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ELECTRICAL PROPERTIES OF SOL-GEL DERIVED SEMICONDUCTING COBALT SILICATE GEL-GLASS

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Measurements of electrical conductivity of the semiconducting cobalt silicate gel-glass prepared by the sol-gel route are reported for the first time. The analysis of the results shows that the small polaron hopping model is consistent with the temperature dependence of the electrical conductivity of these gel-glasses.

Keywords: A. semiconductors.

TRANSITION metal oxide gels and glasses [1–6] are of recent interest because of their technological applications, namely, optical and electrical memory switching [1, 7], etc. These gels and glasses exhibit semiconducting behavior arising from the presence of the transition metal ions in more than one valency state [1–6]. Electron–phonon interaction in these materials is very strong, giving rise to the formation of small polarons [8, 9]. The electrical conduction in these glasses normally occurs by the hopping of small polarons between two different valency states of the transition metal ions [8, 9]. Most of the glasses studied so far were prepared with various glass formers like P_2O_5, GeO_2, etc. by quenching the melts [10]. However, preparation of transition metal oxide glasses with SiO_2 as a glass former by quenching the melts is very difficult due to high viscosity of the melts and high tendency towards phase separation. We have circumvented these difficulties in preparing homogeneous gel-glasses in the cobalt silicate system using the sol-gel route [11]. Here we report the results of electrical measurements of these gel-glasses. It is important to note that these gel-glasses are highly porous compared to the melt-quenched glasses and the porosity has a great influence on the electrical properties.

Sol-gel glassy samples of compositions xCoO–$(100-x)$$SiO_2$ where $x = 10$–40 mol%, were prepared from the reagent grade chemicals, $Si(OC_2H_5)_4$ [TEOS] and $Co(NO_3)_2 6H_2O$ [cobalt nitrate hexahydrate]. Ethanol and HCl were used as a common solvent and catalyst respectively. The solutions were prepared in the molar ratio of TEOS : solvent : water: catalyst = 1 : 4 : 20 : 0.03. First, solutions of cobalt nitrate in ethanol were prepared and stirred for 2 h. TEOS, water and HCl were then added to the solutions so that the pH of the resulting solutions was within 3–4. The resulting solutions were stirred for 4 h and were kept in polypropylene Petri dishes at room temperature for gelation. After 30–40 days, the dried gels of thickness ~ 1 mm and area ~ 10–60 mm^2 were obtained. The dried gels were heat treated stepwise in an electric furnace at temperatures in the range 50–600°C for about 12–15 h at each temperature to achieve gel to glass conversion. Amorphous nature of the prepared samples was confirmed by X-ray diffraction, differential thermal analysis and infrared spectroscopy. Density of the samples heat treated at 600°C for 15 h was measured by displacement method and was found to lie in the range 1.70–1.88 g cm^{-3} depending on composition. It may be noted that these values of density are less than that of the pure silica glass, suggesting clearly porous nature of the gel-glasses. The porosity of these gel-glasses in

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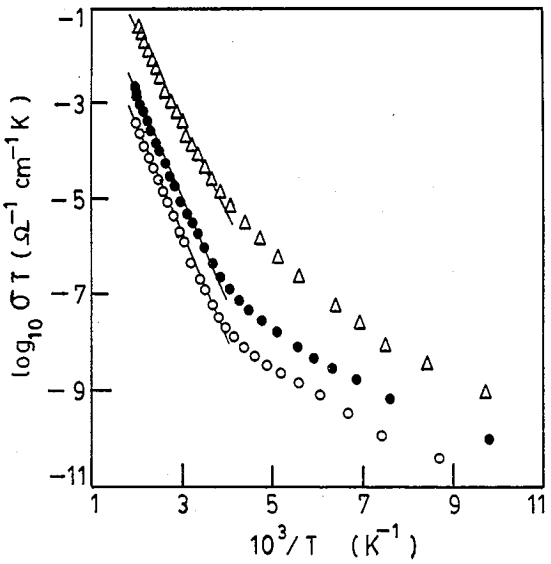

Fig. 1. Temperature dependence of the conductivity for cobalt silicate-gel glasses heat treated at 600 °C for 15 h: ○, 20 mol% CoO; ●, 30 mol% CoO; △, 40 mol% CoO. The solid lines are the best fits to equation (1).

comparison with the pure silica glass was estimated to be within ~20%.

