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Transport properties of semiconducting $CuO–Sb_2O_3–P_2O_5$ glasses

Aswini Ghosh and D Chakravorty
Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, India

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Abstract. Both DC and AC electrical conductivities for glasses in the system $CuO–Sb_2O_3–P_2O_5$ have been measured over the temperature range 80–450 K. The DC conductivity data at higher temperatures indicate that a phonon-assisted hopping conduction mechanism is operative. The low-temperature data are characterized by a variable-range hopping model. The AC conductivities of all the samples are consistent with the classical hopping model.

1. Introduction

The electrical behaviour of oxide glasses containing transition-metal ions has attracted considerable attention in recent years because of their semiconducting properties (Hirashima *et al* 1987). The electrical conductivity in these systems arises because of the strong electron–phonon interaction which results in the formation of small polarons. The hopping of the latter between the low- and the high-valence sites of the transition-metal ions has been shown to control the transport properties of the glasses. A recent investigation has shown that the presence of Bi_2O_3 increases the conductivity of $CuO–P_2O_5$-based glasses (Ghosh and Chakravorty 1990a). The presence of Sb_2O_3 in silicate glasses had earlier shown interesting electrical properties which were explained on the basis of a two-polaron hopping conduction mechanism (Chakravorty *et al* 1979). We have now investigated the electrical behaviour of glasses in the system $CuO–Sb_2O_3–P_2O_5$. The results are reported in this paper.

2. Experiment

The samples (table 1) were prepared by melting reagent-grade $Cu(NO_3)_2 \cdot 3H_2O$, $(NH_4)_2HPO_4$ and Sb_2O_3 in alumina crucibles at 1273 K for 2 h in an ordinary atmosphere. The melt was subsequently quenched by pressing between two polished brass plates. The amorphous nature of the samples was confirmed from x-ray diffraction studies.

The concentrations of the total Cu ions present in the samples were determined by atomic absorption spectroscopy (Varian model AA 1745). The concentrations of the Cu^{2+} ions were obtained from the measurements of magnetic susceptibility (EG and G Parc magnetometer model 155). The concentrations of the total and the reduced copper ions and the ratio $C([Cu^+]/([Cu^+] + [Cu^{2+}]))$ and other physical parameters are shown in table 1.

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Table 1. Glass compositions investigated and some of their physical and chemical characteristics.

Glass composition (mol%)			Density	N	$[Cu^+]$		R
CuO	P_2O_5	Sb_2O_3	($g\,cm^{-3}$)	($10^{22}\,cm^{-3}$)	($10^{22}\,cm^{-3}$)	C	(Å)
60	20	20	5.23	1.77	1.51	0.85	3.84
70	20	10	4.71	3.28	2.82	0.87	3.12
80	15	5	4.52	4.18	3.67	0.88	2.88

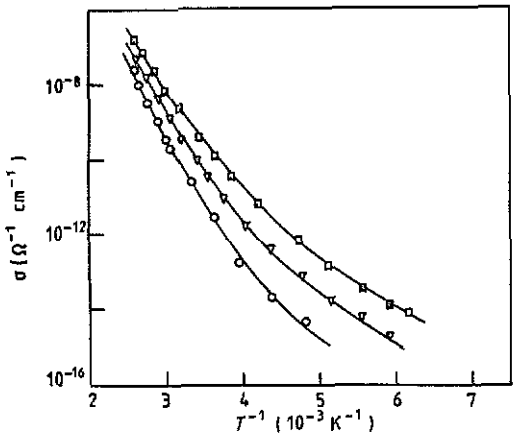

Figure 1. Temperature dependence of the DC conductivity for three glass compositions: ○, 60 mol% CuO; ▽, 70 mol% CuO; □, 80 mol% CuO; ———, theoretical fits to equation (1).

