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Tunneling of large polarons in semiconducting zinc vanadate glasses

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Abstract
The ac electrical properties of several compositions of the semiconducting zinc vanadate glasses have been studied in the frequency range 10 Hz–2 MHz and in the temperature range 93–423 K. It has been observed that the ac conductivity shows power law dependence. The experimental data for the conductivity have been analyzed in the framework of several theoretical models based on quantum mechanical tunneling and classical hopping over barriers in order to determine the conduction mechanism. It has been observed that the model based on the tunneling of large polarons, out of the several models discussed, could explain adequately the temperature and frequency dependence of the ac conductivity and its power law exponent. The parameters obtained from the fits of this model with the experimental results are reasonable.

1. Introduction

Transition metal oxide glasses show semiconducting properties, which arise from the presence of more than one valence state of the transition metal ions [1–3]. These glasses have drawn much attention due to their possible application as optical and memory switching devices, etc [4–7]. The dc electrical conduction in these semiconductors was observed to be due to the hopping of either electrons or polarons with strong temperature dependence of the corresponding activation energy [8–14]. The frequency dependent loss in amorphous semiconductor containing transition metal ions has also been studied [15–21]. However, it becomes the subject of much controversy depending on materials studied and the temperature range considered [15–17]. In most studies [15–21] it was observed that the frequency dependent ac conductivity in amorphous semiconductor shows sub-linear frequency dependence at low frequencies and temperatures. Several models [1, 3, 22–24] based on the relaxation caused by the hopping or tunneling of electrons (polarons) or atoms between equilibrium sites have been developed to explain the frequency and temperature dependence of the ac conductivity in different limited temperature ranges. However, more studies in different glassy materials are necessary in order to give more insight into the hopping mechanisms predicted in these models.

In this paper the ac conductivity of a glass series, prepared using V_2O_5 as the network former and ZnO as the network modifier, has been investigated in the frequency range 10 Hz–2 MHz and in the temperature range 93–423 K to determine the mechanism for the ac conductivity by examining the observed experimental results in terms of the existing theoretical models. It has been observed that the tunneling of the overlapping large polarons is the dominant mechanism for the ac conductivity in these glasses.

2. Experimental procedure

The details of the preparation of several glass compositions in the system xV_2O_5–$(1-x)$ZnO for $x = 0.5$–0.8 have been reported elsewhere [26]. The sample compositions were prepared from the reagent grade chemicals V_2O_5 and ZnO (Aldrich Chem. Co). The mixtures of these chemicals in appropriate amounts were melted in a platinum crucible in an electrical furnace at 900 °C for 2 h. The melts were occasionally stirred for homogenization and were finally poured on an aluminum block and pressed immediately by another aluminum block. X-ray diffraction (XRD) patterns of the powdered samples, recorded in an x-ray diffractometer (Seifert, model XRD-3000P), confirmed the amorphous nature of these samples (figure 1). For electrical measurements samples of diameter ∼10 mm and thickness ∼1 mm were prepared and both sides of them were coated with gold to serve as the electrode. The capacitance and conductance of the gold-coated samples were measured in an RLC meter (QuadTech, Model 7600) in the frequency range 10 Hz–2 MHz. The

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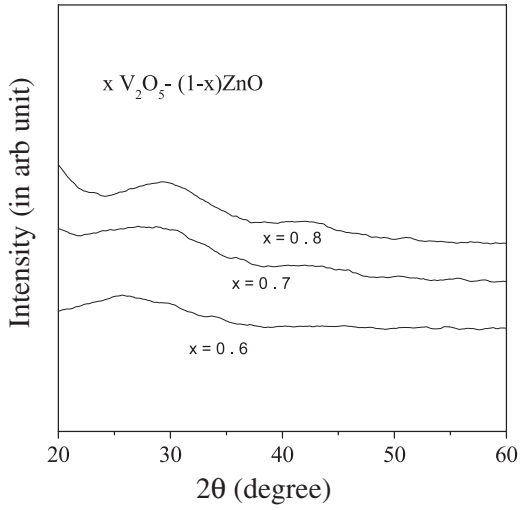

Figure 1. X-ray diffraction patterns of some prepared samples of compositions $x\mathrm{V_2O_5}$–$(1-x)$ZnO shown in the inset.

