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Investigation of DC Conductivity and Non-Adiabatic Small Polaron Hopping in V_2o_5-Seo_2-Zno Glass Nanocomposites

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Abstract: ***Transition metal oxide doped semiconducting glass nanocomposites with common nomenclature xV_2O_5-(1-x) ($0.05SeO_2$-$0.95ZnO$) for x= 0.3, 0.5, 0.7, and 0.9 have been synthesized through melt quench route. Dc electrical conductivity has been measured for wide temperature range. It is perceived that Dc conductivity increases with an increment in V_2O_5concentration and with temperature rise, revealing semiconducting nature. The non-adiabatic hopping of small polaron is accountable for Dc electrical conduction process that is an effect of hopping of the polaron from V^{+4} to V^{+5} valence state in all the glassy system. The activation energies at low and high temperature, the density of states at the Fermi level, the frequency of optical phonons and Debye temperature have been estimated. The Schnakenberg's multi-phonon supported small polaron hopping model is the best-suited model to describe the temperature dependency of the activation energy and Dc conductivity over the completely experimental temperature range. The polaron hopping parameters, for instance, polaron radius, polaron-hopping energy, polaron bandwidth etc. have been calculated. The electron-phonon coupling constant values are higher (24.4-6.64), revealing strong electron phonon interaction. It is also noteworthy that the calculated values of hopping carrier mobility and hopping carrier concentration are composition and temperature dependent.***

Keywords: Glass nanocomposites, Dc conductivity, polaron hopping, polaron bandwidth, electron-phonon coupling constant, hopping carrier mobility, hopping carrier concentration.

I. INTRODUCTION

Transition metal oxide (TMO) such as V_2O_5-doped semiconducting glass nanocomposites have attracted much attention in the study of their conduction mechanism, extensive investigations have been accomplished on their electrical conduction [1]-[11]. The small polaron hopping model [12], [13], has assumed the conduction mechanism. Semiconducting glass nanocomposites have significant applications such as gas sensors, solar cells, laser diodes, optics to catalysis and photo catalysis. Such glasses also exhibit many fascinating physical properties such as electrical threshold, switching phenomenon, electro chromic properties, etc. [2]-[5]. In TMO-doped glasses, excess charge carriers may couple with distortions of nearby ions and excess charge carriers become localized, which leads to polaron formation. It is reported that the activation energy required for hopping conduction is affected by glass forming oxides [8]-[10]. The cause for interest in these glassy systems are that amorphous materials with random structure can be obtained for a wide composition range, wherein V_2O_5 acts as a unique glass network former along with modifier. The conduction in TMO-doped glassy systems occurs by means of transfer of small polarons from V^{4+} to V^{5+} valence state [14]. Since the unpaired electron causes a polarization around the ionic transition metal, the conductivity can be interpreted with regard to a polaron-based model. Vanadium usually exhibits three types of coordination modes, VO_4 tetrahedron, square pyramid or trigonal bipyramid structure of $VO_5$and VO_6 octahedron. ZnO is widely used as a key catalyst in many significant photo catalytic processes as it is easy to produce a pair of electron-hole pair through exposure to ultraviolet (UV) light that is needed for photo processes. ZnO exhibits three-dimensional network consisting of ZnO_4, ZnO_5 and ZnO_6 polyhedra that is edge and corner shared. SeO_2 based glassy systems reveal the local coordination environment of selenium [15], [16]. It is observed that the coordination of selenium changes from Se^{4+} to Se^{6+} valence state, which are attributed to the conversion of oxygen rich selenate phase to oxygen deficit selenite phase with a rise in SeO_2 content in the glassy systems and consequently affecting the network structure [15]. The modification of the network structure occurs from layers to chains with risingSeO_2concentration. At low SeO_2 content, the SeO_2 is dissolved in the network structure whereas at high content, the network-forming tendency increases [15]. Therefore, the formation of glasses of various

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selenite compounds is related to the creation of a disorder in the SeO_3 chains of the polyhedron modifier in an appropriate composition ratio.

In this article, the glassy system with general nomenclaturexV_2O_5-(1-*x*) (0.05SeO_2-0.95ZnO) for *x*= 0.3, 0.5, 0.7 and 0.9 have been prepared by melt quench method. The Dc electrical conductivity has been studied with reference to the model based on small polaron hopping. The various polaron-hopping parameters, hopping carrier mobility (μ) and hopping carrier concentration (N_C) have been estimated of all the as-prepared glass nanocomposites formed with other non-traditional glass modifier such as SeO_2.

II. EXPERIMENTAL PROCEDURE

TMO-doped semiconducting glass nanocomposites with common nomenclature xV_2O_5-(1-*x*) (0.05SeO_2-0.95ZnO) for *x* = 0.3, 0.5, 0.7 and 0.9 have been develop by conventional melt quench technique. We have used proper molar ratio of precursors vanadium pentoxide (V_2O_5) (purity 99.9%, Loba Chemie), selenium oxide (SeO_2) (purity 99.5%, Sigma Aldrich) and zinc oxide (ZnO) (purity 99.9%, Loba Chemie). The suitable quantities of precursors have been thoroughly weighed, assorted, and preheated in an alumina crucible and the assortments are then liquefied in a high temperature electric furnace in the temperature range from 840^0 C to 940^0 C contingent upon the composition. It is asserted that with rising concentration of V_2O_5 the melting temperature of the glass composition drops. The liquefies have been equilibrated for 25 minutes and rapidly quenched between two aluminum plates at room temperature, thus, glassy plates of thickness ~0.5-0.7 mm have been obtained. Density (ρ) of the as-quenched samples have been determined by Archimedes principle by means of acetone as an immersion liquid. For electrical measurements, both sides of the samples are coated with silver paste to serve as the electrode. The resistance of samples coated with silver paste is measured by a Metravi digital meter at different temperatures and the measurements are made using two-probe method.

