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Classical hopping in sol–gel cobalt silicate glass

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Abstract. The complex AC conductivity of the sol–gel-derived cobalt silicate gel-glasses is reported for the frequency range 10^2–10^5 Hz and temperature range 80–300 K. The experimental results were analysed in terms of theoretical models based on quantum tunnelling and classical hopping theories. It has been observed that classical hopping theory is the best model to explain the results for these glasses and that not all sites participate in the AC hopping mechanism.

1. Introduction

Semiconducting transition metal oxide gels and glasses [1–6] have aroused recent interest because of their technological applications, namely optical and electrical memory switching, cathode materials in batteries and so on [1, 7, 8]. There have been extensive reports on the electrical properties of the glasses based on conventional glass formers like P_2O_5 [6, 9, 10]. However, reports are scarce for the electrical properties of the transition metal oxide glasses based on the glass former SiO_2, because of the difficulty in preparing glasses with SiO_2 as a glass former due to the high viscosity of the melts and the high tendency of the melts towards phase separation. We have circumvented these difficulties in preparing these glasses by using a recently developed sol–gel method [11]. The glass formation and the DC electrical properties of the CoO–SiO_2 gel-glasses have recently been reported [12, 13]. It was observed that the DC electrical conduction in these gel-glasses occurs by the hopping mechanism. In this paper we report the AC electrical properties of the CoO–SiO_2 gel-glasses in the temperature range 80–300 K and in the frequency range 10^2–10^5 Hz.

2. Experimental details

Cobalt silicate gel-glass samples of compositions $(CoO)_x(SiO_2)_{100-x}$, where $x = 10$–30 mol% (table 1) were prepared from the reagent grade chemicals $Si(OC_2H_5)_4$ and $Co(NO_3)_2 \cdot 6H_2O$ as starting materials, using ethanol as the common solvent of these chemicals. The solutions were prepared in the molar ratio $Si(OC_2H_5)_4$:C_2H_5OH (solvent):H_2O:HCl (catalyst) = 1:4:20:0.03. First, solutions of $Co(NO_3)_2 \cdot 6H_2O$ in ethanol were prepared and stirred for 2 h. $Si(OC_2H_5)_4$, water and HCl were then added to the solutions so that the pH values of the resulting solutions were within the range 3–4. The resulting solutions were then stirred for 4 h and were kept in polypropylene Petri dishes at 35 °C for gelation and drying. Fractured and dried gels of thickness about 1 mm and area

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about 8–10 mm^2 were obtained after 30–40 days depending on the composition. The gels were heat-treated in an electrical furnace sequentially at different temperatures in the range 50–600 °C for 12 h and gel-glasses obtained finally in this way were used in the electrical measurements.

Table 1. Parameters obtained by fitting the experimental results to the classical hopping theory and the DC activation energy.

Glass composition (mol%)		W_M	τ_0	N	W^a
CoO	SiO_2	(eV)	(s)	(cm^{-3})	(eV)
10	90	2.26	1.2×10^{-13}	2.10×10^{21}	0.49
20	80	1.56	0.5×10^{-13}	2.20×10^{21}	0.45
30	70	1.19	2.6×10^{-13}	2.25×10^{21}	0.42

[a] From [13].

The amorphous nature of these samples obtained finally after heat treatment at 600 °C was confirmed by x-ray diffraction and scanning electron microscopy. For electrical measurements, gold electrodes were deposited on both surfaces of the samples by vacuum evaporation. The gold-coated samples were heat-treated at 150 °C for 2 h for stabilization of the gold electrodes. Electrical measurements of the samples were performed in a Gen Rad (model 1615A) capacitance bridge in the frequency range 10^2–10^5 Hz. Measurements were performed in the temperature range 80–300 K. For low-temperature measurements, sample cells were inserted in a liquid nitrogen cryostat.

3. Results and discussion

The real part of the AC conductivity of the $10CoO–90SiO_2$ gel-glass composition is shown in figure 1 as a function of reciprocal temperature at three frequencies, whereas in figure 2 the same is shown as a function of frequency at three temperatures. It is observed in figures 1 and 2 that the frequency- and the temperature-dependences of the conductivity are not very strong throughout the entire temperature range of measurement, in contrast to the case of melt-quenched oxide glasses [5, 6]. It is also clear from figure 2 that the measured conductivity follows the empirical relation [14, 15]

$$\sigma_1(\omega) = A\omega^s \tag{1}$$

where $\sigma_1(\omega)$ is the real part of the complex conductivity $\sigma(\omega)$ at frequency ω, A is a constant dependent on temperature and the frequency exponent s is generally less than or equal to unity. It may be mentioned that several authors [14, 15] have obtained the AC conductivity by subtracting the DC conductivity from the measured AC conductivity, assuming that the AC and DC processes arise from separate mechanisms. However, in the present cases the DC conductivity is lower by about two orders of magnitude than the AC conductivity and thus the measured conductivity represents effectively the frequency-dependent AC conductivity. The frequency exponent s was obtained from the least-squares straight-line fits and is shown in figure 3 as a function of temperature for a particular glass composition. It is evident in figure 3 that the frequency exponent decreases very slowly with increasing temperature. Other glass compositions also showed similar behaviour except for the differences in the magnitudes of the AC conductivity and frequency exponent. It has been observed that the AC conductivity at a fixed frequency and temperature increases,

whereas the frequency exponent decreases with increasing CoO content in the gel-glass compositions.