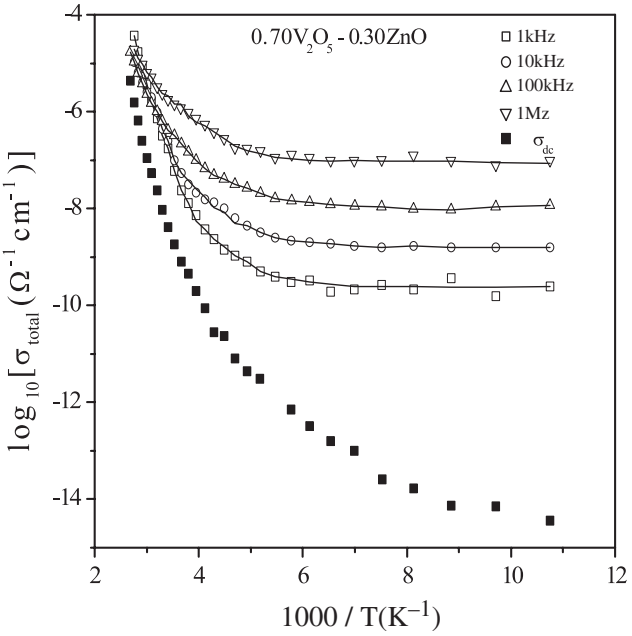

Figure 2. Measured total conductivity for the $0.7\mathrm{V_2O_5}$–0.3ZnO glass composition, shown as a function of inverse temperature at four different frequencies. The measured dc conductivity from an earlier report [26] is also shown. The solid lines in the figure are the best fits obtained from the overlapping large polaron tunneling model (equation (7)).

measurements were carried out in a closed cycle cryostat in the temperature range 93–423 K with a stability of ±0.10 K.

3. Results and discussion

The measured total conductivity (σ_{total}) at four frequencies is shown in figure 2 as a function of reciprocal temperature for the $0.7\mathrm{V_2O_5}$–0.3ZnO glass composition. The dc conductivity, σ_{dc} from earlier report [26] is also included in the figure for comparison. At low temperatures the temperature dependence of σ_{total} is much less than that of σ_{dc} and is not activated in nature. However, at high temperatures the temperature dependence of σ_{total} becomes strong and its frequency dependence becomes small and they almost coincide with the σ_{dc}. The temperature dependence of the measured conductivity σ_{total} at a fixed frequency for different compositions is shown in figure 3. It may be noted that all compositions show similar temperature dependences.

The frequency dependence of the measured conductivity at different temperatures is shown in figure 4. The results are very similar to those for many other amorphous semiconductors including semiconducting glasses [3, 22]. It is noted that at low temperatures the frequency dependence of the measured conductivity for all temperatures is not significant. However, at higher frequencies the conductivity shows dispersion. It is noted that the dispersion starts at a higher frequency as the temperature is increased.

In general, the frequency dependence of the total conductivity measured within a fixed frequency window can be expressed as [3, 22]

$$\sigma_{\mathrm{total}}(\omega) = \sigma'(\omega) + \sigma_{\mathrm{dc}}, \tag{1}$$

where $\sigma'(\omega)$ is the ac conductivity. A frequency dependent ac conductivity $\sigma'(\omega)$ has been observed in semiconducting glasses similar to many amorphous semiconductors [22] and invariably has the power law form [25]