III.RESULTS AND DISCUSSION

Fig. 1(a) depicts Dc conductivity of all the glass compositions with reference to reciprocal temperature. All glassy samples show a smooth variation of the conduction, which specifies that the activation energy is temperature dependent that is the feature of the small polaron hopping conductivity [3], [10], [17], [18]. It is also recognized that the Dc conductivity increases with temperature rise, indicating typical semiconducting behaviour. In glassy systems doped with TMO, Mott [12], [18] has studied theoretically the hopping conduction with regard to phonon-assisted small polaron hopping concerning localized states. Mott has derived the following expression of Dc conductivity for nearest neighbour hopping process in the non-adiabatic regime is expressed by [12], [18]

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

and pre-exponential factor σ_0 of Eq. 1 in non-adiabatic regime can be given as

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

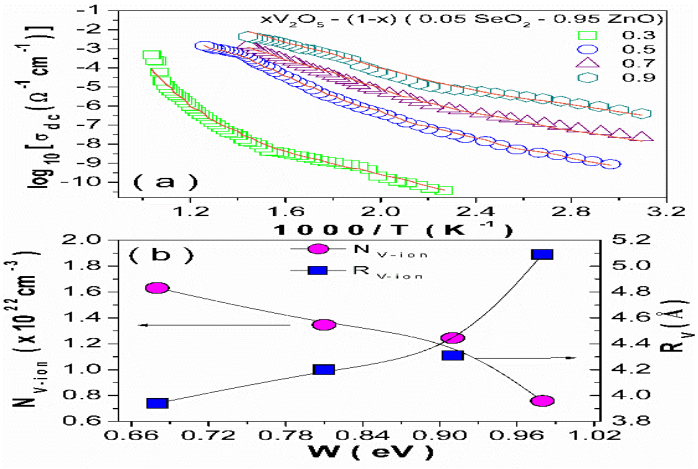


Fig. 1 (a) The reciprocal temperature dependence of Dc electrical conductivity of glass nanocompositesxV_2O_5-(1-*x*) (0.05SeO_2-0.95ZnO) for x = 0.3, 0.5, 0.7 and 0.9. The solid lines are best-fit data of Schnakenberg model (Eq. 11),(b) Effect of R_V and concentration of V-ion ($N_{V\text{-ion}}$) on activation energy (W) for different values of *x*.

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Whereν_0 is the longitudinal optical phonon frequency, R is the average inter-site separation, α is the inverse localization length presumed to define the localized states (the ratio of wave function decay). Here C is the occupancy of electron or polaron in fraction of sites, N is known as transition metal ion density, e is the electronic charge, K_B is the Boltzmann constant and W is the activation energy for hopping conduction. However, in high and low temperature region, from the slope of the plot, the values of activation energy are estimated and the values are listed in Table 1. It is observed from Table 1 that the activation energy and Dc conductivity have negative correlation, which is in accordance with the theory of small polaron hopping. It asserts that Dc electrical conductivity rises with the rising V_2O_5concentration of all as-quenched glassy samples. The plot of log σ_{dc} with 1000/T is observed to be non-linear in nature, which is ascribed to mechanism comprising several similar activation energies and conduction by polarons or variable range hopping (VRH) of carriers [3].

TABLE I

Density (ρ), Low temperature, high temperature activation energy (W), concentration of V-ion ($N_{V\text{-}ion}$), 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 $N(E_F)$ ofall the glass nano-composites for different values of *x*.

x	Density ρ (gm/cm^3)	Low T Activation Energy W_1 (eV)	High T Activation Energy W_2 (eV)	$N_{V\text{-}ion}$ ($\times 10^{22}$ 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)	$N(E_F)$ ($\times 10^{21}$ $eV^{-1}cm^{-3}$)
0.3	3.816	0.71	0.98	0.75	5.09	2.05	1.85	888	1.84
0.5	3.762	0.47	0.93	1.24	4.31	1.73	1.89	909	3.21
0.7	2.904	0.36	0.81	1.34	4.21	1.69	1.92	925	3.98
0.9	2.737	0.31	0.68	1.63	3.94	1.58	1.97	947	5.74

The phonon-assisted hopping of electrons or polarons is an outcome of the valence change between V^{4+} ion and V^{5+} ion in these glassy systems. In hopping process, the spacing between V^{4+} and V^{5+} ions (R_V) affects the activation energy and Dc electrical conductivity. The activation energy of Dc conduction shows a strong dependence on R_V.The assertion of the relation between temperature dependent activation energy (W) and R_V, the value of V-ion density ($N_{V\text{-}ions}$) is estimated first using the following expression [19]

$$N_{V-ions} = 2 * \left(\frac{d * Wt V_2O_5}{MW\ V_2O_5}\right) N_A \quad (3)$$

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 estimated values of $N_{V\text{-}ions}$ are listed in Table 1. The value of the mean spacing between V^{4+} and V^{5+} ions (R_V) is calculated [19] using the relationship

$$R_V = \left(\frac{1}{N_{V-ions}}\right)^{\frac{1}{3}} \quad (4)$$

Fig. 1(b) shows the relation between activation energy (W) and mean spacing between V^{4+} and V^{5+} ions (R_V) of all the glassy samples. Fig. 1(b) also exhibits the deviation of activation energy (W) with reference to V-ion density ($N_{V\text{-}ions}$). It is established from Fig. 1(b) that the values of activation energy rise with an increment of mean spacing between V^{4+} and V^{5+} ions (R_V), which makes Dc conductivity to drop. It is also perceived from Fig. 1(b) that with increasing values of V-ion density ($N_{V\text{-}ion}$), the mean spacing between V^{4+} and V^{5+} ions (R_V) reduces that makes Dc conductivity to increase. Similar results have been observed for other glassy systems [5, 20]. The afore-mentioned results directly point out the validation of activation energy dependence with the mean spacing between V^{4+} and V^{5+} ions (R_V), suggestive of the hopping of small polaron between V-ions. Using the value of R_V, the value of polaron radius (R_p) can be assessed in relation to the following expression [21] and the estimated values of R_P are tabulated in Table. 1.

$$R_P = \left(\frac{\pi}{6}\right)^{\frac{1}{3}} \left(\frac{R}{2}\right) \quad (5)$$

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Table 1 ascertains that smaller the polaron radii, the Dc conductivity becomes higher. The Fermi level density of states ($N(E_F)$) can be determined using the expression [22]

$$N(E_F) = \frac{3}{(4\pi R^3 W)} \quad (6)$$

The results of $N(E_F)$ are presented in Table 1. The values of $N(E_F)$ are judicious for localized states [20]-[22]. Table 1 asserts that with a rise in conductivity, the values of Fermi level density of states$N(E_F)$ increase, this kind behavior is expected, which is caused by the creation of more defects in the glassy system.

