ac relaxation in silver vanadate glasses

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The frequency dependent ac conductivity of semiconducting silver vanadate glasses has been studied in the temperature range 87–423 K and in the frequency range 10 Hz–2 MHz. The experimental results have been analyzed with reference to various theoretical models based on quantum mechanical tunneling and classical barrier hopping. The analysis shows that the temperature dependence of the ac conductivity is consistent with the overlapping large polaron tunneling model at temperatures below 275 K in the measured frequency range. The frequency exponent data show a departure from the theoretically expected values above 275 K. A scaling of the conductivity spectra with respect to temperature is attempted for these glasses at high temperatures. It is observed that at temperatures above 275 K the conductivity spectra show a time-temperature superposition principle consistent with the temperature independence of the frequency exponent in this temperature region.

I. INTRODUCTION

The general condition for the semiconducting behavior of the oxide glasses containing transition metal ions is that the transition metal ions should be capable of existing in more than one valence state (e.g., V^{+5} and V^{+4} in vanadate glasses) so that conduction can take place by the transfer of electron from low to high valence state.[1–3] Like many other amorphous materials,[1,3,4] a frequency dependence of the ac conductivity and loss has been observed in semiconducting glasses containing transition metal ions,[5–7] and has been the subject of much controversy. The dc electrical conduction in this semiconducting glasses was observed to be due to the hopping of either electrons or polarons with a strong temperature dependence of the corresponding activation energy.[8–12] It was observed that at low temperatures, the ac conductivity $\sigma(\omega)$ at frequency ω behaves as ω^s where the frequency exponent s is generally less than or equal to unity and dependent on the temperature. Several models[1,3,4] 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 and s within different limited temperature ranges. However, fewer studies[5,6,10,13,14] were made on the frequency dependent conductivity of transition metal oxide semiconducting glasses in light of these existing theoretical models. In this present work, we have made a comprehensive study of the frequency and temperature dependence of the ac conductivity of various compositions of silver vanadate semiconducting glasses over the frequency range 10 Hz–2 MHz and the temperature range 87–423 K.

II. EXPERIMENT

Glass samples of compositions $xV_2O_5-(1-x)Ag_2O$, where $x=0.5$, 0.6, 0.7, and 0.8, were prepared by melting the AgNO$_3$ (99.9%) and V$_2$O$_5$ (99%). The appropriate amounts of AgNO$_3$ and V$_2$O$_5$ powders were thoroughly mixed and preheated in an alumina crucible at 450 °C for 2 h for calcination of AgNO$_3$. The mixtures were then melted

in the temperature range from 900 to 1000 °C depending upon the composition. The melts were equilibrated for 30 min and quenched between two plates. Glass samples of thickness ∼0.1 mm were obtained for $x=0.5-0.8$. The samples were annealed at 150 °C for 1 h. The absence of crystallinity was verified by x-ray diffraction (Seifert, model 3000P) studies. The density of the samples was measured by Archimedes' principle using acetone as an immersion liquid. The total vanadium ion concentration (N) was estimated from the glass composition and density. For electrical measurements, gold electrodes were deposited on both surfaces of the polished samples of diameter ∼10 mm. The electrical measurements such as capacitance and conductance of the samples were carried out in the frequency range 10 Hz −2 MHz using a RLC meter (QuadTech, model 7600) interfaced with a computer in the temperature range 87−423 K. The ionic contribution to the total conductivity for different glass compositions was determined using Wagner's polarization cell technique.[15] We observed that the ionic contribution to the total conductivity was ∼0.2%. Thus the measured conductivity was primarily electronic in nature.