For electrical measurements, disc-shaped samples of approximate thickness 0.5 mm and approximate diameter 10 mm were cut and polished. Gold electrodes were deposited on both faces of the samples by vacuum evaporation. To stabilize the gold contact, the gold-coated samples were heat treated at about 393 K for 2 h. The DC conductivities of the samples were measured using a Keithley electrometer (model 617). Before the measurements, ohmic behaviour at the contacts was ascertained from the linearity of the current–voltage characteristics. The AC measurement was carried out in a General Radio capacitance bridge (model GR-1615A) which measures equivalent parallel conductance and capacitance of a sample for frequencies between 20 and 10^5 Hz in a three-terminal arrangement. Measurements were made in a cryostat in the temperature range 80–450 K with a stability of ±0.5 K.

3. Results and discussion

3.1. DC conductivity

The DC conductivities σ of the various sample compositions are shown in figure 1 as a function of reciprocal temperature. It is clear from figure 1 that the DC conductivity shows an activated behaviour above about 280 K. However, below 280 K, the behaviour of the DC conductivity is non-linear, indicating a temperature-dependent activation energy, characteristics of small polaron hopping conduction (Mott 1968, Austin and Mott 1969, Schnakenberg 1968, Ermin and Holstein 1969). The activation energy decreases with decreasing temperature. Mott (1968) investigated the conduction pro-

Table 2. Activation energy, phonon frequency, decay constant and polaron radius obtained from experimental data.

CuO in sample (mol%)	W (eV)	ν_0 (10^{13} s^{-1})	α (Å^{-1})	r_p (Å) From equation (3)	r_p (Å) From equation (4)
60	0.82	1.5	0.13	1.46	1.55
70	0.71	2.0	0.12	1.30	1.26
80	0.63	3.0	0.11	1.27	1.16

cesses in transition-metal ion glasses in terms of phonon-assisted hopping of small polarons between localized states. The DC conductivity in the Mott model for the nearest-neighbour hopping in the high-temperature limit ($T > \Theta_D/2$) is given by

$$\sigma = \nu_0[e^2C(1-C)/k_BTR]\exp(-2\alpha R)\exp(-W/k_BT) \tag{1}$$

where ν_0 is the longitudinal optical phonon frequency, R is the average site separation, α is the spatial decay parameter for the s-like wavefunction assumed to describe the localized state at each site, C is the fraction of sites occupied by an electron or polaron and therefore is the ratio of the ion concentration in the low-valence state to the total transition-metal ion concentration, W is the activation energy, k_B is the Boltzmann constant and T is the absolute temperature. Austin and Mott (1969) showed that

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

where W_H is the polaron hopping energy, W_D the disorder energy arising from the energy difference of the neighbouring sites and Θ_D the Debye temperature.

Equation (1) can be well fitted to the high-temperature ($T > 280$ K) electrical data presented in figure 1. The best fits are obtained for the values of W, α and ν_0 shown in table 2. The values of the average copper ion separation are used for R in the calculation. It may be noted that the values of α indicate strong localization in the CuO–Sb_2O_3–P_2O_5 glasses (Mott and Davis 1979). The values of ν_0 are also close to the phonon frequencies estimated from the infrared spectra of these glasses (Ghosh and Chakravorty 1990b).

An experimental estimate of the polaron radius r_p may be obtained within the framework of the Mott model which predicted that (Austin and Mott 1969)

$$W_H = e^2/4\varepsilon_p r_p \tag{3}$$

where ε_p is the effective dielectric constant. On the assumption that $W = W_H$, the values of r_p obtained from equation (3) are shown in table 2. The values of ε_p used in the calculation were obtained from the Cole–Cole plot of the complex dielectric constant. Bogomolov *et al* (1968) showed theoretically that for the case of a non-dispersive system of frequency ν_0 the polaron radius is given by

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

Equation (4) is obviously oversimplified for a complex system but the infrared spectra of the present glass system suggest that this approximation may fit this system well. The values of polaron radius calculated from equation (4) are shown in table 2. It is observed from table 2 that the theoretical and experimental values of r_p are comparable.