$$\sigma'(\omega) = A\omega^s, \tag{2}$$

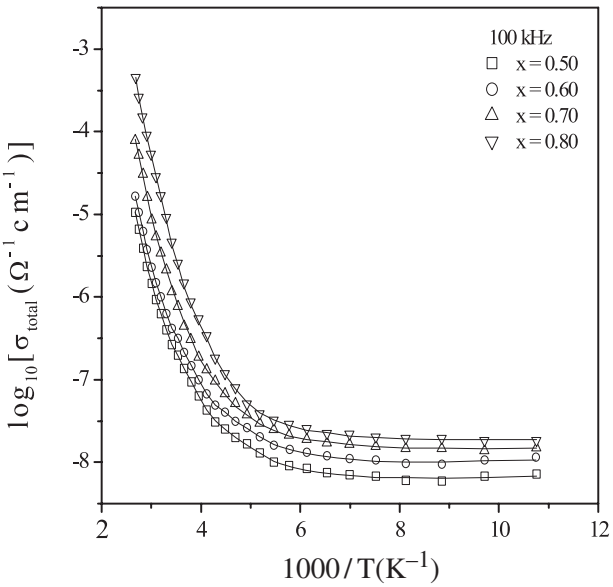

Figure 3. Measured total conductivity at 100 kHz for $x\mathrm{V_2O_5} - (1-x)$ZnO glass compositions shown as a function of inverse temperature. The solid lines in the figure are the best fits obtained from the overlapping large polaron tunneling model (equation (7)).

where A is a constant dependent on temperature and the power law exponent s is generally equal to or less than unity.

Figure 5 shows the ac conductivity $\sigma'(\omega)$ at different temperatures, obtained by subtracting the dc conductivity from the measured total conductivity, as a function of frequency for a glass composition. The ac conductivity $\sigma'(\omega)$ for different

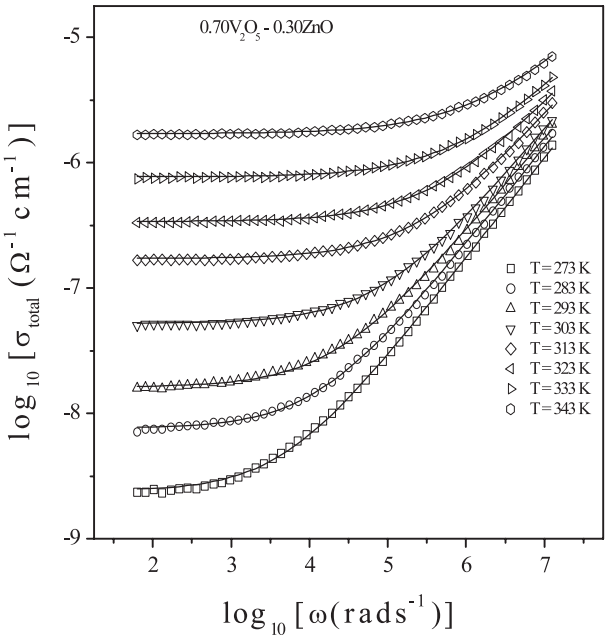

Figure 4. Frequency dependence of the measured total conductivity at different temperatures shown in the inset for the $0.7V_2O_5$–$0.3ZnO$ glass composition.

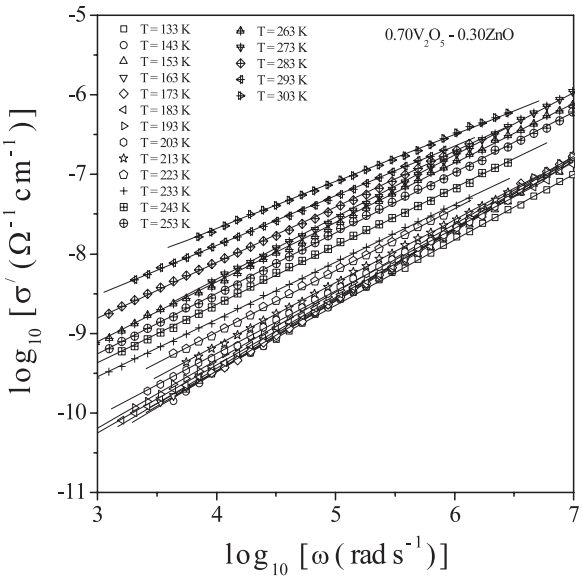

Figure 5. The frequency dependent ac conductivity, obtained by subtracting the dc conductivity from the measured total conductivity, for the $0.7V_2O_5$–$0.3ZnO$ glass composition shown at different temperatures. The solid lines are the least square straight line fits of the data.