The presence of two regions (as depicted in Fig. 1(a)), one at lower temperature and another comparatively at higher temperature are clearly observed. These two regions are almost linear and intersect at a definite temperature (T_X) varying with reference to the composition (x). It is hypothetical that vanadium ion modifies the structure of glassy system at such definite temperature. As stated by Hirashima [23]

$$T_X = \frac{\theta_D}{2} \quad (7)$$

where θ_D is the characteristic Debye temperature that defined by [23]

$$h\nu_0 = K_B\theta_D \quad (8)$$

Here, his Planck's constant, υ_0 is the optical phonon frequency and $K_B$is Boltzmann constant. The calculated θ_D and υ_0 values are tabulated in Table 1. The Debye temperature (θ_D) and optical phonon frequency (υ_0) values show a gradual increment with rising concentration of V_2O_5. The increasing values of θ_D owe to rising V_2O_5 content in consequence of the opening of the glass network structure created by the large V^{4+} or V^{5+} volume, which increases the network thermal vibration. Due to increase in glass network thermal vibration, the optical phonon frequency and the vibration amplitude of the glassy network increase.

Based on Schnakenberg's polaron hopping model [24], polaron disordered energy ($W_D \neq 0$) is described by optical multi phonon hopping process at higher temperature, while at lower temperature, the dc conductivity is influenced by the acoustical single phonon assisted hopping process. The temperature dependent Dc conductivity of this model is expressed by the relation

$$\sigma = T^{-1}\left[\sinh\left(\frac{h\nu_0}{K_B T}\right)\right]^{0.5} \exp\left[\left(\frac{-4W_H}{h\nu_0}\right)\tanh\left(\frac{h\nu_0}{4K_B T}\right)\right]\exp\left(\frac{W_D}{K_B T}\right) \quad (9)$$

It is worth noting that Eq. 9 predicts a temperature dependent hopping energy, which drops with a temperature rise in consistent with the data presented in Fig. 1(a). Dc conductivity data have been fitted to Eq. 9 and the solid lines in Fig. 1(a) shows the best-fit data of Schnakenberg model. In the fitting process, optical phonon frequency (ν_0), polaron hopping energy (W_H) and disordered energy (W_D)are utilized as fitting parameters. The best fits of the data have been obtained and the values of the fitting parameters are presented in Table 2. It is notable that the values of ν_0 are much higher than those values obtained from Dc electrical conductivity spectra. However, Schnakenberg's model yields lower values of W_H than the values of the estimated high temperature activation energies as presented in Table 1 of all the different glassy samples. Perusal of Schnakenberg model and Dc electrical conductivity results reveal that optical phonon frequency (ν_0) and polaron hopping energy (W_H) rises with increasing conductivity. The disorder energy (W_D) is nothing but the energy difference of successive localized states. In addition, it is also perceived that the values of disorder energy (W_D) drop as the conductivity increases.

TABLE II

The values of Dc conductivity ($\log \sigma_{dc}$) at 553K, $N(E_{FM})$ using Mott's model (Eq. 11), $N(E_{FG})$ using Greaves model (Eq. 13), hopping distance (R_{hop}), hopping energy (W_{hop}) at 373K, Greaves threshold temperature (T_{HG}) and parameters obtained by fitting the conductivity results to the Schnakenberg's polaron hopping model (Eq. 9) ofall the glass nanocomposites.

x	$\log \sigma_{dc}$ (Ω^{-1} cm^{-1}) At 553K	$N(E_{FM})$ (x 10^{29} eV^{-1} cm^{-3}) Mott Model	$N(E_{FG})$ (x 10^{28} eV^{-1} cm^{-3}) Greaves Model	R_{hop} (at 373K) (nm)	W_{hop} (at 373K) (m eV)	Greaves Threshold Temperature (T_{HG}) (K)	ν_o (Phonon Frequency) (10^{13} S^{-1})	W_H (Hopping Energy) (eV)	W_D (Disorder Energy) (eV)
0.3	-8.57	0.184	0.156	2.79	0.592	913	3.71	0.113	0.094
0.5	-5.59	0.218	0.338	2.67	0.567	692	6.47	0.416	0.092
0.7	-4.51	0.351	1.707	2.38	0.504	612	7.15	0.458	0.086
0.9	-3.41	1.238	2.378	1.73	0.368	523	9.94	0.527	0.079

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At low temperatures, Mott [25] has proposed a variable range hopping model, which is given by the relation

$$\sigma_{dc} = A \exp\left[-\left(T_0/T\right)^{0.25}\right] \quad (10)$$

where A and T_0 are constants and T_0 is given by

$$T_0 = \frac{16\,\alpha^3}{k\,N(E_{FM})} \quad (11)$$

Here, $N(E_{FM})$ is the Fermi level density of states. In Fig. 2(a), Dc conductivity is plotted as functions of $T^{-0.25}$. It is worth noting that the plot is linear over a considerable temperature range consistent with the variable range-hopping model. In Fig. 2(a), the investigational results are fitted to Eq. 10. The value of α^{-1} = 10 Å is assumed [22]. Using the slope (as presented in Fig. 2(a) by solid lines) attained from this linear relation, the values of $N(E_{FM})$ has been estimated using Eq. 11 and values are presented in Table 2. The values of $N(E_{FM})$ increase with composition (x), which justifies Dc conductivity results. The $N(E_{FM})$ values appear higher than those for the other molybdate [17] and vanadate glasses [26]. Again, Fermi level density of states of Mott's model ($N(E_{FM})$) [25], [27] can also be derived using investigational results and is plotted as functions of temperature, which is presented in Fig. 2(b). It is observed from Fig. 2(b) that the values of $N(E_{FM})$ rise gradually with temperature rise and the values of $N(E_{FM})$ do not increase sharply. It is also perceived that the values of$N(E_{FM})$ is composition dependent. These results recommend that the inclusion of V_2O_5play a significant role in the conductivity.

