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Ac conductivity of strontium vanadate semiconducting glasses

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Abstract

We have studied the ac conductivity of several compositions of strontium vanadate semiconducting glasses in the frequency range 10 Hz–2 MHz and in the temperature range 80–450 K. We have analysed the experimental results in the framework of the quantum tunnelling and classical hopping models. We observe that tunnelling of the overlapping large polarons is the most suitable mechanism for the ac conductivity of the strontium vanadate glasses.

1. Introduction

Transition metal oxide glasses have drawn much attention due to their possible application as optical and memory switching devices etc [1–3]. These glasses show semiconducting properties which arise from the presence of more than one valence state of the transition metal ions [4]. Although the transition metal ion glasses based on conventional network formers have been studied extensively [4–7], there are a few reports on the glasses containing transition metal oxides as glass network formers [8]. Recently the compositional dependence of the structural properties [9, 10] of some alkaline earth vanadate glasses has been reported in which V_2O_5 acts as the network former. The network structure in these glasses is made up of unaffected VO_5 groups as in vitreous V_2O_5 and affected VO_5 groups with alkaline earth ions [9] in contrast to the vanadate glasses formed by conventional network formers in which only unaffected VO_5 groups are present [8]. The structural changes as a function of composition are also reflected in the dc electrical and other physical properties [9, 10].

The objective of the present work is to study the ac conductivity of the strontium vanadate glasses in the temperature range 80–500 K. We have observed the tunnelling of the overlapping large polarons as the dominant mechanism for the ac conductivity in these glasses.

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2. Experiment

Glass samples of compositions $(100-x)\text{SrO}-x\text{V}_2\text{O}_5$ (table 1) were prepared from the reagent grade chemicals SrO and V_2O_5 . The appropriate mixtures of these chemicals in 10 g batches were melted for 1 hour in air in alumina crucibles in an electrical furnace at temperatures in the range 850–1000 °C depending on compositions. The melts were poured onto a twin-roller. Glassy flakes of thickness $\sim 0.01\text{--}0.03$ cm were obtained for $x = 50\text{--}90$ (mol%). The samples were annealed at a temperature which is 50 °C below the glass transition temperature T_g (table 1) determined by the differential thermal analysis [9]. The amorphous nature of the samples was confirmed from x-ray diffraction studies. The average intersite separation (R) between vanadium ions was estimated from the glass composition and density (table 1).

Table 1. Density, average intersite separation and the glass transition temperature for different compositions of strontium vanadate glasses.

Composition V_2O_5 (mol%)	Density (g cm^{-3})	R (\AA^{-1})	T_g (°C)
50	3.47	4.29	305
60	3.44	4.07	295
70	3.33	3.98	270
80	3.19	3.85	270
90	3.03	3.78	250

For electrical measurements, gold electrodes were deposited on both surfaces of the polished samples by vacuum evaporation. The gold coated samples were heat treated at 150 °C for the stabilization of the electrodes. Electrical measurements such as capacitance and conductance of the samples were measured using an *RLC* meter (Quad-Tech, model 7600) in a wide frequency range of 10 Hz to 2 MHz. Measurements of the dc conductivity of the samples were carried out in a Keithley electrometer (model 617). The dc conductivity was also obtained from the complex impedance plots. The dc conductivities measured by these two methods agreed perfectly well. Measurements below room temperature were taken by placing the sample cells in a cryogenic unit in the temperature range 80–500 K with a stability of ± 0.5 K.

3. Results and discussion

Figure 1 shows the measured total conductivity, $\sigma_t(\omega)$, as a function of reciprocal temperature for a glass composition. It is clear from the figure that the dc contribution is significant at low frequencies and high temperatures, while the frequency dependent term dominates at high frequencies and low temperatures. The other glass compositions also showed similar behaviour.