III. RESULTS AND DISCUSSION

The measured conductivity $\sigma_{total}(\omega)$ of $0.6V_2O_5-0.4Ag_2O$ glass composition for four fixed frequencies is shown in Fig. 1(a) as a function of reciprocal temperature. The variation of the dc conductivity σ_{dc} with the temperature is also included in this figure. At low temperatures, the temperature dependence of $\sigma_{total}(\omega)$ is much less than that of the dc conductivity σ_{dc} and is not activated in nature. However, at high temperatures the temperature dependence of $\sigma_{total}(\omega)$ becomes strong and its frequency dependence becomes small. At higher temperatures the conductivity for all frequencies almost coincides with σ_{dc}. The conductivity at higher frequencies tends to coincide with σ_{dc} at higher temperatures. A similar behavior was observed for the other glass compositions with a difference in the temperature at which the measured conductivity becomes equal to the dc conductivity. In Fig. 1(b) the temperature dependence of the
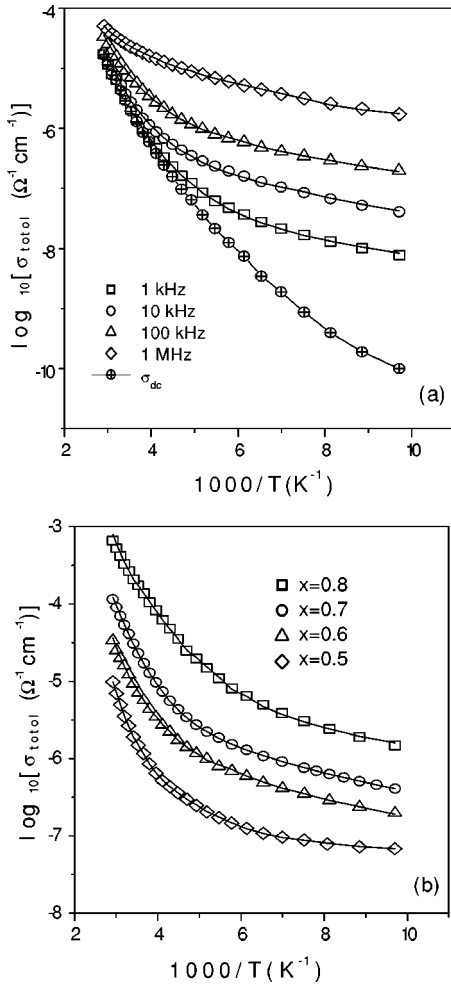
FIG. 1. (a) Measured total conductivity for the sample composition $0.6V_2O_5-0.4Ag_2O$ shown as a function of inverse temperature at four frequencies shown. The measured dc conductivity is also shown (Ref. 12). (b) Measured total conductivity for the sample compositions $xV_2O_5-(1-x)Ag_2O$ for $x=0.8$, 0.7, 0.6, and 0.5 as a function of inverse temperature at the 100-kHz frequency shown. The solid lines in both cases are the best fits to the overlapping large polaron model [Eq. (7)].

FIG. 2. (a) The frequency-dependent real ac conductivity, for $0.6V_2O_5-0.4Ag_2O$ glass composition obtained by subtracting the dc conductivity from the measured total conductivity, shown as a function of frequency at different temperatures shown in the inset. (b) The frequency-dependent real ac conductivity, at a fixed temperature (133 K) for the various compositions as in Fig. 1(b), shown as function of frequency. The solid lines in both cases are the least-squares straight line fits.

conductivity at 100 kHz for all the compositions is shown. It is observed that the conductivity is the highest for those glasses with the highest V_2O_5 content. The above results have been analyzed below in light of appropriate theoretical models.

For several low mobility amorphous and crystalline materials[1] a frequency dependent real ac conductivity has been observed to follow the relation

$$\sigma'(\omega)=A\omega^s, \tag{1}$$

where A is a constant dependent on temperature and the exponent s is, generally, equal to or less than unity. In particular, an approximately linear frequency dependence of $\sigma'(\omega)$ is predicted if the distribution of relaxation times is inversely proportional to relaxation times τ. Any departure from linearity carries information on a particular type of loss mechanism involved. However, recent investigations showed val-