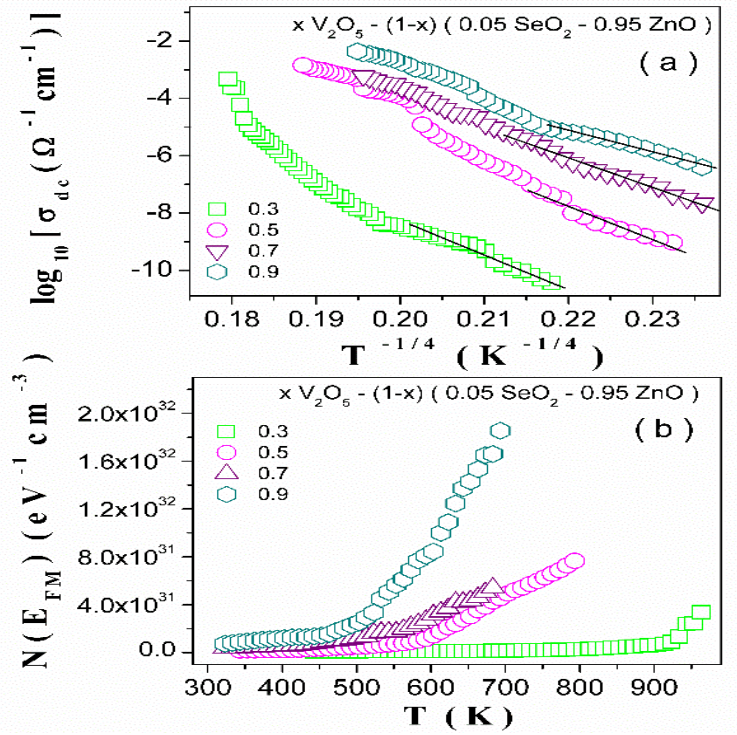


Fig. 2 (a) Variation of dc conductivity at low temperatures as a function of $T^{-0.25}$, solid lines indicate the best fitted straight lines fit; (b) The variation of density of states at Fermi level ($N(E_{FM})$) of Mott's model as a function of temperature.

At higher temperature, the temperature dependence Dc conductivity cannot be interpreted using Mott's model. However, Greaves [28] has predicted a temperature dependent variable range hopping model, which is dominant in high temperature region. Greaves has derived the following Dc conductivity expression at higher temperatures

$$\sigma_{dc} T^{1/2} = A' \exp\left[-\left(T_0'/T\right)^{0.25}\right] \quad (12)$$

Here A' and T_0' are constants and $T_0'$is given by

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$$T_0' = \frac{19.4\,\alpha^3}{k\,N(E_{FG})} \quad (13)$$

Fig. 3(a) depicts the plot of log ($\sigma T^{1/2}$) with reference to $T^{-0.25}$. Fig. 3(a) ascertains that Greaves's model yields good fits to the investigational results using Eq. 12. The value of α^{-1} = 10 Å is assumed for localized states, using the slope (as depicted in Fig. 3(a) by solid lines) obtained from this linear relation is used to calculate the values of $N(E_{FG})$ using Eq. 13 and values are tabularized in Table 2. The values of $N(E_{FG})$ increase with rise in V_2O_5 concentration (x), which agrees with Dc conductivity. Table 2 asserts that the density of state values estimated from Mott's model [$N(E_{FM})$] and Greaves model [$N(E_{FG})$] are nearby though they are functioning in dissimilar temperature ranges. It is also ascertained that with a rise in Dc conductivity, the values of density of state at Fermi level $N(E_{FM})$ and $N(E_{FG})$ also rise. With increasing temperature, thermal energy rises, which makes polaron hopping assisted by optical phonons, thus, possible collision take place between phonon and nanoclusters within the glass matrix. Due to collision, a part of energy may loss, which retains the values of $N(E_{FM})$ and $N(E_{FG})$ nearby. The density of states at Fermi level of Greaves model ($N(E_{FG})$) [28] can also be computed using experimental results and is plotted with regard to temperature as shown in Fig. 3(b). It is perceived from Fig. 3(b) that the values of $N(E_{FG})$ almost constant in lower temperature region and rises sharply at a specific temperature symbolized as Greaves threshold temperature (T_{HG}) and the values of T_{HG} are listed in Table 2. It is asserted that the T_{HG} values are higher than half of Debye temperature (θ_D) is, whereas the values of T_{HG} drops with rising V_2O_5 content, while Dc conductivity rises.

