Electrical conduction in some sol-gel silicate glasses

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Measurements are reported for the electrical conductivity of different compositions of silicate glasses containing copper and vanadium in the temperature range 200–500 K. The experimental results for the two systems are found to be very similar and are analyzed with respect to theoretical models existing in the literature. At high temperatures, Mott's model of phonon-assisted small-polaron hopping between nearest neighbors is consistent with the data, while at low temperatures the variable-range-hopping model appears to be valid. The generalized polaron-hopping model of Schnakenberg and the percolation model applied to the small-polaron-hopping regime of Triberis and Friedman can also predict the temperature dependence of the conductivity data. The various model parameters obtained from the best fits are found to be consistent with the glass compositions.

I. INTRODUCTION

Recently the study of transition-metal (TM) oxide gels,[1] amorphous TM oxides,[2] and glasses containing TM ions[3–6] has received considerable attention. These materials show semiconducting behavior arising from the presence of TM ions in multivalent states[1–6] and have technological applications, namely, electrical memory and optical switching devices,[1,7] cathode materials in a battery,[8] etc. In these materials small polarons are formed due to strong electron-phonon interaction[9] and the electrical conduction occurs by the hopping movement of small polarons between two different states of the TM ions.[9,10] Most of the glasses studied so far were prepared with various glass formers by the melt-quenching technique.[11] However, difficulty arises in preparing binary TM ion glasses with SiO_2 as a glass former, because of the highly viscous melt and high tendency towards phase separation. We have circumvented the difficulties in preparing these glasses by a recently developed sol-gel route.[12] We have studied the electrical properties of silicate glasses containing TM ions, namely, Cu and V, for different compositions prepared by this method. However, the results of the electrical measurements are found to be very similar to these two systems. Here we report the results of electrical measurements emphasizing the copper silicate system. The experimental procedure is briefly described in Sec. II. In Sec. III, the results are presented and analyzed in the light of theoretical models also discussed briefly in this section.

II. EXPERIMENTAL PROCEDURE

Copper-silicate glass samples of compositions $x\mathrm{CuO}\cdot(100-x)\mathrm{SiO_2}$, where $x=5-30$ mol%, were prepared using the reagent grade chemicals $Cu(NO_3)_2\cdot 3H_2O$ and $Si(OC_2H_5)_4$ as starting materials. For a vanadium-silicate system, vanadyl acetylacetonate and $Si(OC_2H_5)_4$ were used.[12] The solutions were prepared in the molar ratio of $Si(OC_2H_5)_4$:C_2H_5OH (solvent):water:HCl (catalyst) = 1:4:20:0.03. First, the solutions of $Cu(NO_3)_2\cdot 3H_2O$ (or vanadyl acetylacetonate) in water and C_2H_5OH were prepared and stirred for 4 h. $Si(OC_2H_5)_4$ and 1*N*-HCl were then added to the solutions. The resulting solutions were stirred for 6 h at 308 K and were kept in polypropelyne Petri dishes for gelation. After drying and gelation for 6 days, the gels were heat treated stepwise in an electrical furnace at 323–973 K for 12 h at each temperature. Glassy samples of thickness 0.2–0.5 mm with black color were obtained.

The amorphous nature of the samples was confirmed from x-ray diffraction, scanning electron microscopy, differential thermal analysis, and infrared spectroscopic studies. Total copper ion concentrations (N) in the samples were estimated from atomic absorption spectroscopy (Varian, model AA1475), while the Cu^{2+} ion concentration was obtained from magnetic susceptibility measurements (PARC, model 155). The density of the samples was measured by Archimedes's principle. The average intersite separation (R) between Cu ions was obtained from the glass composition and density. The various

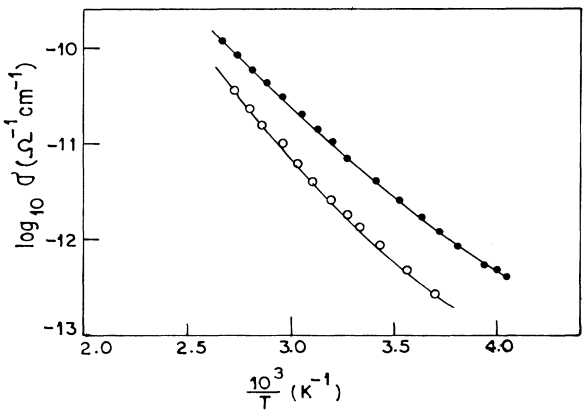

FIG. 1. Temperature dependence of the conductivity for copper-silicate glasses: ●, 20 mol % CuO; ○, 10 mol % CuO. The solid lines are the fits to Mott's model [Eq. (1)].