At low temperatures, Mott (1969) suggested a variable-range hopping mechanism.

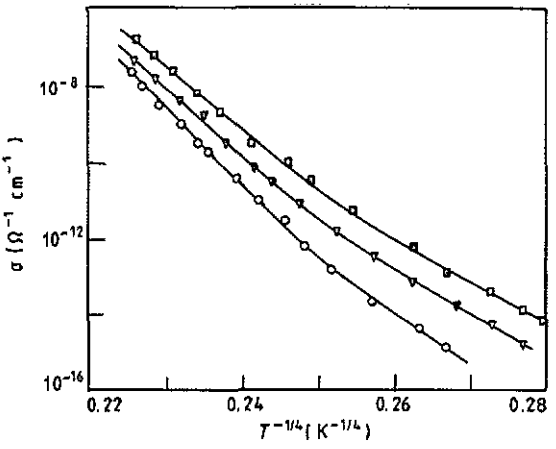

Figure 2. DC conductivity versus $T^{-1/4}$ for different glass compositions: ○, 60 mol% CuO; △, 70 mol% CuO; □, 80 mol% CuO; ———, theoretical fits to equation (5).

Table 3. Density of states and decay constant obtained from variable-range hopping model analysis.

CuO in sample (mol%)	Below 250 K		Above 250 K	
	$N(E_F)$ (10^{19} eV^{-1} cm^{-3})	α (Å^{-1})	$N(E_F)$ (10^{19} eV^{-1} cm^{-3})	α (Å^{-1})
60	4.0	0.14	1.0	0.14
70	5.0	0.12	1.0	0.12
80	5.0	0.11	1.0	0.10

The conductivity for the variable-range hopping is given by

$$\sigma = A \exp(-B/T^{1/4}) \tag{5a}$$

where A and B are constants and B is given by

$$B = 2.1[\alpha^3/k_B N(E_F)]^{1/4} \tag{5b}$$

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

Semilogarithmic plots of the DC conductivity versus $T^{-1/4}$ are shown in figure 2, which shows two linear regions below and above 250 K. The solid lines in figure 2 are the theoretical fits to equation (5) for the values of $N(E_F)$ and α shown in table 3. It is noted that the fits are reasonable. It should also be noted from table 3 that the values of α in the two temperature regions are consistent with the previous estimate of α (table 2) from the high-temperature electrical data. The values of $N(E_F)$ differ slightly in the two temperature regions; however, these values are reasonable for localized states (Mott and Davis 1979). It is interesting to note that the $T^{-1/4}$ behaviour in the high-temperature region in the present system is in agreement with the recent prediction of Triberis and Friedman (1985) who applied percolation theory to obtain this result. Their model predicts that the value of B should be lower in the high-temperature region compared with that at lower temperatures. In the present system, however, the behaviour exhibited is opposite to that expected from their model. No explanation is available at present for this discrepancy.