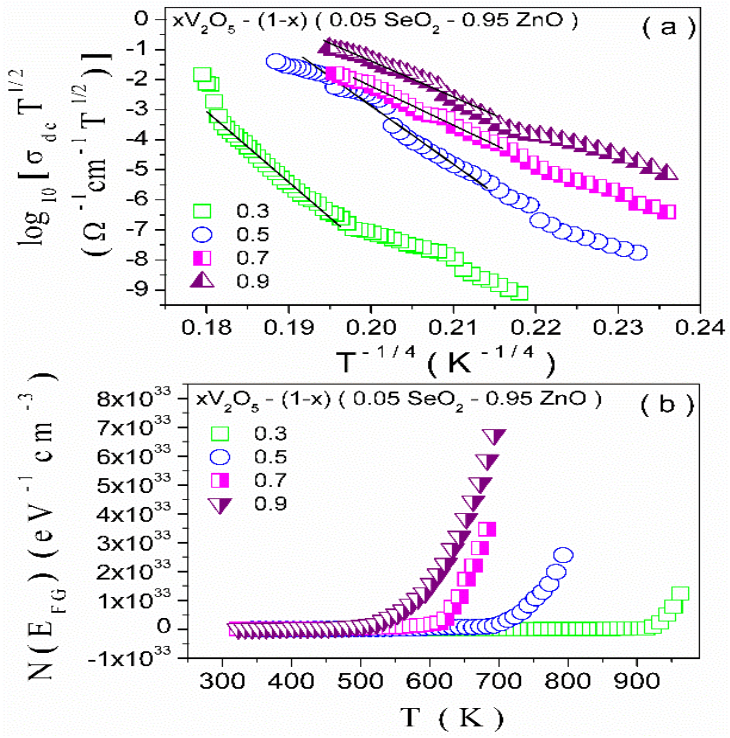


Fig. 3 (a) Variation of $\sigma_{dc}\,T^{1/2}$ at high temperatures as a function of $T^{-0.25}$, solid lines indicate the best fitted straight lines fit; (b) The variation of density of state at Fermi level (N (E_{FG})) of Greaves's model as functions of temperature.

The polaron hopping parameters, for instance, the temperature-dependent hopping distance (R_{hop}) and average hopping energy (W_{hop})can be estimated using the value of density of state of Mott's modelN(E_{FM}), which are expressed as [22]

$$R_{hop} = \left[\frac{9}{8\pi N(E_{FM})\,\alpha\,K_B\,T}\right]^{1/4} \quad (14)$$

and

$$W_{hop} = \frac{3}{4\,\pi\,R_{hop}^3\,N(E_{FM})} \quad (15)$$

The R_{hop} and W_{hop} values are estimated at 373 K of all the glass nanocomposites and listed in Table 2. The condition $R_{hop}\,\alpha \geq 1$ and $W_{hop} > K_B T$of Mott's VRH model are evidently fulfilled. Fig. 4(a) illustrates the variation of R_{hop}as functions of temperature. Fig.

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4(a) ascertains that with temperature rise, the values of hopping distance (R_{hop}) drops, while Dc conductivity increases. Fig. 4(b) shows the variation of R_{hop} and W_{hop} against V_2O_5 concentration (x).It is established that with inclusion of V_2O_5 content, the values of $R_{hop}$and W_{hop} drop, which makes Dc conductivity to rise, as polaron requires less hopping energy W_{hop} and the hopping distance $R_{hop}$of polaron is also lesser.

In view of strong interaction of electron-phonon, Mott and Davis [22]proved that

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

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

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, which is the energy difference between two neighboring sites, arising owing to deviation in the local arrangement of ions. Mott has suggested that due to interaction of polarons with optical phonons, the activation energy drops, which is the dominant process. If Eq. 1 is V_2O_5 concentration dependent, the hopping process is known as non-adiabatic hopping and if it varies with concentration of V_2O_5, is recognized as adiabatic hopping process. In adiabatic hopping process, the tunneling term exp (–2αR) in Eq. 1 becomes unity and the conductivity is expressed by [3], [8], [18]

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

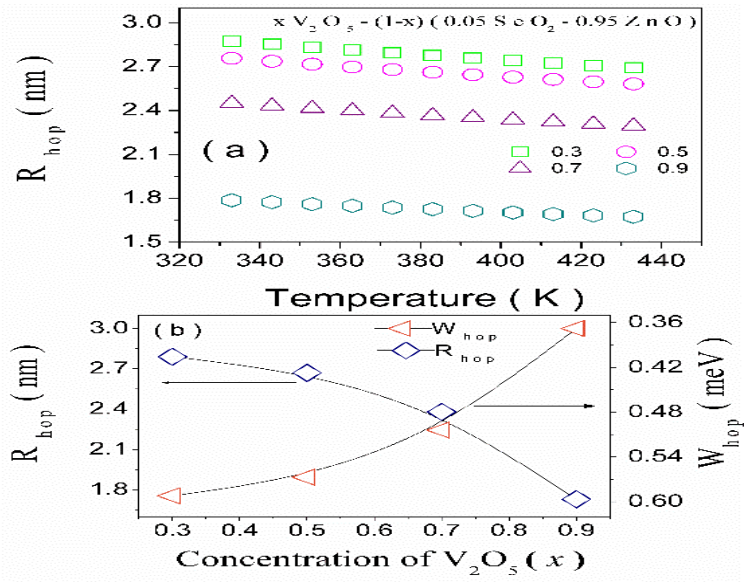


Fig. 4 (a) The variation of hopping distance (R_{hop}) as functions of temperature for different values of x;(b) The temperature-dependent hopping distance, R_{hop}, and average hopping energy, W_{hop}, of all the glass nanocomposites at a temperature (373K).

If Eq. 18 is independent of V_2O_5 concentration, then the nature of hopping conduction is adiabatic type [29]-[31].If the tunneling factor in Eq. 1, exp (–2αR), is neither constant nor equal to one, which means that σ_0 varies with composition, specifying non-adiabatic nature of hopping conduction [17], [32]. The term pre-exponential factor (σ_0) is estimated by means of the experimental results, explicitly the intercept of log σ_{dc} versus1000/T plot at 1000/T = 0 [33]. Fig. 5(a) depicts the effect of V_2O_5 concentration on pre-exponential factor (σ_0).As discussed formerly, it is asserted that the conduction in these as-quenched glassy samples owe to the non-adiabatic small polaron hopping process in both low and high temperature region. The nature of hopping mechanism at high temperature region, where dc conductivity is thermally activated, can also be determined from the plot of log σ_{dc} versus W at an arbitrary experimental temperature [3], [34]. If the estimated temperature from the slope of such plot is near to experimental temperature, it is supposed to be of adiabatic type. Otherwise, the hopping would be of non-adiabatic type [33], [35]. Fig. 5(b) presents the plot of log σ_{dc} against activation energy (W) at two dissimilar experimental temperatures 500K and 444K. The corresponding values of estimated temperatures from the slope (–1/2.303*K_BT) of the plots are found to be 369K and 387K

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respectively, which are very much different from experimental temperatures. Therefore, the validation of the non-adiabatic polaron hopping conduction mechanism of all the glassy samples is justified.