TABLE I. Physical parameters of copper-silicate glasses.

Glass compositions (mol %) CuO	SiO_2	Density ($g\,cm^{-3}$)	N (10^{21} cm^{-3})	$[Cu^{2+}]$ (10^{21} cm^{-3})	R (Å)
5	95	2.42	1.19	1.15	5.82
10	90	2.69	2.61	2.54	4.50
20	80	3.21	6.03	5.35	3.41

physical parameters of the copper-silicate glasses are shown in Table I. For electrical measurements gold electrodes were deposited on both surfaces of the samples by vacuum evaporation. Electrical measurements of the samples were carried out using a Keithley electrometer (model 617). The absence of barrier layers at the contacts was ascertained from the linear I-V characteristics before measurements. For low-temperature measurements the sample cell was inserted in a cryogenic unit. Measurements were made in the temperature range 100–500 K with a stability of ± 0.5 K. However, due to high resistances of the samples below 200 K, the data below this temperature were not reliable and are not reported.

III. RESULTS AND DISCUSSION

The temperature dependence of the logarithmic conductivity is shown in Fig. 1 as a function of reciprocal temperature for two compositions of the copper-silicate glasses. It is observed that the plot is not linear, indicating temperature-dependent activation energy, characteristic of small-polaron-hopping conduction.[9–14] The activation energy decreases with temperature. Other glass compositions also showed similar behavior with a difference that the conductivity of the glass compositions containing higher CuO content was found to be higher. Vanadium-silicate glasses exhibited similar behavior.

Mott[9,10] has investigated theoretically the hopping conduction in glasses containing TM ions in terms of phonon-assisted hopping of small polarons between localized states and obtained the following expression for the conductivity for the nearest-neighbor hopping in the nonadiabatic regime at high temperatures ($T > \Theta_D/2$):

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

where ν_0 is the optical phonon frequency, α^{-1} is the localization length of the s-like wave function assumed to describe the localized states at each TM ion site, R is the average intersite separation, C is the fraction of sites occupied by an electron or a polaron and is therefore the ratio of the TM ion concentration in the low valence states to the total TM ion concentrations, and W is the activation energy for the hopping conduction. Assuming a strong electron-phonon interaction, Austin and Mott[10] have shown that

$$W = \begin{cases} W_H + W_D/2 & \text{for } T > \Theta_D/2 \\ W_D & \text{for } T < \Theta_D/4 , \end{cases} \quad (2)$$

where W_H is the polaron-hopping energy, W_D is the disorder energy arising from the variation of the local arrangements of the ions, and Θ_D defined by $h\nu_0 = k\Theta_D$ is the characteristic Debye temperature. In the adiabatic limit the overlap integral $J \approx \exp(-2\alpha R)$ in Eq. (1) reduces to unity.

The conductivity data above 300 K presented in Fig. 1 can be interpreted in terms of this model. Equation (1) is fitted to the experimental data in Fig. 1 using ν_0, α, and W as variable parameters. The best fits are observed for the values of the parameters shown in Table II. The values of the activation energy W increase with the decrease of CuO content in the glass compositions. The values of ν_0 obtained from the fitting are consistent with their estimate from the infrared studies.[15] The values of α are reasonable for localized states and indicate strong localization in the silicate glasses.[9] An estimate of the polaron radius r_p can be obtained experimentally within the framework of the Austin-Mott model[9] from the relation

$$W_H = e^2/4\epsilon_p r_p , \quad (3)$$

where ϵ_p is the effective dielectric constants given by $\epsilon_p^{-1} = \epsilon_\infty^{-1} - \epsilon_0^{-1}$, where ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants, respectively, which were estimated from the complex conductivity plot (Table II). Assuming $W \simeq W_H$, the calculated values of r_p from Eq. (3) are included in Table II. It has been shown theoreti-

TABLE II. Parameters obtained by fitting the high-temperature data to Mott's model.