The total conductivity $\sigma_t(\omega)$ measured in a given ac experiment at a particular frequency ω and temperature can be written as [11]

$$\sigma_t(\omega) = \sigma_1(\omega) + \sigma_{dc} \quad (1)$$

where $\sigma_1(\omega)$ is the real part of the frequency dependent ac conductivity and σ_{dc} is the dc conductivity. Here, it is assumed that the dc and ac contributions arise from completely separate mechanisms. However, if dc and ac contributions arise from the same mechanism the dc conductivity is given by $\sigma_1(\omega)$ in the limit $\omega \rightarrow 0$.

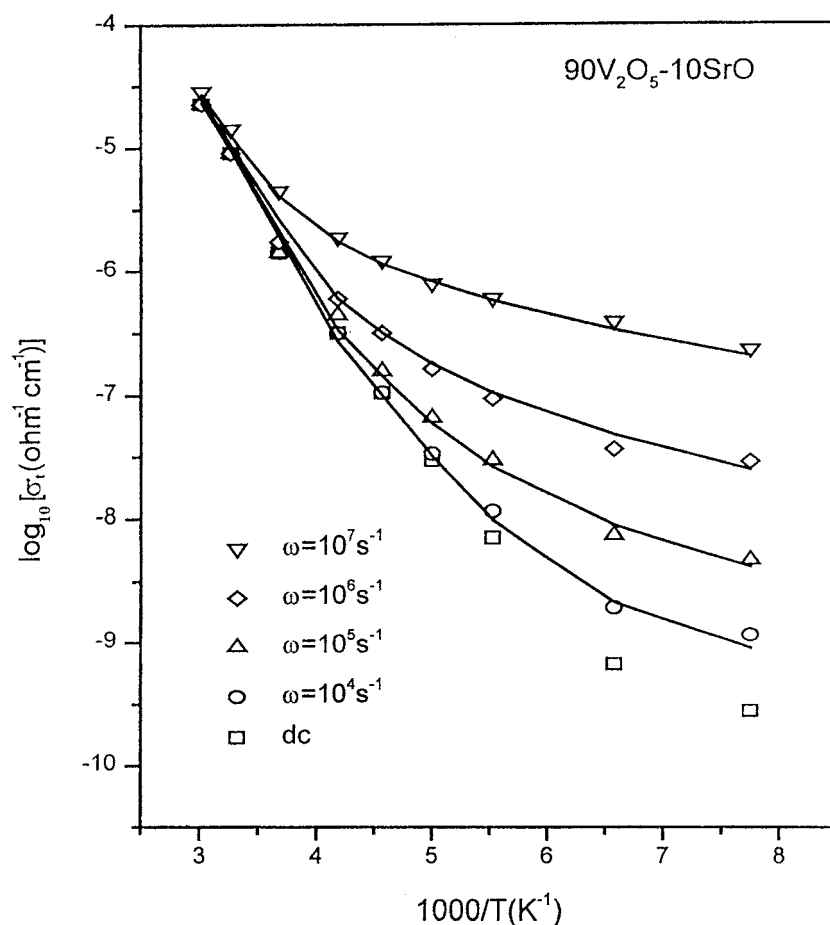


Figure 1. The measured conductivity shown as a function of reciprocal temperature for different frequencies. The solid curves are the best fits to equations (1) and (8).

The variation of ac conductivity $\sigma_1(\omega)$, obtained by subtracting the dc contribution σ_{dc} from $\sigma_t(\omega)$ (equation (1)), with frequency at several temperatures is shown in figure 2 for a glass composition. It is observed that the ac conductivity increases with the increase of temperature and frequency. A similar trend was also observed for other glass compositions. The logarithmic variation of the ac conductivity, for all glass compositions, is almost linear with the variation of logarithmic frequency, which clearly indicates that the ac conductivity $\sigma_1(\omega)$ obeys the power law

$$\sigma_1(\omega) = A\omega^s \quad (2)$$

where A is a temperature dependent constant and exponent s is less than unity. The frequency exponent s was obtained from the least-square straight-line fits of the data in figure 2. The temperature dependence of the frequency exponent s is shown in figure 3 for two glass compositions. It is clear from the figure that the exponent decreases with increasing temperature. In the investigated frequency range, significant frequency dependence of s was not observed. The above results have been analysed below in the framework of the quantum tunnelling and classical hopping models.