Alternatively, the value of the tunneling factor, α, which is the ratio of the wave function decay, according to Eq. 2, can be determined from the slope of log σ_0 versus R_V plot [3]. The result of such assessment is shown in Fig. 6(a) and the value of slope is (–2α). The estimated value of α is 1.169×10^{8} cm $^{-1}$, which is lesser than the values of that of some other semiconducting glassy systems [3], [33]. The value of R_V is plotted against the concentration of V_2O_5 (*x*) as shown in Fig. 6(b). The values of R_V reduce with the inclusion of V_2O_5. Consequently, Dc conductivity increases as an effect of polaron hopping from V^{+4} site to V^{+5} site.

Alternatively, Holstein has suggested the nature of hopping mechanism by small polaron hopping model [36].As stated by Holstein's model, the nature of hopping process depends on inequality conditions, which are expressed using the following relation

$$J > J^{*} \quad \text{adiabatic} \quad (19)$$

$$J < J^{*} \quad \text{non-adiabatic} \quad (20)$$

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

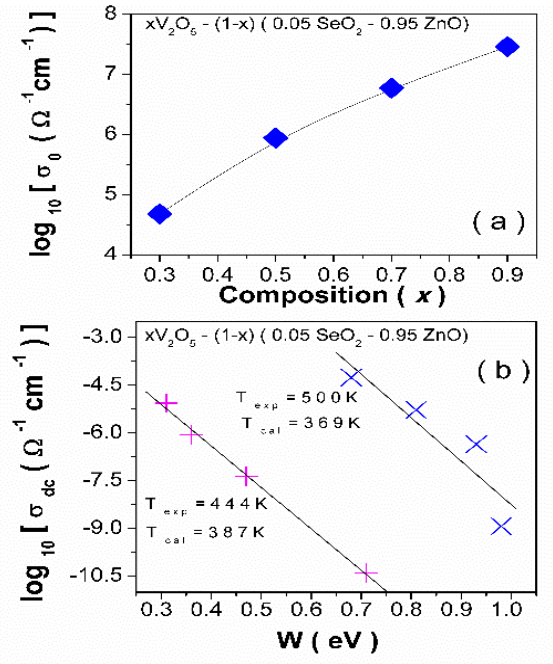


Fig. 5 (a) Effect of V_2O_5 concentration on pre-exponential factor, σ_0, for different values of*x*; (b) The dc conductivity at experimental temperatures (T) 444 K and 500 K versus the activation energy for different compositions of glass nanocomposites. Symbols represent experimental data and solid lines represent the linear fit.

Here, J is the overlapping of electron wave function on the neighboring sites known as polaron bandwidth and W_H is polaron hopping energy. The W_H values is estimated using the Eq. 16 taking the values of W_D from Schnakenberg model and J is calculated by the following relation [36]-[38]

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

The values of J, J^{*} and W_H are listed in Table. 3. As stated by Mott and Davis [22] at low temperature, the polaron hopping energy W_H^{*} is derived as

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

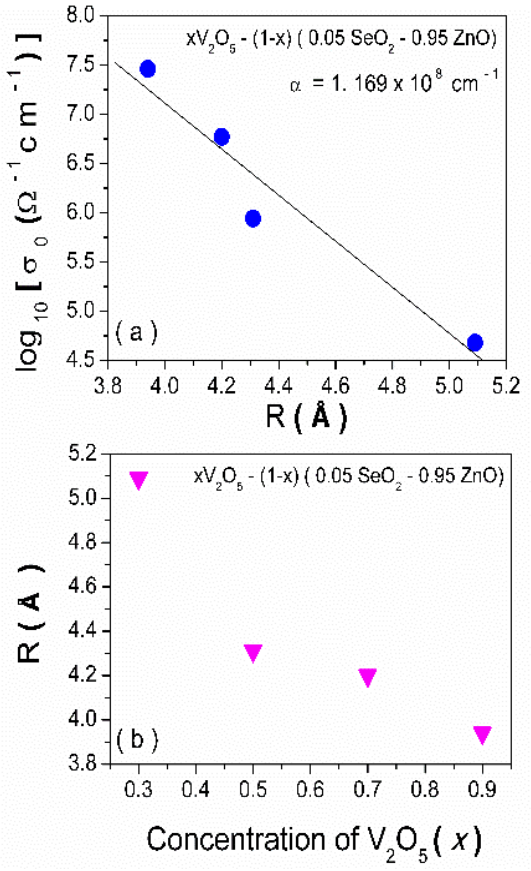


Fig. 6 (a) Relationship between log σ_0 and mean V-ion site spacing (R_V) for different values of *x*. Solid line represents linear fit data, the slope of these line is (−2α); (b) Relationship between mean V-ion site spacing (R_V) and V_2O_5 concentration (*x*).

Table 3 reveals that the inequality Eq. 20 ($J < J^*$, non-adiabatic) is valid of all the glassy samples, which consecutively support our assertion that polaronic conduction of the presently studied glassy samples is non-adiabatic in nature. The small polaron hopping condition that is $J < W_H / 3$ is also fulfilled in both high and low temperature regions [36], [39]. A measure of interaction between electron and optical phonon is known as small polaron coupling constant (γ_P), which is expressed by [22] [32], [39]

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

The estimated values of γ_P are tabularized in Table 3. It is revealed from Table 3 that at high temperature (641K) γ_P values are in the range of 24.4-15.7 and at low temperature (444K) γ_P values are in the range of 17.3-6.6, which directly specify a very strong electron-phonon interaction in all the glassy samples as $\gamma_P > 4$ directs a strong electron-phonon interaction [32], [39]. However, it is also ascertained from Table 3 that small polaron coupling constant (γ_P) values drop with a rise in V_2O_5 concentration. The relation of polaron mass (m_p) to rigid lattice effective mass (m^*) is obtained by [32]