The temperature dependence of the DC conductivity, similar to the Mott model, is

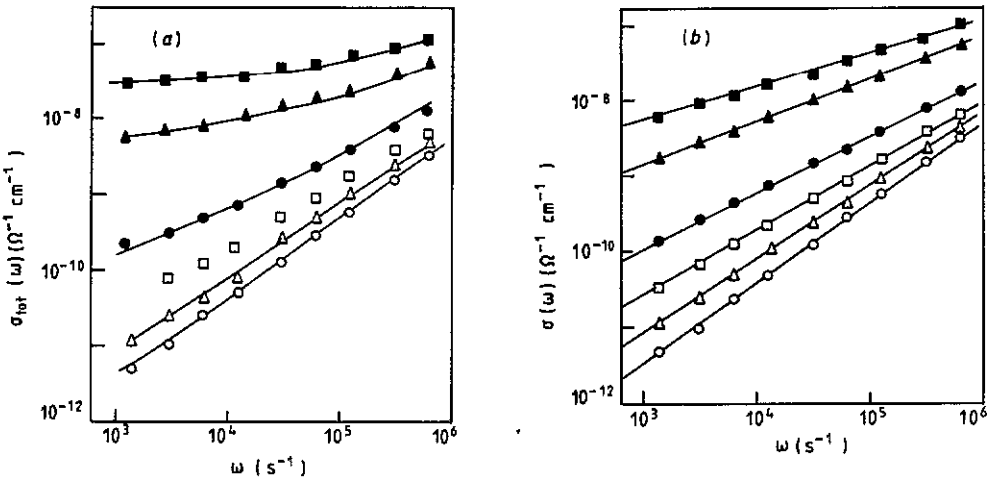

Figure 3. (*a*) Frequency dependence of the measured total conductivity for the glass composition containing 60 mol% CuO at several temperatures: ■, 384 K; ▲, 357 K; ●, 295 K; □, 252 K, △, 170 K; ○, 87 K; ———, theoretical fits to the classical hopping model. (*b*) The frequency-dependent conductivity obtained by subtracting DC conductivity from the data shown in (*a*).

also predicted by the Holstein model (Holstein 1959, Emin and Holstein 1969) in the high-temperature region. An independent check of the nature of hopping is also provided by this model. The overlap integral J must satisfy the relation

$$\left.\begin{matrix} J > \\ J < \end{matrix}\right\} (k_B T W_H/\pi)^{1/4}(h\nu_0/\pi)^{1/2} \qquad \text{for} \begin{cases} \text{adiabatic hopping} \\ \text{non-adiabatic hopping} \end{cases} \tag{6}$$

with the condition for the existence of small polaron being $J \leqslant W_H/3$. The limiting value of J estimated from the right-hand side of (6) using the values of ν_0 and $W_H \simeq W$ from table 2 at 400 K is in the range 0.052–0.068 eV for all compositions. An upper limit of J can be deduced by assuming that the entire concentration dependence of the activation energy is due to the variation in J. For the present glass systems, this corresponds to a change in W from 0.63 to 0.82 eV (table 2), leading to a possible variation in J of about 0.19 eV. However, since W is likely to change with composition, the true value is probably smaller than this, although it is large enough for the adiabatic hopping theory to be most appropriate for describing the polaronic conduction in the present cuprate glasses.

3.2. AC conductivity

The measured total conductivity $\sigma_{tot}(\omega)$ as a function of frequency at various temperatures is shown in figure 3(*a*) for one glass composition. It is clear that the DC contribution is significant at low frequencies and high temperatures, while the frequency-dependent term dominates at low temperatures and high frequencies. Other glass compositions also showed similar behaviour.

The measured total conductivity $\sigma_{tot}(\omega)$ can be decomposed into two components:

$$\sigma_{tot}(\omega) = \sigma(\omega) + \sigma \tag{7}$$

where σ and $\sigma(\omega)$ are the DC and frequency-dependent AC conductivities, respectively,

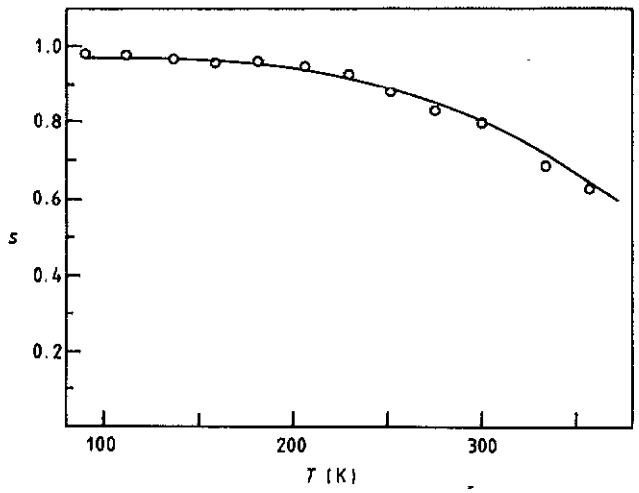

Figure 4. Temperature dependence of the frequency exponent for the sample composition containing 60 mol% CuO: ———, fit to the classical hopping model.

and it is assumed that the DC and AC contributions arise from separate mechanisms. However, when DC and AC conductivities are due to the same process and σ is simply $\sigma(\omega)$ in the limit $\omega \rightarrow 0$, the separation given in equation (7) is no longer valid (Elliott 1987).