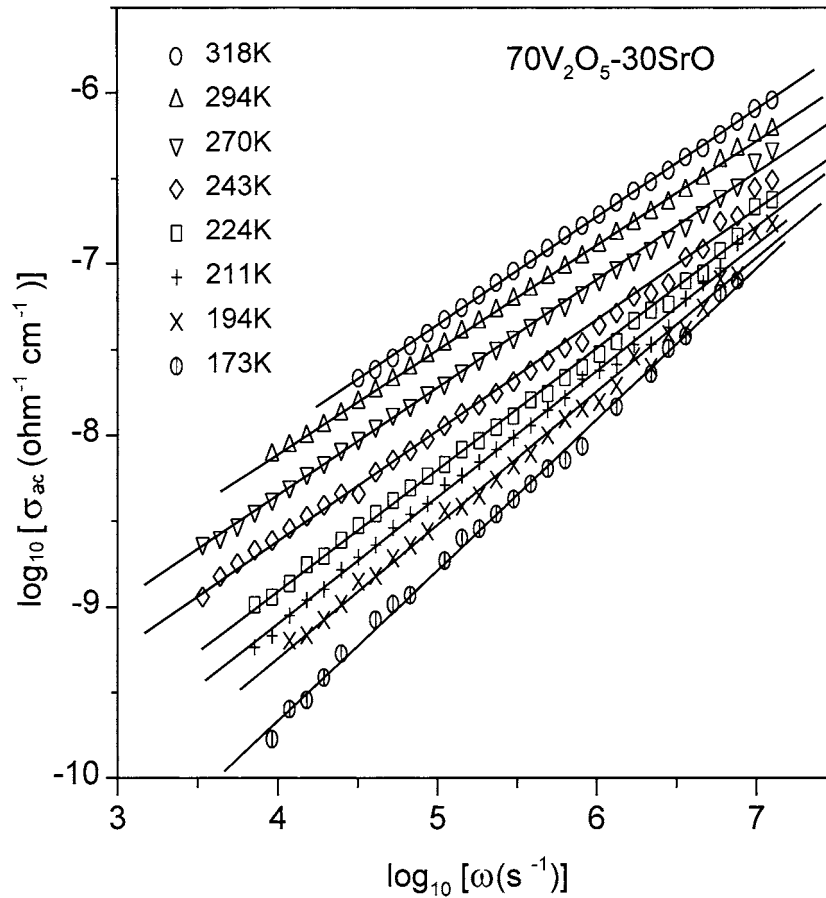


Figure 2. The frequency dependent ac conductivity obtained by subtracting the dc conductivity from the measured total conductivity shown as a function of frequency at several temperatures.

3.1. Quantum mechanical tunnelling models

The quantum mechanical tunnelling models were widely used to explain the ac conductivity of chalcogenide as well as the oxide semiconducting glasses. The quantum mechanical tunnelling models [4, 11–14] were developed for that type of material whose dc conductivity exhibited an $\exp(-T^{-1/4})$ temperature dependence believed to result from the variable range phonon-assisted tunnelling between defect states. For electron tunnelling the conductivity and the frequency exponent are given by [11]

$$\sigma_1(\omega) = (Ce^2k_B T/\alpha)N(E_F)^2\omega R_\omega^4 \quad (3)$$

and

$$s = 1 - 4/\ln(1/\omega\tau_0) \quad (4)$$

where C is a constant, α is the decay constant of the electron wave function, $N(E_F)$ is the density of states at the Fermi level, τ_0 is given by $\tau_0 = \nu_0^{-1}$, where ν_0 is the optical phonon frequency, and R_ω is the tunnelling distance given by [11]

