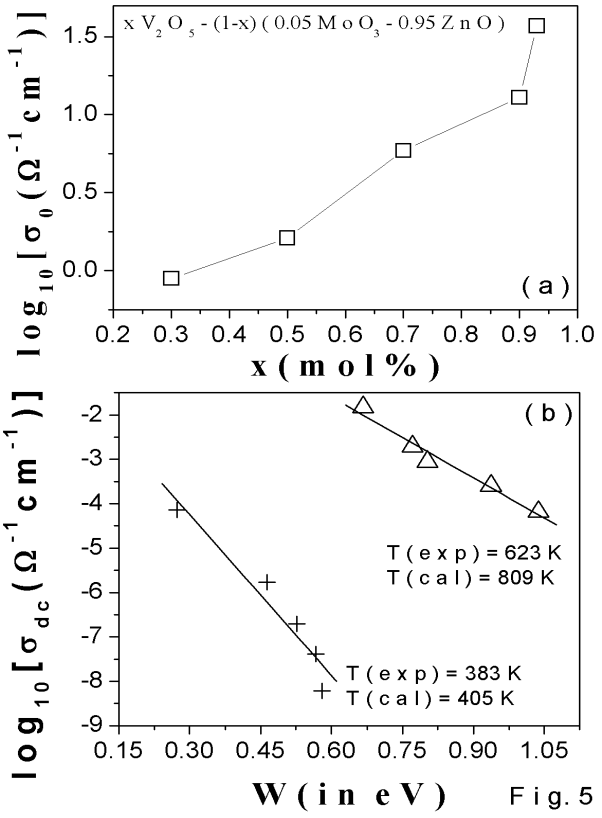

Fig. 5 (a) Effect of V_2O_5 concentration on pre-exponential factor, σ_0, for different compositions of xV_2O_5–(1–x) ($0.05MoO_3$–0.95ZnO) glass nano-composites; (b) The dc conductivity at experimental temperatures (T) 383 K and 623 K versus the activation energy for all the glass nanocomposites. Symbols represent experimental data and solid lines represent the linear fit.

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 localized sites due to variation in the local arrangement of ions. Mott suggested that the dominant process decreasing the activation energy is an interaction between polarons and optical phonons. If Eq. 14 is totally dependent on V_2O_5 concentration, it is said to be in non-adiabatic regime and if it varies with V_2O_5 content, it is said to be in adiabatic regime. In the case of adiabatic hopping, the tunneling term exp (–2αR) in Eq. 14 reduces to unity and the conductivity is given by [13, 23, 27]

$$\sigma_{dc} = \frac{\nu_0 N e^2 R^2}{K_B T} [C(1-C)] \left[\exp\left(\frac{-W}{K_B T}\right)\right] \quad (18)$$

If Eq. 18 is independent of V_2O_5 concentration, then it indicates adiabatic nature of hopping conduction [31–33]. If it is found that the tunneling factor in Eq. 14, exp (–2αR), is neither constant nor equal to one for different compositions of the glassy systems, as evidenced by the fact that pre-exponential factor (σ_0) varies with composition, indicating thereby non-adiabatic nature of hopping conduction [12, 34]. The term of pre–exponential factor (σ_0) can be evaluated using the experimental values, namely the intercept of log σ_{dc} versus (1000/T) plot at (1000/T) = 0 [1]. Fig. 5(a) shows the effect of V_2O_5 concentration depend on pre-exponential factor (σ_0). As previously discussed, we can conclude that conduction is due to the 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 σ_{dc} vs W plots is close to experimental temperature,