compositions at a fixed temperature (203 K) is also shown in figure 6. It is noted that the plots in figures 5 and 6 are almost linear, satisfying the power law expression (equation (2)). The frequency exponent s was obtained from the least square straight line fits of the data. The data for s are shown in figure 7(a) as a function of temperature for different glass compositions. It is noted that s decreases from close to unity to an almost fixed value with increasing temperature. It is also

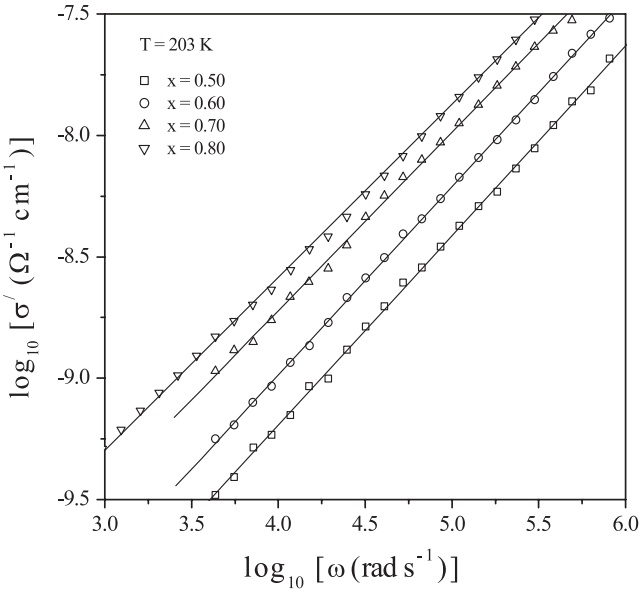

Figure 6. The frequency dependent ac conductivity for different compositions of xV_2O_5–$(1-x)$ZnO glasses at a fixed temperature (203 K).

observed in figure 7(a) that s decreases with the increase of V_2O_5 content in the compositions.

The specific mechanism for the ac conductivity operating in the present system has been obtained by analyzing the temperature dependence of the ac conductivity and its frequency exponent predicted by various existing theoretical models based on quantum mechanical tunneling and hopping over a barrier of charge carriers. The detailed analysis is considered below.

Several authors [2, 3, 23] have evaluated, within the pair approximation, the ac conductivity for single electron motion undergoing quantum mechanical tunneling and have obtained an expression for s as

$$s = 1 - 4/(1/\omega\tau_0). \tag{3}$$

Thus this model predicts that s (about 0.81) is temperature independent but frequency dependent. A temperature dependent s can be obtained within the framework of the quantum mechanical tunneling model in the pair approximation by assuming that the carriers form non-overlapping (small) polarons [23] i.e. the total energy of a charge carrier is lowered by the polaron energy, W_p, resulting from the lattice distortion accompanying the occupation of the site by the carrier. The transpose of an electron between degenerate sites having random distribution of separations generally involves an activation energy, i.e. the polaron hopping energy $W_H \approx W_p/2$. In this case, the frequency exponent becomes

$$s = 1 - 4/[\ln(1/\omega\tau_0) - W_H/k_B T]. \tag{4}$$

Now it is noted that s is temperature dependent, but increases with increasing temperature. However, the variation of the data for s with temperature presented in figure 7(a) shows opposite