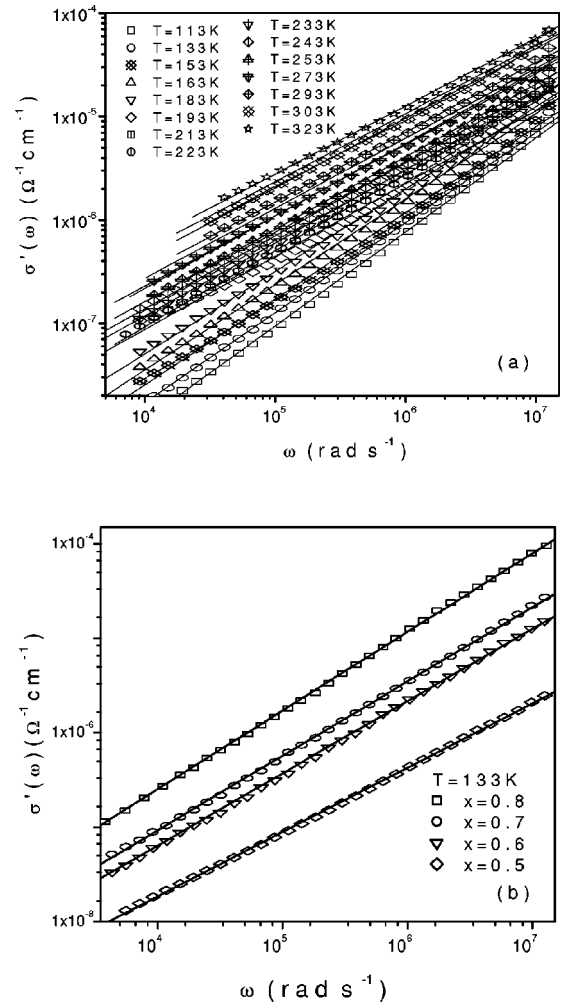ues of s larger than unity in some cases.[16,17] It should be noted that what is measured in a given ac experiment is the total conductivity $\sigma_{total}(\omega)$ of the sample at a particular frequency and temperature. In general, this can be written as[4]

$$\sigma_{total}(\omega)=\sigma'(\omega)+\sigma_{dc}. \tag{2}$$

It is tacitly assumed that the dc and ac conductivities arise from completely different processes. Figure 2(a) shows the frequency dependent conductivity $\sigma'(\omega)$ (real part), at different temperatures for the glass composition $0.6V_2O_5-0.4Ag_2O$, obtained by subtracting the dc conductivity from the measured total conductivity, as a function of frequency. In Fig. 2(b) the above variation is shown for different silver vanadate glass compositions at a fixed temperature of 133 K. The solid lines are the least square straight line fits of the ac conductivity data, the slope of which ac-
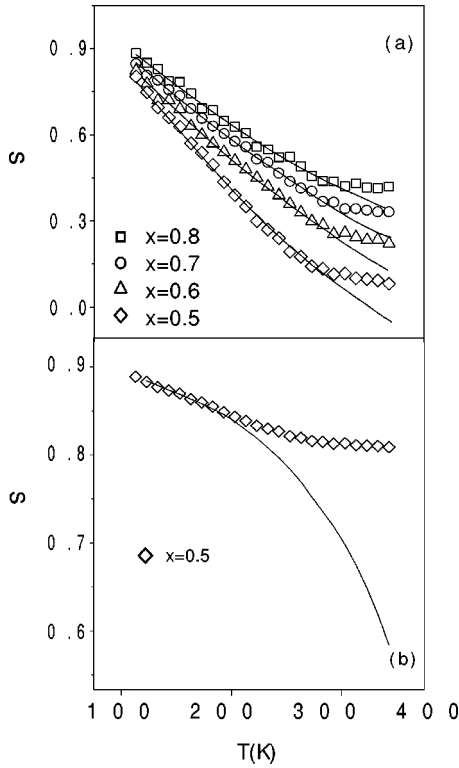
FIG. 3. (a) The frequency exponent s for the various glass compositions as in Fig. 1(b) shown as function of temperature. The solid curves are best fits to the overlapping large polaron model [Eq. (7)]. (b) shows the fits of the data to the correlated barrier hopping model [Eq. (13)]

cording to Eq. (1) gives the values of the frequency exponent s. It can be seen in Fig. 3 that s decreases from close to unity to an almost fixed value with increasing temperature. It is also observed in Fig. 3 that s increases with the increase of V_2O_5 content in the glass. Frequency dependence of s was not observed within the investigated frequency region (Fig. 2).