$$R_\omega = (2\alpha)^{-1} \ln(1/\omega\tau_0). \quad (5)$$

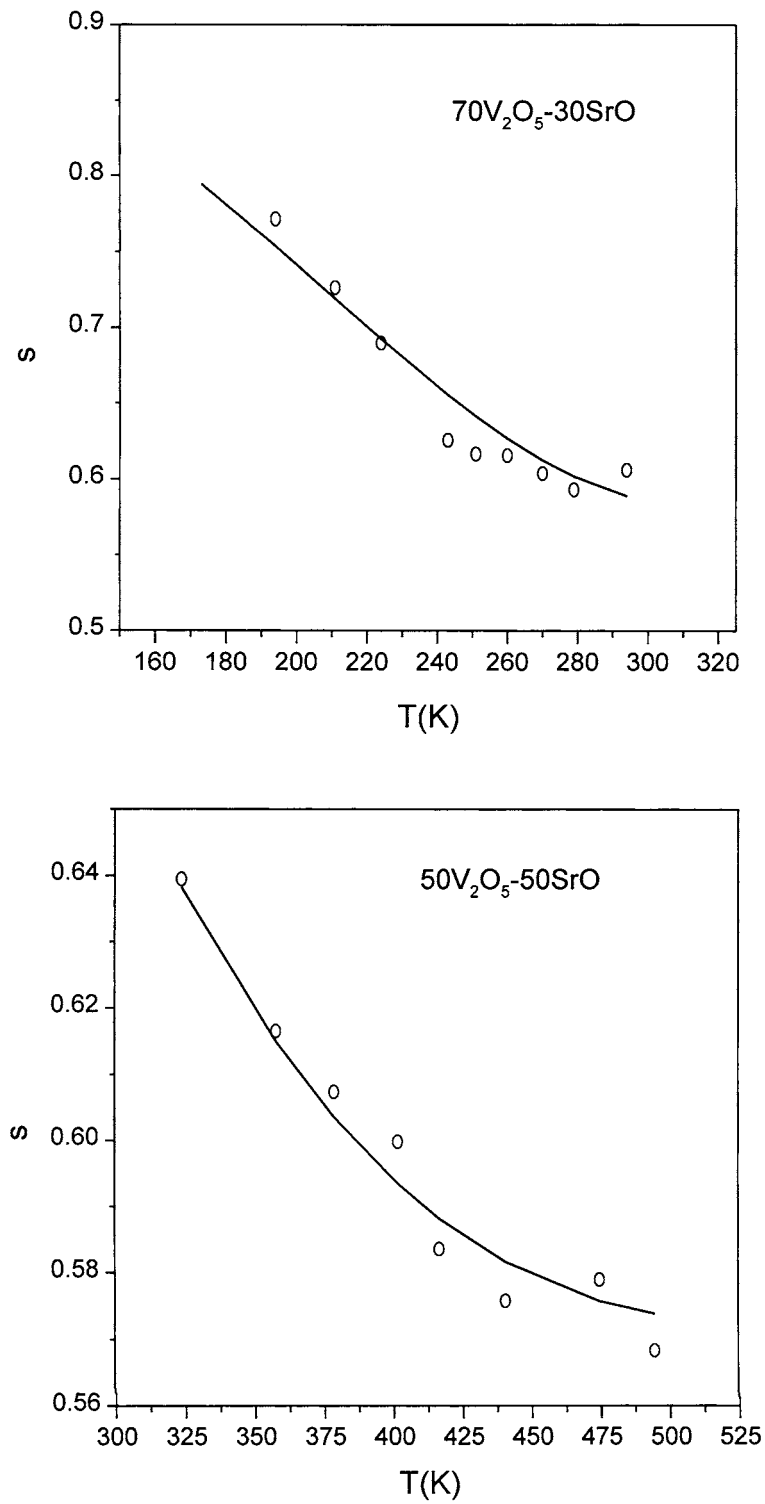


Figure 3. The frequency exponent shown as function of temperature for two compositions. The solid curves are the best fits to equation (10).