Compositions (mol % CuO)	W (eV)	α ($Å^{-1}$)	ν_0 (10^{12} s^{-1})	r_p (Å) from Eq. (3)	r_p (Å) from Eq. (4)	ϵ_p [a]
5	0.61	0.97	6.5	2.45	2.33	2.4
10	0.49	0.90	7.2	1.93	1.80	3.8
20	0.40	0.78	7.9	1.45	1.36	6.6

[a]From the Cole-Cole plot of the complex dielectric constants (Ref. 15).

TABLE III. Parameters obtained by fitting the variable-range-hopping and percolation models to the data.

Glass compositions (mol % CuO)	α (Å^{-1})	$N(E_F)$ (10^{19} $\text{eV}^{-1}\text{cm}^{-3}$)	N_0 (10^{19} $\text{eV}^{-1}\text{cm}^{-3}$)
5	1.00	4.0	2.9
10	0.80	5.5	2.0
20	0.63	7.1	1.5

cally by Bogomolov, Kudinov, and Firsov[16] that for the case of nondispersive system of frequency ν_0 the polaron radius is given by

$$\gamma_p = \tfrac{1}{2}(\pi/6)^{1/3}R \ . \tag{4}$$

Equation (4) is obviously oversimplified for a complex system, but the infrared spectra of the present glass compositions suggest that this approximation fits these glasses fairly well. The values of polaron radius calculated from Eq. (4) using the values of R from Table I are shown in Table II. It is clear from the table that the experimental and theoretical values of r_p are comparable.

At lower temperatures where the polaron binding energy is small, Mott[17] has proposed that hopping may occur preferentially beyond nearest neighbors. The conductivity for the so-called variable range hopping is predicted to be

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}] \ , \tag{5a}$$

where σ_0 and T_0 are constants and T_0 is given by

$$T_0 = 19.44\alpha^3/kN(E_F) \ , \tag{5b}$$

where $N(E_F)$ is the density of states at the Fermi level.

A plot of the logarithmic conductivity versus $T^{-1/4}$ is shown in Fig. 2 for the copper-silicate glasses. It is clear that the plot is linear over a considerable temperature range, consistent with Eq. (5). Experimental points are fitted in Fig. 2 to Eq. (5) by the least-squares fitting procedure. The values of α and $N(E_F)$ obtained from the fitting are shown in Table III. These values are reasonable for localized states.[9,18] It might be noted that the value of $N(E_F)$ increases with the increase of copper ion content in the glass compositions.

The temperature dependence of the conductivity, similar to Mott's model, is also predicted by a generalized polaron-hopping model proposed by Holstein and others.[14] This model also provides an independent check of the nature of hopping. The criterion for the nature of hopping is expressed by

$$J \gtrless (kTW_H/\pi)^{1/4}(h\nu_0/\pi)^{1/2} \ , \tag{6}$$

where the signs $>$ and $<$ are for adiabatic and nonadiabatic hopping, respectively. The condition for the formation of a small polaron is also given by $J < W_H/3$. The limiting values of J estimated from the right-hand side of (6) at 400 K, using the values of ν_0 and W_H from Table II, are in the range 0.03–0.04 eV. An estimate of J can be made from the following expression:[18]

$$J \approx e^3[N(E_F)/\epsilon_p^3]^{1/2} \ . \tag{7}$$

Using the values of $N(E_F)$ and ϵ_p (Tables II and III), Eq. (7) gives $J \approx 0.01$–0.02 eV. Thus the hopping in these glasses occurs by the nonadiabatic processes.

Schnakenberg[13] has considered a more general polaron-hopping model in which an optical multiphonon process determines the conductivity at high temperatures, while at low temperatures charge carrier transport is an acoustical one-phonon-assisted hopping processes. The temperature dependence of the conductivity in this model has the form

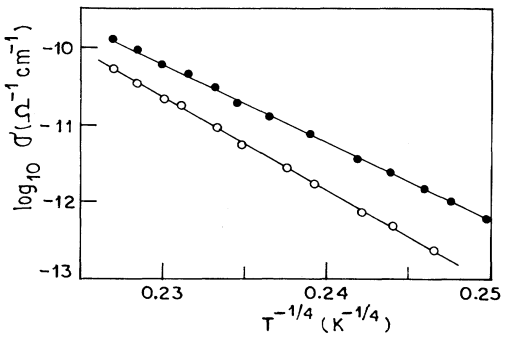

FIG. 2. Conductivity shown as a function of $T^{-1/4}$ for the same glass compositions as in Fig. 1. The solid lines are fits to Eq. (5).