We now discuss the temperature dependence of the frequency exponent within the frame work of various theoretical models. Several theories based on classical hopping as well as quantum mechanical tunneling have been developed to account for the ac conductivity and its frequency exponent. For the simple quantum mechanical tunneling model, several authors[1–3] have evaluated, within the pair approximation, the ac conductivity, and obtained an expression for s as

$$s = 1 - 4/\ln(1/\omega\tau), \tag{3}$$

which shows that s is temperature independent but frequency dependent and thus this model is unable to explain the experimental results presented in Fig. 3 for the silver vanadate glasses.

A temperature dependent frequency exponent can be obtained within the framework of the quantum mechanical tunneling model in the pair approximation by assuming that the charge carriers form nonoverlapping small polarons,[1] i.e., the total energy of a charge carrier is lowered by the polaron binding energy W_P resulting from the lattice distortion ac-

companying the occupation of the site by the carrier. Transposing an electron between degenerate sites having random distributions of separations will, generally, involve an activation energy, the polaron hopping energy $W_H \approx W_P/2$. In this case, the frequency exponent becomes

$$s = 1 - 4/[\ln(1/\omega\tau_0) - W_H/k_BT], \tag{4}$$

Now it is noted that s is temperature dependent, increasing with temperature. But this model is also not applicable in the present case, since experimental results (Fig. 3) show opposite trends.

Long[3] has proposed 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. The resultant excitation is called a large polaron. Because of the long-range Coulomb interaction, its potential well of a site will extend over many interatomic distances and overlap with the well of other sites. This has important consequences for the frequency dependent loss because the activation energy associated with charge transfer between the overlapping sites will be reduced[2,3] according to

$$W_H = W_{HO}\left(1 - \frac{r_p}{R}\right), \tag{5}$$

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

$$W_{H0} = e^2/4\varepsilon_p r_p, \tag{6}$$

where ε_p is the effective dielectric constant. It is assumed that W_{HO} is constant for all sites, whereas the intersite separation R is a random variable. The ac conductivity for the overlapping large polaron tunnelling model[3] is given by

$$\sigma'(\omega) = \frac{\pi^4}{12} \frac{e^2(k_BT)^2[N(E_F)]^2\omega R_\omega^4}{2\alpha k_BT + W_{HO}r_p/R_\omega^2}, \tag{7}$$

where α is the decay parameter for the localized wave function, and R_ω is the hopping length at a frequency ω determined by the quadratic equation

$$R_\omega'^2 + [\beta W_{HO} + \ln(\omega\tau_0)]R_\omega' - \beta W_{HO}r_p' = 0 \tag{8}$$

where $R_\omega' = 2\alpha R_\omega$, $r_p' = 2\alpha r_p$, and $\beta = 1/k_BT$. Using the above expressions for the dependence of the conductivity on R_ω, it is straightforward to evaluate an expression for s:

$$s = 1 - \frac{8\alpha R_\omega + 6W_{HO}r_p/R_\omega k_BT}{[2\alpha R_\omega + W_{HO}r_p/R_\omega k_BT]^2}. \tag{9}$$

It is found that functional form of the temperature dependence of $\sigma'(\omega)$ predicted by the overlapping large polaron tunnelling model [Eq. (7)] is complicated and cannot be expressed simply as $\sigma' \propto T^n$ with n constant over a wide temperature range. Also, the overlapping large polaron tunneling model predicts that s should decrease with an increase in temperature. For large values of r_p', s continues to decrease with increasing temperature, eventually tending to a value of s predicted by the simple quantum mechanical tunnelling model of nonpolaron forming carriers. Thus it ap-

TABLE I. Parameters obtained from fits of the ac conductivity and the requency exponent data to the large polaron tunneling model for the $x\mathrm{V_2O_5}-(1-x)\mathrm{Ag_2O}$ glasses.