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

The calculated values of m_p/m^* are tabulated in Table 3, which are very large values both in high temperature (641K) and low temperature (444K) and once again it asserts strong electron-phonon interaction [22]. Table 3 shows that the values of m_p/m^* decrease with rising V_2O_5 concentration. Scrutinizing of data listed in Table 3 it can be concluded that the values of polaron hopping parameters are temperature and composition dependent. We have also incorporated the polaron hopping parameters of $40V_2O_5$-$40Bi_2O_3$-20ZnO [40] and VN-PbO-TeO_2 [41] glassy systemsfor comparisonin Table. 3. It is perceived that values of small polaron coupling constant (γ_P) and m_p/m^* of present glassy systems are much higher than $40V_2O_5$-$40Bi_2O_3$-20ZnO [40] and VN-PbO-TeO_2 [41] glassy systems, which points out strong electron-phonon interaction in the presently studied glassy systems.

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TABLE III

Polaron hopping parameters of xV2O$_5$-(1-x) (0.05SeO$_2$-0.95ZnO) for x = 0.3, 0.5, 0.7 and 0.9 glass nanocomposites and comparing those data with 40V$_2$O$_5$-40Bi$_2$O$_3$-20ZnO glassy system (Ref. 40) and VN-PbO-TeO$_2$ glassy systems (Ref. 41).

Glass Composition		Parameters					
	T	W_H (eV)	J^*	J	W_H^* (eV)	γ_P	m_P / m^*
x=0.3	444K	0.663	0.055	0.0431	0.661	17.3	3.3×10^{7}
	641K	0.933	0.067	0.0472	0.931	24.4	3.9×10^{10}
x =0.5	444K	0.424	0.050	0.0437	0.423	10.8	5.1×10^{4}
	641K	0.884	0.066	0.0479	0.882	22.6	6.6×10^{9}
x =0.7	444K	0.317	0.047	0.0442	0.316	7.98	2.9×10^{3}
	641K	0.767	0.064	0.0485	0.765	19.3	2.4×10^{8}
x =0.9	444K	0.271	0.045	0.0451	0.269	6.64	7.6×10^{2}
	641K	0.641	0.062	0.0495	0.639	15.7	6.7×10^{6}
40V$_2$O$_5$-40Bi$_2$O$_3$-20ZnO (Ref. 40)		0.32	0.034	0.023	0.31	15.3	4.5×10^{6}
VN-PbO-TeO$_2$ (Ref. 41)		0.18	0.051	0.031	0.17	14.1	1.4×10^{6}

The hopping carrier mobility (μ) for non-adiabatic hopping conduction is expressed as [18], [22], [42]

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

Here hopping carrier mobility (μ) values are estimated with the data of W, R, J and W_H presented in Table 1 and Table 3 and the values of hopping carrier mobility (μ) for the temperature 444K and 641K are tabulated in Table. 4. The hopping carrier mobility (μ) of all the glassy samples is very small, signifying localization of electrons or polarons around V-ions [16], [35]. As the conduction of localization for conductive electrons is generally $\mu < 10^{-2}$ cm^{2}V^{-1}s^{-1} [4], the conduction owing to hopping mechanism in all the glassy samples is established. Fig. 7(a) presents the deviation of hopping carrier mobility (log μ) with reference to temperature (T). It is realized that μ values rise with a rise in V_2O_5 concentration and with temperature rise, thus the conductivity also increases. Therefore, we can conclude that μ of as-prepared glassy samples are temperature and composition dependent. The hopping carrier concentration (N_C) is then estimated using the well-known formula [36]

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

The values of N_C are listed in Table. 4 and it is observed that the values N_C are of very high order. Fig. 7(b) depicts the deviation of N_C with respect to composition (x). Fig. 7(b) clearly indicates that N_C values increase with rising V_2O_5 content and with a rise in temperature. The small hopping carrier mobility (μ) and higher hopping carrier concentration (N_C) values confirm that hopping of electrons/polarons arise in consequence ofthe localization at V-ion sites. The values of μ and N_C increase with increasing V_2O_5 concentration in consequence of the continuous decrease in effective mass of polarons as one goes from x= 0.3 to x = 0.9. From Table 4, it can be concluded that μ and N_C is temperature and composition dependent same as the conductivity of the as-quenched glassy samples.

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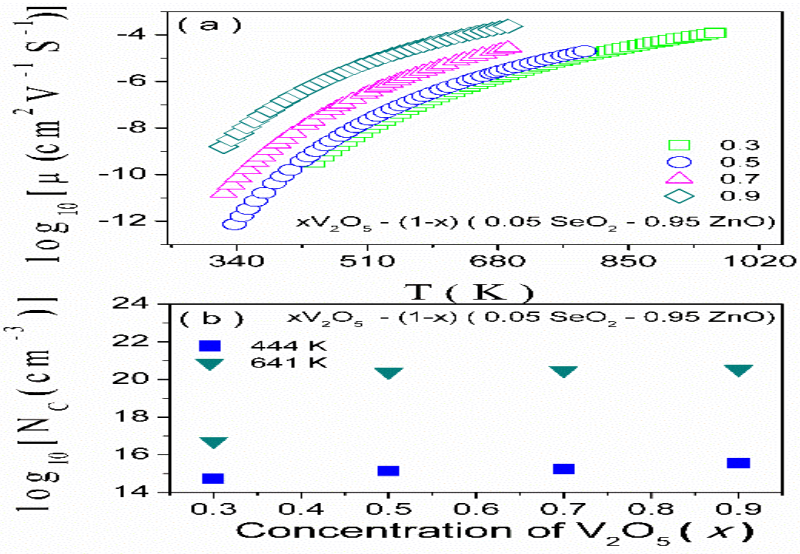


Fig. 7 (a) The plot of hopping carrier mobility (log μ) versus temperature (T) for various glassy compositions; (b) Effect of V_2O_5 content on hopping carrier concentration (log N_C) at 444 K and 641 K for different values of *x*.