In many amorphous semiconductors and insulators (Mott and Davis 1979) the variation in AC conductivity with frequency invariably has the form

$$\sigma(\omega) = A\,\omega^s \tag{8}$$

where A is a constant dependent on temperature and s is a frequency exponent which is generally unity or less.

The frequency dependence of $\sigma(\omega)$ obtained by subtracting the DC conductivity from the measured total conductivity at various temperatures is shown in figure 3(b) for the same glass composition as in figure 3(a). It is clear that the frequency dependence of $\sigma(\omega)$ follows equation (8) well. The frequency exponent s was obtained from the straight-line fits by the least-squares fitting procedure and is shown in figure 4 as a function of temperature. The frequency exponent s decreases smoothly with increasing temperature and is independent of frequency in the investigated frequency range.

Many different theories (Long 1982, Elliott 1987) for AC conduction in amorphous semiconductors have been proposed. It is commonly assumed that the dielectric loss occurs owing to localized carrier motion within a pair of sites. In essence, two distinct processes have been proposed for the relaxation mechanism, namely quantum mechanical tunnelling through the barrier and classical hopping over the barrier. In the following sections, the results presented in figures 3 and 4 are examined using these models.

3.2.1. Quantum mechanical tunnelling models. In the tunnelling process, three carriers are distinguished, namely electrons, small polarons and large polarons.

For electron tunnelling, various workers (Austin and Mott 1969, Pollak 1971, Pollak and Geballe 1961) have evaluated the following expression for the AC conductivity:

$$\sigma(\omega) = Ce^2 k_B T \alpha^{-1} [N(E_F)]^2 \omega R_\omega^4 \tag{9}$$

where C is a numerical constant and R_ω is hopping distance at frequency ω given by

$$R_\omega = (2\alpha)^{-1} \ln(1/\omega\tau_0) \tag{10}$$

where τ_0 is a characteristic relaxation time. The frequency exponent s is also given by

$$s = 1 - 4/\ln(1/\omega\tau_0). \tag{11}$$

Thus, for the electron-tunnelling model, $\sigma(\omega)$ is linearly dependent on temperature and s is temperature independent but frequency dependent. For typical values of the parameters, namely $\tau_0 \simeq 10^{-13}$ s and $\omega = 10^4\ s^{-1}$, a value of $s = 0.81$ is deduced from equation (11). However, it is clear from figure 4 that, for the present glass system, s decreases smoothly with increasing temperature, thereby conflicting with the predictions of the electron-tunnelling model.

For the small-polaron-tunnelling model the expression for conductivity remains the same with some modification in the hopping length R_ω (Elliott 1977). However, the temperature dependence of s as predicted by this model is not consistent with our experimental data. The large-polaron-tunnelling model (Long 1982) predicts that s decreases initially with increasing temperature, shows a minimum at a particular temperature and subsequently increases with increasing temperature. However, figure 4 shows no minimum for the present glass system. The temperature dependence of $\sigma(\omega)$ predicted by this model is of the order of T^6 at low temperatures, which is also much higher than that shown by experimental data (figure 3). Thus the large-polaron-tunnelling model is not consistent with the results for the present glass system.