x	W_{HO} (eV) (± 0.01)	r_p cm ($\pm 0.04 \times 10^{-8}$)	$1/\alpha$ cm ($\pm 0.03 \times 10^{-8}$)	τ_0 (s) ($\pm 0.05 \times 10^{-13}$)	$N(E_F)$ (eV^{-1} cm^{-3}) ($\pm 0.06 \times 10^{23}$)
0.8	0.59	1.25×10^{-8}	1.61×10^{-8}	1.95×10^{-13}	2.27×10^{23}
0.7	0.55	1.12×10^{-8}	1.69×10^{-8}	1.88×10^{-13}	2.83×10^{23}
0.6	0.52	1.13×10^{-8}	1.45×10^{-8}	1.63×10^{-13}	2.55×10^{23}
0.5	0.51	0.90×10^{-8}	1.33×10^{-8}	1.10×10^{-13}	2.87×10^{23}

pears that the overlapping large polaron tunneling model might be an appropriate theory to explain the data presented here.

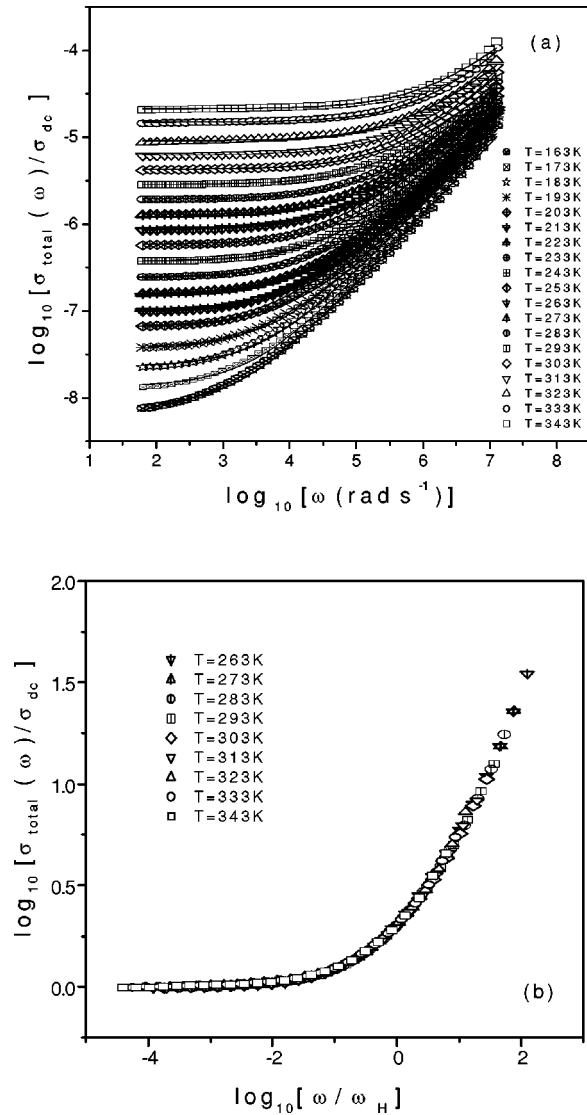In Fig. 3 the experimental data for frequency exponent s

FIG. 4. (a) Conductivity spectra of $0.6\mathrm{V_2O_5}-0.4\mathrm{Ag_2O}$ glass composition at different temperatures shown in the inset. The solid lines are best fits to Eq. (14). (b) Plots of $\log(\sigma_{total}/\sigma_{dc})$ vs $\log(\omega/\omega_H)$ for the $0.6\mathrm{V_2O_5}-0.4\mathrm{Ag_2O}$ glass composition for different temperatures shown in the inset.

are fitted with the predictions of the overlapping large polaron tunnelling model using Eq. (9). The best fit of the experimental data is observed for temperatures below 275 K for the different values of the parameters shown in Table I. At sufficiently higher temperatures (above 275 K) the experimental points show a disagreement with the theoretical values obtained by the large polaron tunneling model. The reason for the discrepancy is not known at present. However, we speculate that a separate mechanism might be operative above 275 K. The experimental data for $\sigma_{total}(\omega)$ at different fixed frequencies are fitted to the ac conductivities calculated from Eq. (7). The best fit of the above model to the total conductivity data for different frequencies is exhibited as solid lines in Fig. 1(a). Reasonable fits were also observed for other glass compositions. It may be noted from Table I that values of the parameters obtained from the best fits are reasonable.