TABLE IV

Hopping carrier mobility (μ) and hopping carrier concentration (N_C) of all theglass nanocomposites at 641K and 444K for different values of *x*.

x	μ ($cm^2 V^{-1} s^{-1}$) at 444K	N_C (cm^{-3}) at 444K	μ ($cm^2 V^{-1} s^{-1}$) at 641K	N_C (cm^{-3}) at 641K
0.3	4.42×10^{-07}	$5.37 \times 10^{+14}$	5.84×10^{-07}	$5.28 \times 10^{+16}$
0.5	2.17×10^{-04}	$1.37 \times 10^{+14}$	1.10×10^{-06}	$2.48 \times 10^{+20}$
0.7	4.42×10^{-03}	$1.77 \times 10^{+15}$	1.01×10^{-05}	$3.04 \times 10^{+20}$
0.9	1.58×10^{-02}	$3.52 \times 10^{+15}$	1.06×10^{-04}	$3.47 \times 10^{+20}$

IV. CONCLUSION

The temperature dependent Dc conductivity of the semiconducting glass nanocomposites with general nomenclaturexV_2O_5-(1-*x*)($0.05SeO_2$-$0.95ZnO$) for *x* = 0.3, 0.5, 0.7 and 0.9 have been investigated in the wide temperature range. Dc conductivity is analyzed in the framework of Mott and Greaves model. Schnakenberg's optical multi-phonon hopping model is persistent with the temperature dependent activation energy. It is ascertained that Dc conduction occurs owing to small polaron hopping in non-adiabatic regime and in consequence of polaron hopping from V^{+4} to V^{5+} valence state. The electron-phonon interaction is strong and dominant over entire temperature range. The various judicious values of physical parameters, for instance, polaron hopping energy, disorder energy, optical phonon frequency, density of states at the Fermi level, polaron bandwidth, etc. have been estimated by fitting the investigational outcomes to theoretical models. The Dc conductivity and hopping carrier mobility (μ) increases with rise in V_2O_5 concentration and with rising temperature. The hopping carrier concentration (N_C) is composition and temperature dependent.

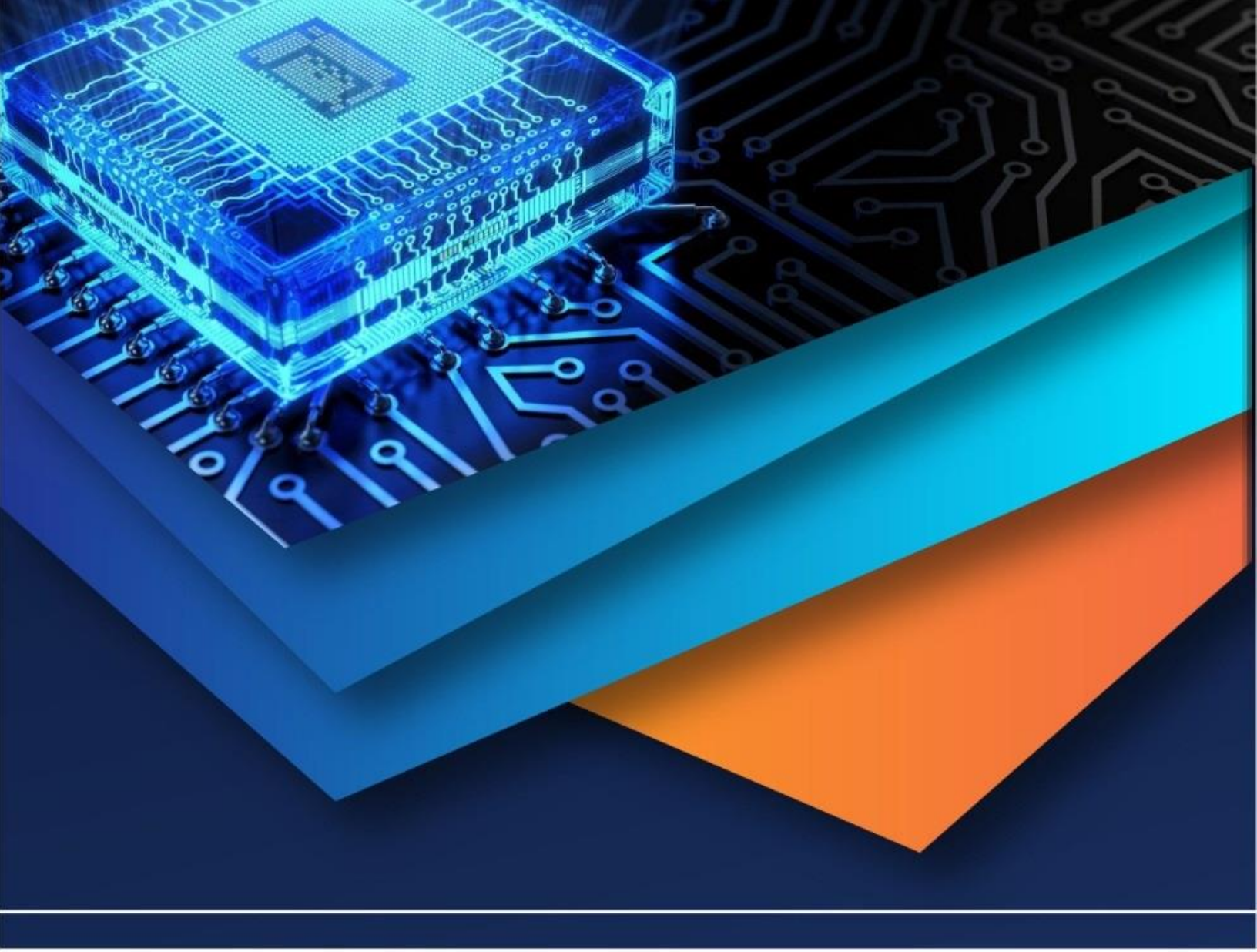
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