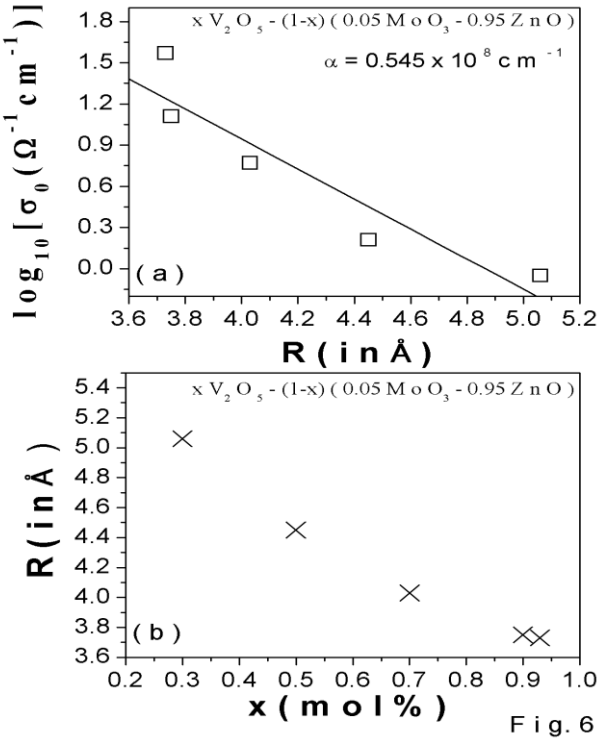

Fig. 6 (a) Relationship between log σ0 and mean V-ion site spacing (R) for different compositions of xV_2O_5–(1–x) ($0.05MoO_3$–0.95ZnO) glasses. Solid line represents linear fit data, the slope of these line is (−2 α); (b) Relationship between mean V-ion site distance (R) with V_2O_5 concentration (x mol %) of xV_2O_5–(1–x) ($0.05MoO_3$–0.95ZnO) glassy systems.

otherwise, the hopping would be of non–adiabatic type [20, 35]. Fig. 5(b) shows plots of log σ_{dc} with W at two different experimental temperatures 383K and 623K. The calculated values of temperatures from slopes ($-1/2.303*K_BT$) of these plots are found to be 405K and 809K, 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 are justified. On the other hand, we can evaluate approximately the value of the tunneling factor, α, according to Eq. 15, α can be calculated from the slope of log σ_0 with R (mean spacing between V_{ions}) plot [1], result of such calculation is shown in Fig. 6(a) and the value of slope is (-2α). The obtained value of α is 0.545×10^8 cm $^{-1}$, which is much lower than the order of that for some other semiconducting glassy systems [1,35]. The mean site distance of V_{ions} (R) has been plotted for different concentrations of V_2O_5 as shown in Fig. 6(b). The mean site distance of V_{ions} (R) is found to decrease with increasing content of V_2O_5. Thus, it is confirmed that conductivity is due to polaron hopping from V^{+4} to V^{+5} valence states, then with decrease of mean site distance of V_{ions} (R) the increase of dc conductivity can be expected.

The nature of hopping mechanism may be determined by a small polaron hopping model suggested by Holstein [36] also. According to this model, nature of hopping can be expressed by using the following inequalities

$J > J^*$ adiabatic (19)

$J < J^*$ non–adiabatic (20)

Glass Composition (x)	Parameters					
	W_H (eV)	J^*	J	W_H^* (eV)	γ_P	m_P / m^*
0.3	0.563	0.0508	0.0409	0.562	14.7	$2.4\text{x}10^6$
0.5	0.528	0.0503	0.0410	0.527	13.6	$8.4\text{x}10^5$
0.7	0.488	0.0498	0.0415	0.487	12.3	$2.3\text{x}10^5$
0.9	0.426	0.0486	0.0422	0.425	10.5	$3.9\text{x}10^4$
0.93	0.308	0.0452	0.0427	0.307	7.5	$1.8\text{x}10^3$
$40V_2O_5$–$40Bi_2O_3$–20ZnO (Ref. 40)	0.32	0.034	0.023	0.31	15.3	$4.5\text{x}10^6$
VN–PbO–TeO_2 (Ref. 41)	0.18	0.051	0.031	0.17	14.1	$1.4\ \text{x}10^6$