The overlapping large polaron tunneling model [Eq. (9)] also predicts the frequency dependence of s. A detailed analysis shows that in the low temperature region ($k_B T/W_{HO} > 0.04-0.05$), s should increase with frequency. An opposite and more significant behavior should be observed in the high temperature region ($k_B T/W_{HO} > 0.05$). In the present work, however, the frequency dependence of s was not observed.

The experimental data presented in Figs. 1 and 3 show some similarity with the results predicted by the correlated barrier hopping model, which was developed initially by Pike[18] for single electron hopping and later extended by Elliott[4] for two electrons hopping simultaneously. For neighboring sites at a separation R, the Coulomb wells overlap, resulting 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[4]

$$W = W_M - e^2/\pi\epsilon\epsilon_0 R. \qquad (10)$$

The ac conductivity (real part) in this model, in the narrow band limit is expressed by

$$\sigma'(\omega) = \frac{\pi^3}{24} N^2 \omega R_\omega^6 \epsilon\epsilon_0, \qquad (11)$$

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

$$R_\omega = e^2/\pi\epsilon\epsilon_0[W_M + k_B T ln(\omega\tau_0)], \qquad (12)$$

The frequency exponent s for this model is evaluated as[15]

$$s = 1 - 6k_B T / [W_M + k_B T ln(\omega \tau_0)] \qquad (13)$$

Thus, in this model a temperature dependent exponent is predicted, with s increasing towards unity as T tends to zero. We have attempted to fit our data this model [Eq. (13)], but poor fits to the experimental data were obtained [Fig. 3(b)], indicating that the correlated-barrier-hopping model is not applicable to the present glasses.

Now we discuss the scaling of the conductivity spectra at high temperatures. Recently, the study of the conductivity spectra of several glasses at different temperatures led to a scaling law which results in a time-temperature superposition.[19–22] The frequency dependence of the total measured conductivity $\sigma_{total}(\omega)$ at different temperatures for the glass composition $0.6V_2O_5 - 0.4Ag_2O$ is shown in Fig. 4(a). It is noted that the frequency dispersion starts at a higher frequency as the temperature is increased. Other glass compositions also showed a similar behavior. It has been reported that the following expression can be used to describe the frequency dispersion of the real part of the ac conductivity in glasses[21,22]:

$$\sigma_{total}(\omega) = \sigma_{dc} \left[1 + \left(\frac{\omega}{\omega_H} \right)^s \right], \qquad (14)$$

where σ_{dc} is the dc conductivity, ω_H is the hopping frequency of the charge carriers and s is the same frequency exponent as in Eq. (1). The experimental data have been fitted to the above equation to obtain ω_H. We have applied a scaling approach[22] for the present glass compositions by scaling the conductivity axis with respect to σ_{dc} and the frequency axis with respect to the hopping frequency ω_H.

The conductivity spectra scaled in this way for different temperatures above 275 K are displayed in Fig. 4(b) for a glass composition. We note that all the spectra, within a considerably high temperature range, merge on a single curve, indicating a temperature independent relaxation dynamics within this range. It is noteworthy that within this temperature region the frequency exponents s remain independent of temperature, which signifies the time-temperature superposition principle. The conductivity spectra at different temperatures above 275 K of the other glass compositions are also similarly superposed.

IV. CONCLUSIONS

The frequency-dependent (ac) conductivity of the silver vanadate semiconducting glasses has been presented in the frequency range 10 Hz–2 MHz and in the temperature range $87 - 423$ K. Of the various theoretical models for ac conduction in amorphous semiconductors, the overlapping large polaron tunneling model is consistent with almost every respect of the loss data, namely the ac conductivity and its frequency exponent. Fits using this model are in good agreement with the experimental data for the ac conductivity and its exponent for temperatures below 275 K in the measured frequency range. At high temperatures the experimental data show an inconsistency with the theoretical predictions. An attempt to scale the conductivity spectra with respect to temperature is made. It is observed that in the high temperature region (above 275 K) the scaling of the conductivity spectra is independent of temperature, consistent with the temperature independence of the power law exponent in that region.

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