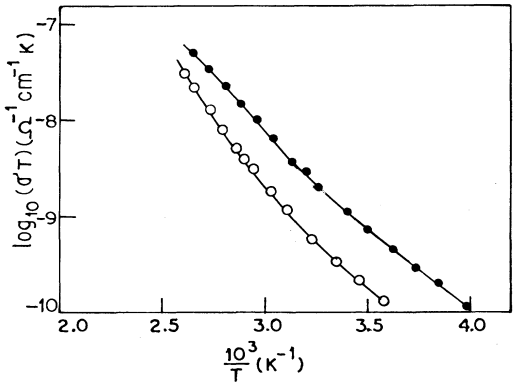

FIG. 3. Plot of $\log_{10}(\sigma T)$ vs $10^3/T$ for the same glass compositions as in Fig. 1. The solid curves are fits to Eq. (8).

TABLE IV. Parameters obtained by fitting Schnakenberg's model to the experimental data.

Glass compositions (mol % CuO)	ν_0 (10^{12} s^{-1})	W_H (eV)	W_D (eV)
5	7.1	0.48	0.16
10	7.3	0.39	0.16
20	8.5	0.32	0.14

$$\sigma \sim T^{-1}[\sinh(h\nu_0/kT)]^{1/2} \exp[-(4W_H/h\nu_0)\tanh(h\nu_0/4kT)] \exp(-W_D/kT) \ . \quad (8)$$

Equation (8) predicts a temperature-dependent hopping energy which decreases with the decrease of temperature in consistence with the data presented in Fig. 1. In Fig. 3 experimental data are fitted to Eq. (8) by the best-fit method. The best fits yield the values of the parameters ν_0, W_H, and W_D as shown in Table IV. It may be noted that the values of ν_0 are close to the estimates from Mott's model. As expected the values of the hopping energy are less than the high-temperature activation energy W. The values of W_D show little variation with glass compositions and are close to the estimates of the disorder energy from the Miller-Abrahams theory.[19] It might be noted that the values of $W_H + W_D/2$ are approximately equal to W consistent with the predictions of Mott's model.

Recently Triberis and Friedman[20,21] have applied percolation theory to the small-polaron-hopping regime and evaluated the conductivity in the disordered systems. Considering correlation due to energy of common sites in a percolation cluster, the following expression for the conductivity has been obtained:

$$\sigma = \sigma_0' \exp[-(T_0'/T)^{1/4}] \ , \quad (9a)$$

where σ_0' and T_0' are constants and T_0' are given by

$$T_0' = 12.5\alpha^3/kN_0 \ , \quad (9b)$$

where N_0 is the density of localized states assumed constant. It might be noted that Eq. (9) is similar to the predictions of Mott [Eq. (5)] for the variable range hopping with a different value of T_0. The data presented in Fig. 2 were also fitted to Eq. (9) yielding the values of N_0 shown in Table III. It may be observed that the values of N_0 are close to the values of $N(E_F)$ obtained from Mott's model.

It may be noted from Tables II–IV that the various parameters obtained from the fittings of the experimental data to the model predictions change systematically with the glass compositions. The value of ν_0 increases as the CuO concentration is raised in the compositions. This is consistent with the fact that the density of the glasses also increases with the increase of CuO. The value of W_H shows a decrease with the increase of CuO content which is adduced for an increase in the value of ϵ_p as the copper concentration is raised in the glasses. The decreasing trend in the value of α implies a stronger localization in the glass compositions with higher CuO content.

IV. CONCLUSIONS

The temperature dependence of the electrical conductivity of silicate glasses containing copper and vanadium ions has been presented. Analysis of the conductivity data shows that the high- and low-temperature conductivity data are consistent with the predictions of the phonon-assisted nearest-neighbor hopping and variable-range-hopping models, respectively, proposed by Mott. Holstein's model indicates that the hopping in the glasses occurs in the nonadiabatic regime. Schnakenberg's generalized polaron-hopping model, and also Triberis and Friedman's percolation model applied to the small-polaron-hopping regime can interpret the temperature dependence of the conductivity. Various physical parameters, such as localization length, density of states, etc., obtained from the best fits of these models are found to be reasonable for localized states and to be consistent with the glass compositions. The behavior of the copper- and vanadium-silicate glasses is found to be very similar with similar trends in the variations of the physical parameters except for slightly different values of these parameters.

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