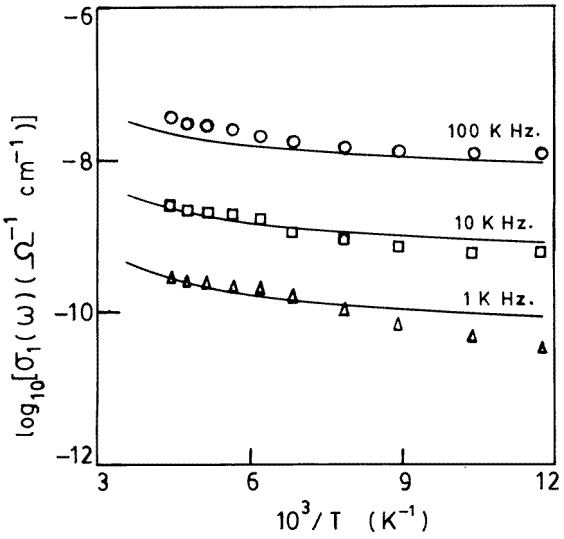

Figure 1. Logarithmic real AC conductivity shown as a function of inverse temperature for three different frequencies for the cobalt silicate glass containing 10 mol% of CoO. Full curves are the best fits predicted by the classical hopping theory.

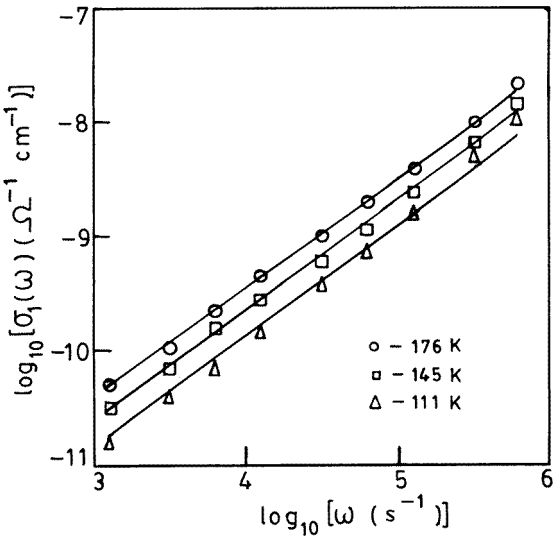

Figure 2. The real AC conductivity shown as a function of frequency for three temperatures for the same composition as in figure 1. Full lines are the best fits to equation (6).

Many theories for the AC conductivity in amorphous materials have been proposed in the literature [14, 16]. It is commonly assumed that the pair approximation is valid, namely

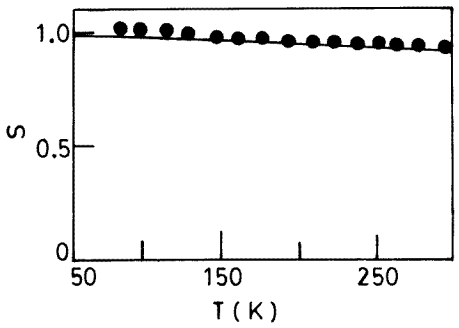

Figure 3. The frequency exponent s shown as a function of temperature for the same glass composition as in figure 1. The full curve is the best fit to equation (8).

that AC transport occurs between pairs of localized states. In essence, two distinct processes have been proposed for the conductivity mechanisms, namely quantum tunnelling through a barrier and classical hopping over a barrier.

The simple quantum tunnelling (QT) theory [9, 15] predicts the following expression for the AC conductivity and the frequency exponent s:

$$\sigma_1(\omega) = \frac{\pi}{3} e^2 kT N^2(E_F) \alpha^{-4} \omega \{\ln[1/(\omega\tau_0)]\}^4 \tag{2}$$

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

where τ_0 is the characteristic relaxation time and is of the order of the inverse phonon frequency, $N(E_F)$ is the density of states at the Fermi level and α^{-1} is the localization length. It is clear from equations (2) and (3) that the simple QT theory predicts a linear temperature-dependence of the conductivity and the temperature-independent exponent s ($s \approx 0.81$). However, the experimental values of the conductivity are not linearly dependent on temperature and the values of s are temperature-dependent, thus ruling out the applicability of the QT model for the present gel-glasses. The QT theories for small and overlapping large polarons are also not consistent with our data [15].