Table III: Polaron hopping parameters of xV_2O_5–(1–x) (0.05 MoO_3–0.95 ZnO), x= 0.3, 0.5, 0.7, 0.9 and 0.93 glass nanocomposites at 363K and comparing those data with $40V_2O_5$– $0Bi_2O_3$– 20ZnO glass (Ref. 40) and VN– PbO–TeO_2 glass (Ref. 41).

$$\text{Where } J^* = \left[\left(\frac{2\,K_B\,T\,W_H}{\pi}\right)^{\frac{1}{4}}\right]\left[\left(\frac{h\,\nu_0}{\pi}\right)^{\frac{1}{2}}\right] \quad (21)$$

Here, J is the polaron bandwidth 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 Eq. 16 taking the value of W_D from Schnakenberg model and J can be obtained the following relation [17, 36, 37]

$$J = \frac{[\,0.67 * h\,\nu_0\,]}{\left[\left(\frac{T}{\theta_D}\right)^{\frac{1}{2}}\right]} \quad (22)$$

The values of J, J^* and W_H are listed in Table III. At low temperature, according to Mott and Davis [26], the polaron hopping energy W_H^* is given as

$$W_H^* = \frac{W_H\left[\tanh\left(\frac{h\,\nu_0}{4\,K_B\,T}\right)\right]}{\left[\left(\frac{h\,\nu_0}{4\,K_B\,T}\right)\right]} \quad (23)$$

Perusal of data listed in Table 3, reveals that the inequality Eq. 20 ($J < J^*$, non–adiabatic) is valid, which in turn support our assertion that conductivity of glassy systems under study is due to non–adiabatic polaron hopping process. The condition for small polaron hopping, that is, $J < \left[\frac{W_H}{3}\right]$ is also satisfied in both low and high temperature regions [36,38]. The small polaron coupling constant (γ_P) is a measure of electron–phonon interaction is given by [38,39]

$$\gamma_p = \frac{2\,W_H}{h\,\nu_0} \quad (24)$$

The calculated values of γ_P are listed in Table III and it is found that the values of γ_P varies from 14.7 to 7.5 for all glass nanocomposites, indicating a very strong electron–phonon interaction [38,39]. However, it is also observed from Table III that this electron–phonon interaction decreases with interaction, as, $\gamma_P > 4$ indicates a strong electron–phonon increasing V_2O_5 content in the present studied glass compositions. The ratio of polaron mass (mp) to rigid lattice effective mass (m*) is obtained by the relation [39]

$$m_p = \left[\left(\frac{h^2}{8\,\pi^2\,J\,R^2}\right)\right]\exp(\gamma_p) = m^*\exp(\gamma_p) \quad (25)$$

The calculated values of mp/m* are tabulated in Table III which are very large for presently studied glass compositions, and once more time it indicates strong electron–phonon interaction in those glassy systems [25]. From Table III, it is observed that the values of m_p/m^* decreases with increasing

V_2O_5 concentration in those as prepared glassy systems. and once more time it indicates strong electron–phonon interaction in those glassy systems [25]. From Table III, it is observed that the values of m_p/m^* decreases with increasing V_2O_5 concentration in those as prepared glassy systems. Scrutinizing of data listed in Table III, it is ascertained that the values of polaron hopping parameters are temperature and composition dependent. We have also included polaron hopping parameters of $40V_2O_5$–$40Bi_2O_3$–20ZnO [40] and VN–PbO–TeO_2 [41] glassy systems for comparison in Table III.

Finally, the hopping carrier mobility (μ) is expressed for non–adiabatic hopping conduction as [22, 26, 42]

$$\mu = \left[\frac{(e\,R^2\,J^2)}{(h\,K_B\,T)}\right]\left[\frac{\pi}{(4\,W_H K_B\,T)}\right]^{1/2} \exp\left(\frac{-W}{K_B\,T}\right) \qquad (26)$$