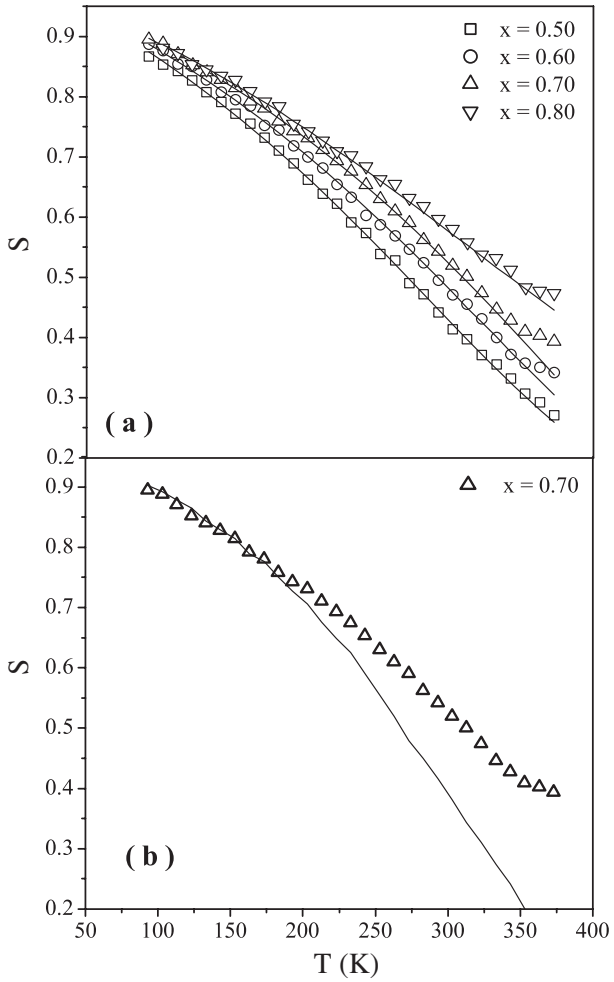

Figure 7. The frequency exponent s for different $xV_2O_5 - (1-x)$ZnO glasses are shown as a function of temperature. (a) The solid curves are the best fits obtained from the overlapping large polaron tunneling model (equation (8)). (b) The fits of the frequency exponent s for a composition to the correlated barrier hopping model (equation (13)).

trends, indicating that the quantum mechanical tunneling models for electrons and small polarons are not applicable to the V_2O_5–ZnO glasses.

A mechanism for the polaron tunneling, where the polaron energy is derived from polarization changes in the deformed lattice as in ionic crystals and glasses was proposed by Long [3]. The resultant excitation is called a large or dielectric polaron. Because of the long range of the Coulomb interaction, its well will extend over many interatomic distances and overlap with the wells of other sites. This has important consequences for the frequency dependent losses because the activation energy associated with charge transfer between the overlapping sites will be reduced [2, 3] according to

$$W_H = W_{HO}(1 - r_p/R) \tag{5}$$

where r_p is the polaron radius, W_{HO} is given by

$$W_{HO} = e^2/4\varepsilon_p r_p, \tag{6}$$

where ε_p is the effective dielectric constant. It is assumed that W_{HO} is constant over sites, but R is a random variable.

Table 1. Parameters obtained from the fits of the ac conductivity data to the large polaron tunneling model for different compositions of xV_2O_5–$(1-x)$ZnO glasses.

x	W_{HO} (eV) (±0.01)	α (Å^{-1}) (±0.02)	τ_0 (10^{-12} s) (±0.05 × 10^{-12})	r_p (Å) (±0.02)	$N(E_F)$ (10^{18} eV^{-1} cm^3) (±0.06 × 10^{18})
0.50	0.33	0.86	2.58	3.40	4.58
0.60	0.30	0.88	2.70	3.68	4.60
0.70	0.38	0.90	2.67	3.81	4.62
0.80	0.37	1.11	2.77	3.70	4.60

Long [3] has obtained the expression for ac conductivity as

$$\sigma'(\omega) = [(\pi^2 e k_B T)^2/12] \times [N(E_F)]2\omega R_\omega^4/[2\alpha k_B T + W_{HO} r_p/R_\omega^2] \tag{7}$$

and the frequency exponent s has been calculated as

$$s = 1 - (1/R'_\omega)(4 + 6\beta W_{HO} r'_p/R'^2_\omega)/(1 + \beta W_{HO} r'_p/R'_\omega)^2. \tag{8}$$