We observe from equation (3) that the ac conductivity varies with temperature as $\sigma_1(\omega) \propto T^n$ where n is unity. However, from figure 4 it is clear that either the plots are non-linear or n is always greater than one. It thus appears that electron tunnelling is not a suitable model for the ac conduction in the strontium vanadate glasses. This is also evident from the s versus T plots in figure 3, where a gradual decrease in frequency exponent s is observed with the increase of temperature, in contrast to the electron tunnelling model, which predicts a temperature independent s (~ 0.81) (equation (4)).

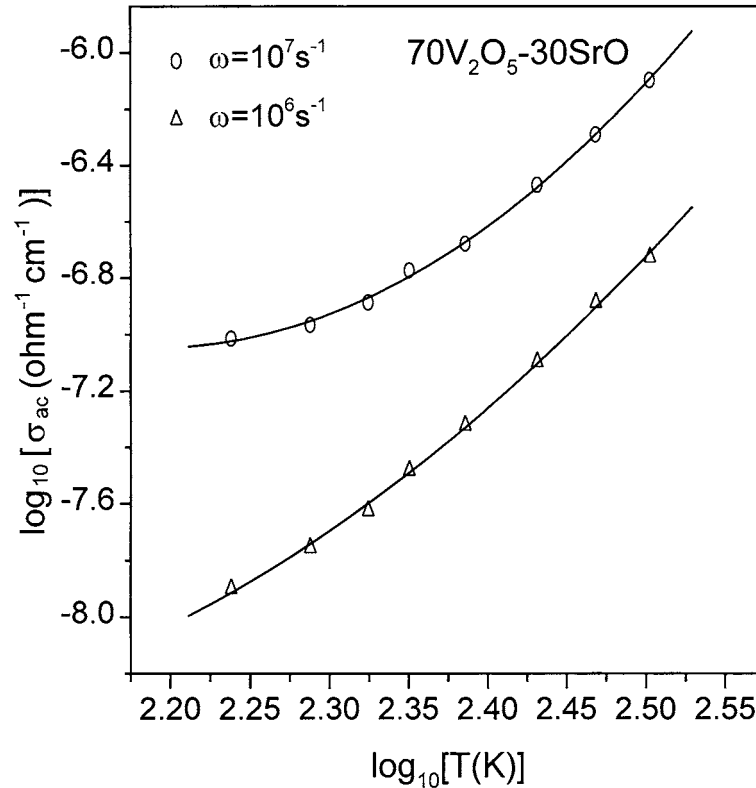


Figure 4. The ac conductivity shown as a function of logarithmic temperature for two frequencies.

The small polaron tunnelling model suggests that a large degree of lattice distortion lowers the total energy of the system and the distortion cloud do not overlap. The conductivity in this model is given by equation (3) with the following values of the tunnelling distance R_ω and the frequency exponent s :

$$R_\omega = (1/2\alpha)[\ln(1/\omega\tau_0) - (W_H/k_B T)] \quad (6)$$

and

$$s = 1 - 4/[\ln(1/\omega\tau_0) - W_H/k_B T] \quad (7)$$

where W_H is the polaron hopping energy. From equation (7) it is obvious that s increases with the increase of temperature in sharp contrast to the experimental observation for the strontium vanadate glass compositions (figure 3). Also the large variation of s with frequency predicted by the small polaron tunnelling model is absent in this glass system.