Electrical measurements were carried out in a Keithley 617 electrometer in the temperature range 100–500 K, using evaporated gold as an electrode material. Ohmic contacts were ascertained from the linear I–V characteristics. Figure 1 shows the temperature dependence of the electrical conductivity plotted as $\log \sigma T$ vs T^{-1} for three compositions of the cobalt silicate gel-glasses. It is clear that the plot is not linear, indicating temperature dependent activation energy, characteristic of small polaron hopping conduction [8, 9]. It may be noted that the conductivity increases with the increase of CoO content in the glass compositions, similar to other transition metal oxide glasses [1–6]. However, the increase of the conductivity with composition is much less than those for glass compositions prepared by the conventional method. The electrical conductivity of the transition metal oxide glasses has been interpreted earlier in the framework of the phonon-assisted hopping of small polarons proposed by Mott [8]. The conductivity in the high temperature limit ($T > \theta_D/2$) in this model is given by

$$\sigma = [\nu_0 e^2 C(1-C)/kTR] \exp(-2\alpha R) \exp(-W/kT), \quad (1)$$

where ν_0 is the optical phonon frequency, α is the decay constant of the localized wave function, R is the average hopping distance, C is the fraction of sites occupied by a polaron and W is the activation energy

Table 1. Parameters obtained by fitting the conductivity data to Mott's small polaron hopping model [equations (1) and (4)]

Glass composition (mol% CoO)	W (eV)	$N(E_F)$ (eV^{-1} cm^{-3})
20	0.45	1.25×10^{20}
30	0.42	1.16×10^{20}
40	0.40	3.80×10^{19}

given by [9]

$$W = W_H + W_D/2 \quad \text{for } T > \theta_D/2,$$
$$= W_D \quad \text{for } T < \theta_D/4, \quad (2)$$

where W_H is the polaron hopping energy, W_D is the disorder energy and θ_D is the Debye temperature.

It may be observed in Fig. 1 that the activation energy decreases with the decrease of temperature. However the variation of activation energy with temperature in the high temperature region (250–500 K) is extremely small and thus $\log \sigma T$ vs T^{-1} plots in this region may be approximated by straight lines. Fits of the data in this temperature region yield activation energies (W) which are shown in Table 1. Although the data for W for the corresponding melt-quenched glasses are not available for comparison, these values of W are lower than those of the phosphate glasses containing even higher CoO content prepared by the conventional method [6] and are attributed to the porous nature of these gel-glasses.

At lower temperatures, Mott [12] has proposed that charge transport may occur beyond nearest neighbour by the variable range hopping. The conductivity for the variable range hopping is given by [12]

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}], \quad (3)$$

where σ_0 and T_0 are constants. T_0 is given by

$$T_0 = 19.4\alpha^3/kN(E_F), \quad (4)$$

where $N(E_F)$ is the density of states at the Fermi level. Plots of $\log_{10} \sigma$ vs $T^{-1/4}$ are shown in Fig. 2 which shows linearity below and above 250 K. The least square fits of the data to equation (3) below 250 K yields $N(E_F) \sim 10^{19}$–10^{20} eV^{-1} cm^{-3} (Table 1) for a reasonable value of $\alpha = 1$ Å^{-1} [13].

A generalised polaron hopping model proposed by Schnakenberg [14] predicts the temperature dependence of the activation energy. In this model, optical multi-phonon and acoustical one-phonon processes determine the conductivity at high and low temperatures respectively. According to this model the d.c.