R'_ω and r'_p are related by the dimensionless equations

$$R'^2_\omega + [\beta W_{HO} + \ln(\omega\tau_0)]R'_\omega - \beta W_{HO} r'_p = 0$$
$$R'_\omega = 2\alpha R_\omega, \qquad r'_p = 2\alpha r_p, \qquad \beta = 1/k_B T. \tag{9}$$

Thus the overlapping large polaron tunneling model (equation (8)) predicts that s is a decreasing function of temperature, which is consistent with the experimental data presented in figure 7(a).

The experimental data for s for different compositions have been fitted to equation (8) predicted by the above model in figure 7(a), where it is noted that the fits of the experimental data are very good. The values of the parameters obtained from the best fits are shown in table 1 for different compositions. The experimental data for $\sigma_{total}(\omega)$ presented in figure 2 at different frequencies have been also fitted to the ac conductivity $\sigma'(\omega)$ calculated from equation (7) plus the experimental dc conductivity. It is noted that the fits in this case are also very good for the values of the parameters used for the fits of s in figure 7(a). It may be noted that the values of W_{HO} are slightly less than the values of high temperature activation energy reported earlier [26]. The values of α and $N(E_F)$ obtained from this model agree well with those values obtained from Mott's model for the dc conductivity [26]. The values of τ_0 obtained from the fits are very close to the values obtained from the infrared spectra [27].

The experimental data for s presented in figure 7(a) are also predicted qualitatively in the framework of the barrier hopping model [22, 24], which correlates the relaxation variable W with the inter-site separation R. For neighboring sites at a separation R, the overlapping of the Coulomb wells results in a lowering of the effective barrier height from W_M to a value W, which for the case of one electron transition is given by [22]

$$W = W_M - (e^2/\pi\varepsilon'\varepsilon_0 R). \tag{10}$$

In this correlated barrier hopping model the ac conductivity is expressed by [22]

$$\sigma_1(\omega) = (\pi^2/24)N^2\varepsilon'\varepsilon_0\omega R_\omega^6 \tag{11}$$

where N is the concentration of pair sites and R_ω is the hopping distance at frequency ω given by

$$R_\omega = e^2/[\pi\varepsilon'\varepsilon_0/\{W_M - k_B T \ln(l/\omega\tau_0)\}]. \quad (12)$$

The frequency exponent in this model can be expressed as [22],

$$s = l - k_B T/[W_M - k_B T \ln(l/\omega\tau_0)]. \quad (13)$$

Thus, in the correlated barrier hopping model the exponent s decreases with increasing temperature similar to the experimental data. We have tried to fit the experimental data for s to equation (13) predicted by the above model. The fit for a glass composition is shown in figure 7(b). It may be noted that the experimental data and the prediction of the correlated barrier hopping model are in agreement only in a limited low temperature range. Also reasonable fits of the experimental data to the barrier hopping model based on two electrons hopping simultaneously [22] were not obtained.

Thus, out of several models discussed above, the large polaron tunneling model is the best to interpret the ac conductivity of the present vanadate glasses. But the reason for the applicability of this particular model for the present system is not clear at present. An adequate knowledge of the local structure of these glasses is necessary to resolve this fact.

4. Conclusions

The ac electrical conductivity of the V_2O_5–ZnO semiconducting glasses has been studied in the frequency range 10 Hz–2 MHz and in the temperature range 93–343 K. Out of the several models discussed above, only the overlapping large polaron tunneling model is consistent with the temperature dependence of the ac conductivity and the power law exponent. Fits using this model are in good agreement with the experimental data for all temperatures and frequencies measured. Other models, such as quantum mechanical tunneling and barrier hopping models are not suitable for zinc vanadate glasses.

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