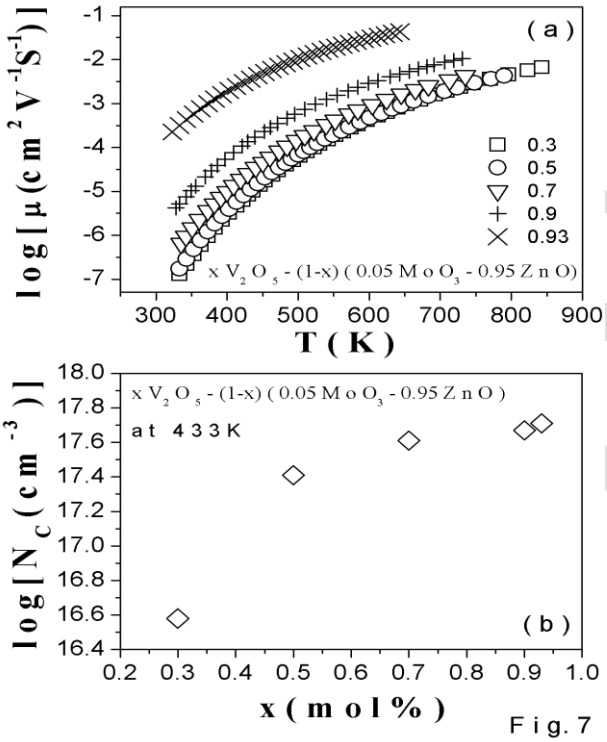

Fig. 7 (a) The plot of carrier hopping mobility (log μ) as a function of temperature (T) for different composition of glass nanocomposites xV_2O_5 – (1–x) (0.05MoO_3–0.95ZnO), x= 0.3, 0.5, 0.7, 0.9 and 0.93; (b) Effect of V2O5 concentration on carrier hopping concentration (log N_C) at 433 K for different composition of glass nanocomposites xV_2O_5 –(1–x) (0.05MoO_3–0.95ZnO), x= 0.3, 0.5, 0.7, 0.9 and 0.93.

Where hopping carrier mobility (μ) values are calculated with the data of W, R, J and W_H given in Table. I and Table. III. The hopping carrier mobility (μ) of present glassy systems is very small, suggesting that electrons or polarons are localized at V-ions [18, 21]. Since the conduction of localization for conductive electrons is generally $\mu < 10^{-2}$ cm^2 V^{-1} s^{-1} [43], the hopping mechanism for conduction in these glassy systems are reconfirmed. Fig. 7(a) shows the variation of hopping carrier mobility (log μ) as a function of temperature (T) for the as prepared glassy systems. It is seen that hopping carrier mobility (μ) of as prepared glassy samples are temperature dependent and as well as composition dependent. The hopping carrier concentration (N_C), can be estimated using the well–known formula [36]

$$\sigma = e\,N_C\,\mu \qquad (27)$$

Fig. 7(b) shows the variation of hopping carrier concentration (log N_C) as a function of mol % of V_2O_5 for the present studied glass systems. Fig. 7(b) clearly indicates that hopping carrier concentration (N_C) increases with increasing V_2O_5 content and also with increasing temperature. The reason of this may be due to continuous decrease in effective mass of polarons as one goes from x=0.3 to x=0.93.

IV. CONCLUSION

The temperature dependence dc conductivity of xV_2O_5 – (1–x) (0.05 MoO_3 – 0.95 ZnO), x= 0.3, 0.5, 0.7, 0.9 and 0.93 semiconducting glasses has been studied in wide temperature range. DC conductivity of presently studied glassy systems is found to increase with increasing temperature and with increasing V_2O_5 concentration. DC conductivity is analyzed in the framework of Mott's model in temperature region lesser than $\theta_D/2$ and Greaves model in temperature region greater than $\theta_D/2$. Schnakenberg's optical multi–phonon hopping model is consistent with the temperature dependence of the 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 and is due to mainly polaron hopping from V^{+4} to V^{5+} valence states. Reasonable values of the various physical parameters, namely, polaron hopping energy, disorder energy, optical phonon frequency, polaron band width, etc., have been obtained by using 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 have been found to depend on concentration of V_2O_5 and temperature.

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