In glasses, hopping between two energetically favourable sites over a potential barrier may occur and the relaxation time for such classical hopping is given by [17]

$$\tau \sim \tau_0 \exp[W/(kT)]. \tag{4}$$

If two favourable sites having separation R are correlated then there is a lowering of the barrier height due to Coulomb interaction, from W_M to W as [18]

$$W = W_M - e^2/(\pi\epsilon\varepsilon_0 R) \tag{5}$$

where ε_0 is the dielectric permittivity of free space and ϵ is the relative dielectric constant of the material. The AC conductivity in the classical hopping theory is given by [16, 18, 19]

$$\sigma_1(\omega) = \frac{\pi^3}{24} N^2 \epsilon\varepsilon_0 \omega R_\omega^6 \tag{6}$$

where N is the density of pair sites and R_ω is the hopping length given by

$$R_\omega = e^2/\{\pi\epsilon\varepsilon_0\{W_M - kT\ln[1/(\omega\tau_0)]\}\}. \tag{7}$$

The exponent s in the theory is estimated as [16]

$$s = 1 - 6kT/\{W_M - kT\ln[1/(\omega\tau_0)]\}. \tag{8}$$

It is to be noted that the classical hopping theory predicts a temperature-dependent exponent s which decreases with increasing temperature consistent with the data presented in figure 3. In figure 2 the conductivity data for the $10CoO–90SiO_2$ gel-glass are fitted to equation (6) by the best-fit method. Reasonably good fits are obtained for the values of the parameters shown in table 1. The data for s for the same glass composition are also fitted to equation (8) in figure 3 using the same values of the parameters W_M and τ_0. The fit in this case is also very good. Other glass compositions also showed similar fits. The values of the parameters W_M, τ_0 and N obtained from the best fits are shown in table 1 for all of the gel-glass compositions. It may be noted that the values of the barrier height W_M decerase with increasing CoO content in the glass composition, consistent with the activation energy (table 1) for the DC conduction [13]. The values of τ_0 obtained from the fits are also reasonable. However, the values of site concentration N do not change significantly, even though the cobalt concentration is changed by a factor of three. This indicates that not all sites in the gel-glasses participate in the hopping mechanism.

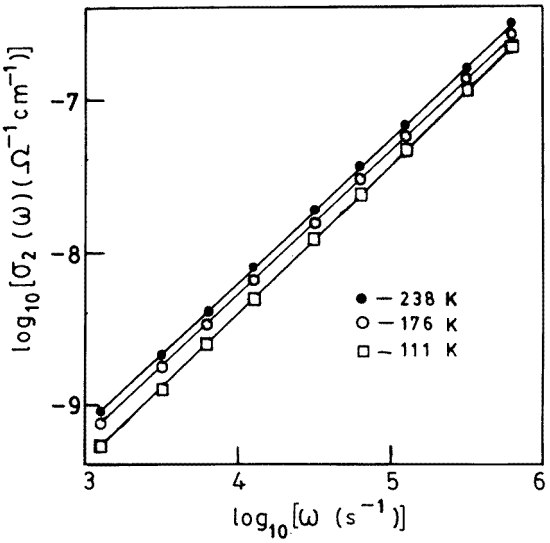

Figure 4. Logarithmic imaginary AC conductivity shown as a function of frequency for three temperatures for the same composition as in figure 1. Full lines are the best fits to equation (9).

Although the real and imaginary parts of the conductivity are related by Kramers–Krönig transformation [14], classical hopping theory [16] makes a specific prediction for the imaginary part of the conductivity $\sigma_2(\omega)$. Also the comparison between theory and experiment is straightforward, since capacitance measurements are inherently much more accurate than conductance measurements. According to classical hopping theory, the imaginary part of the AC conductivity, to a first approximation, is given by

$$\sigma_2(\omega) = \frac{2}{\pi} \ln[1/(\omega\tau_0)]\{1 - (3kT/W_M) \ln[1/(\omega\tau_0)]\}\sigma_1(\omega). \tag{9}$$

The experimental values of $\sigma_2(\omega)$, obtained from capacitance measurements, are shown in figure 4, as a function of frequency for the $10CoO–90SiO_2$ glass composition at three temperatures. The theoretical values calculated from equation (9) are also plotted in figure 4 by best-fit methods. The values of the parameters W_M and τ_0 used for the fits were taken from table 1 and were obtained from the fits of the real part of the conductivity. It may

be noted that the agreement between theory and experiment is very good. Similar fits were also obtained for other glass compositions.

4. Conclusion

The frequency-dependent AC conductivity of the $CoO–SiO_2$ gel-glasses is reported in the temperature range 80–300 K and in the frequency range 10^2–10^5 Hz. It is observed that the AC conductivity for each composition is higher than the DC conductivity. The classical hopping theory predicts quantitatively the temperature-dependence of the AC conductivity and the frequency exponent of these gel-glasses. The values of the site concentration obtained from the fits of this theory to the AC data are lower than the cobalt concentration obtained from the gel-glass composition, suggesting that not all sites are active in the AC hopping mechanism, unlike in the case of the DC conduction mechanism.

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