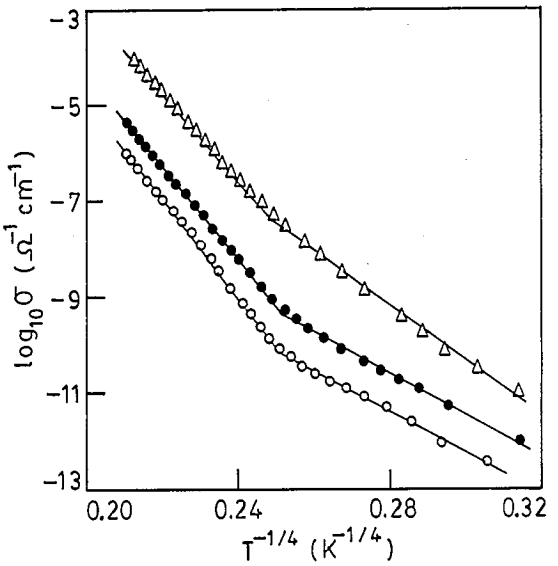

Fig. 2. Plots of $\log\sigma$ vs $T^{-1/4}$ for the same compositions as in Fig. 1. The solid straight lines below 250 K are the fits to equation (3).

conductivity has the form

$$\sigma \sim T^{-1}[\sinh(h\nu_0/kT)]^{1/2}\exp[-(4W_H/h\nu_0) \times \tanh(h\nu_0/4kT)]\exp(-W_D/kT). \quad (5)$$

Equation (5) is fitted to the experimental data in Fig. 3 by the best fit method, using ν_0, W_H and W_D as variable parameters. Figure 3 indicates that the fits are reasonably good. The values of the parameters obtained from the fits are shown in Table 2. The values of ν_0 are very close to the values obtained from infrared spectra [11]. The values of W_H and

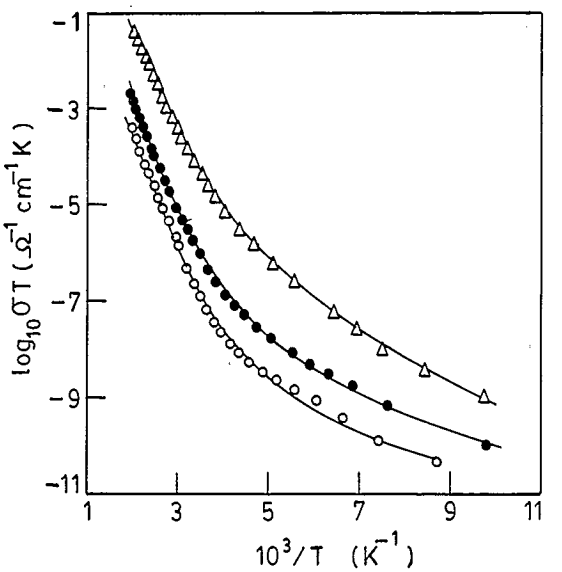

Fig. 3. Fits of Schnakenberg's model [equation (5)] to the experimental data for the same-gel glass compositions as in Fig. 1.

Table 2. Parameters obtained by fitting the conductivity data to Schakenberg's model [equation (5)]

Glass composition (mol% CoO)	W_H (eV)	W_D (eV)	ν_0 (s^{-1})
20	0.83	0.09	2.7×10^{13}
30	0.76	0.11	2.7×10^{13}
40	0.61	0.18	2.6×10^{13}

W_D are also reasonable, but the values of W_H predicted by this model are higher than the high temperature activation energy.

Triberis and Friedman [15, 16] have applied the percolation theory to the small polaron hopping regime in disordered materials. Considering correlation of sites in a percolation cluster, they have obtained

$$\sigma = \sigma_0' \exp[-(T_0'/T)^{1/4}], \quad (6)$$

where σ_0' and T_0' are constants, and T_0' depends on the temperature range and is given by

$$T_0' = 12.5\alpha^3/kN_0 \quad \text{at high temperatures},$$
$$= 17.8\alpha^3/kN_0 \quad \text{at low temperatures}, \quad (7)$$

where N_0 is the constant density of localised states. It may be noted that equation (6) is similar to the prediction of the variable range hopping model of Mott [12]. Figure 2 shows two linear regions in the $\log\sigma$ vs $T^{-1/4}$ plots. However, the slope of the plot above 250 K is higher than that below 250 K, thus contradicting the predictions of the percolation model [equation (7)].

It is thus concluded that the small polaron hopping models can predict quantitatively the temperature dependence of the electrical conductivity of the sol-gel derived cobalt silicate gel-glasses.

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