3.2.2. Classical hopping models. Two models have been considered depending on whether one electron or two electrons simultaneously take part in the hopping mechanism. For single-electron hopping (Pike 1972), the AC conductivity is given by

$$\sigma(\omega) = (\pi^3/24)N^2\varepsilon\varepsilon_0\omega R_\omega^6 \tag{12}$$

where ε and ε_0 are the dielectric constants of the material and the free space, respectively, N is the concentration of pair sites and R_ω is given by

$$R_\omega = e^2/\pi\varepsilon\varepsilon_0[W_M - k_B T \ln(1/\omega\tau_0)] \tag{13}$$

where W_M is the maximum barrier height. The frequency exponent s is also given by

$$s = 1 - 6k_B T/[W_M - k_B T \ln(1/\omega\tau_0)]. \tag{14}$$

For two electrons hopping simultaneously (Elliott 1977, 1987), equations (12) and (13) are multiplied by 2. However, equation (14) remains unaltered.

Equation (14) shows that s decreases monotonically with increasing temperature, which is consistent with the data presented in figure 4. Fits of equation (14) to the experimental data are shown in figure 4 as a function of temperature using W_M and τ_0 as variable parameters. The values of W_M and τ_0 obtained by the least-squares fitting procedure are shown in table 4. In the fitting procedure, a fixed frequency ($\omega = 10^4\ s^{-1}$) is assumed for all compositions. In figure 3(a), the measured total conductivity $\sigma_{tot}(\omega)$ is also fitted to the AC conductivity $\sigma(\omega)$ calculated from equation (12) using the same value of W_M plus the measured value of the DC conductivity. It is observed that the fits appear reasonable over the entire temperature range. The values of the parameters obtained from this model, namely W_M and τ_0, are also reasonable.

It may be mentioned that the activation energies deduced from the low-frequency AC data for the different glasses are found to be of the order of 0.1 eV. This is much

Table 4. Parameters W_M and τ_0 obtained by fitting AC conductivity data to equation (14).

CuO in sample (mol%)	W_M (eV)	τ_0 (10^{-13} s)
60	1.39	1.0
70	1.16	2.0
80	1.03	2.0

smaller than the DC activation energies for these glasses. It is evident therefore that in the present glass system the centres involved in AC conduction are different from those contributing to the DC conductivity.

4. Conclusions

Analysis of the observed DC data shows that at higher temperatures the DC conductivity is consistent with predictions of the phonon-assisted hopping conduction model in the adiabatic approximation, while at low temperatures the variable-range hopping model seems to be valid. The quantum mechanical tunnelling models for the AC conduction are not consistent with the observed AC data. The classical hopping models can predict the temperature dependence of the AC conductivity and its frequency exponent over the entire temperature range.

References

Austin I G and Mott N F 1969 *Adv. Phys.* **18** 41
Bogomolov V N, Kudinov E K and Frisov Y A 1968 *Sov. Phys.–Solid State* **9** 2502
Chakravorty D, Kumar D and Sastry G V S 1979 *J. Phys. D: Appl. Phys.* **12** 2209
Elliott S R 1977 *Phil. Mag.* B **36** 1291
—— 1987 *Adv. Phys.* **36** 135
Emin D and Holstein T 1969 *Ann. Phys., NY* **53** 439
Ghosh A and Chakravorty D 1990a *J. Phys.: Condens. Matter* **2** 931
—— 1990b unpublished
Hirashima H, Watanabe Y and Yoshida T 1987 *J. Non-Cryst. Solids* **95–6** 825
Holstein T 1959 *Ann. Phys., NY* **8** 343
Long A R 1982 *Adv. Phys.* **31** 553
Mott N F 1968 *J. Non-Cryst. Solids* **1** 1
—— 1969 *Phil. Mag.* **19** 835
Mott N F and Davis E A 1979 *Electronic Processes in Non-Crystalline Materials* (Oxford: Oxford University Press)
Pike G E 1972 *Phys. Rev.* B **6** 1572
Pollak M 1971 *Phil. Mag.* **23** 519
Pollak M and Geballe T H 1961 *Phys. Rev.* **122** 1742
Schnakenberg J 1968 *Phys. Status Solidi* **28** 623
Triberis G P and Friedman L R 1985 *J. Phys. C: Solid State Phys.* **18** 2281