The conductivity due to the polaron tunnelling with appreciable overlap has been proposed by Long [15]. The potential wells of the neighbouring sites overlap reducing the polaron

hopping energy, which is given by $W_H = W_{HO}(1 - r_0/R)$ where r_0 is the radius of a large polaron and R the intersite separation. The ac conductivity in the large polaron tunnelling model is given by [15]

$$\sigma_1(\omega) = [(\pi^2 ek_B T)^2 / 12] [N(E_F)]^2 \omega R_\omega^4 / [2\alpha k_B T + W_{HO} r_0 / R_\omega^2] \quad (8)$$

where R_ω can be obtained by solving the following quadratic equation:

$$R_\omega^2 + (2\alpha)^{-1} [W_{HO} / k_B T - \ln(1/\omega\tau_0)] R_\omega - W_{HO} r_0 / 2\alpha k_B T = 0. \quad (9)$$

The frequency exponent in this model is given by

$$s = 1 - (8\alpha R_\omega + 6W_{HO} r_0 / R_\omega k_B T) / (2\alpha R_\omega + W_{HO} r_0 / R_\omega k_B T)^2. \quad (10)$$

Equations (8) and (10) suggest that this model might be the possible mechanism to explain the ac loss in the strontium vanadate glass system. In figures 1 and 3 the experimental data for $\sigma_1(\omega)$ and s are fitted to the ac conductivity calculated from equation (8) plus the measured dc conductivity and equation (10) respectively by the best fit methods for a glass composition. In the calculation the values of R determined from the composition and density (table 1) were used. The values of $\tau_0 = 1/\nu_0$ were taken from [9]. We observe that the fits are reasonably good. Reasonable fits were also observed for other glass compositions. The values of the parameters such as W_{HO} , α , R_ω and $N(E_F)$ obtained from the best fits are shown in table 2 for all glass compositions. We now compare the values of the parameters with those obtained from other experiments. The values of W_{HO} and $N(E_F)$ are consistent with those observed from the dc measurements [16]. However, we note that the values of α differ from those obtained from the dc measurements [16]. This is expected because the parameter α is model dependent. Here it corresponds to a large polaron, while in [16] it corresponds to a small polaron.

Table 2. Parameters obtained from the large polaron tunnelling model for the strontium vanadate glasses.

Compositions V ₂ O ₅ (mol%)	W_{HO} (eV)	α (Å ⁻¹)	R_ω (Å)	$N(E_F)$ (10 ¹⁸ eV ⁻¹ cm ⁻³)
50	0.47	0.029	51	9.0
60	0.41	0.020	53	11.0
70	0.41	0.020	51	11.0
80	0.34	0.019	54	10.0
90	0.31	0.020	52	8.0

3.2. Classical hopping model

The classical hopping over the barrier W_M for thermal activation was first considered by Pollak and Pike [17, 18] for single electron hopping and extended by Elliott [19, 20] for two electrons hopping simultaneously. For neighbouring sites at a separation R , the Coulomb wells overlap, resulting in a lowering of the effective barrier height from W_M to W , which for the single electron hopping is given by $W = W_M - e^2/\pi\epsilon'\epsilon_0 R$, where W_M is the barrier height at infinite site separation, and ϵ' and ϵ_0 are the dielectric constant of the materials and the free space respectively. The ac conductivity and the frequency exponent s in this model is given by [11]

$$\sigma_1(\omega) = (\pi^2/24) N^2 \epsilon' \epsilon_0 \omega R_\omega^6 \quad (11)$$

and

$$s = 1 - k_B T / [W_M - k_B T \ln(1/\omega\tau_0)] \quad (12)$$

where N is the concentration of the charge carriers and R_ω is the hopping distance. It is clear from equation (12) that s decreases with the increase of temperature and with the decrease of frequency, suggesting that classical hopping might be a suitable loss mechanism for the strontium vanadate glasses. We attempted to fit the experimental data presented in figures 1 and 3 to this model and observed that the agreement between theory and experiment was not good and the values of the parameters obtained from the fits were not physically acceptable.

4. Conclusions

The ac electrical properties of different compositions of strontium vanadate glasses were analysed in terms of different theoretical models. We observe that the large polaron tunnelling model is the best to describe the experimental data for the frequency and temperature dependence of the ac conductivity. The values of the activation energy and the density of states at the Fermi level obtained from the fits of the ac conductivity to this model are close to those obtained from the analysis of the dc conductivity. However, the values of the decay parameter obtained from the ac and dc measurements differ because of its model dependent nature.

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