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Electrical conductivity in semiconducting CuO-Bi₂O₃-P₂O₅ glasses

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Abstract. DC electrical conductivity of the semiconducting glasses in the system CuO-Bi₂O₃-P₂O₅ is reported for the first time over the temperature range 80-420 K. The electrical data have been analysed in the light of the theoretical models of polaronic conduction. The analysis shows that the adiabatic hopping theory is the most appropriate to describe the polaronic conduction in the high-temperature region. At lower temperatures, a variable-range hopping mechanism dominates the conduction. Various parameters such as decay constant, density of states at the Fermi level, etc. have been obtained from analysis of the electrical conductivity data.

1. Introduction

The electrical properties of oxide glasses containing transition-metal ions such as V, Fe and W are of great interest because of their switching properties (Hirashima *et al* 1987), their uses as cathode materials in battery applications (Sakurai and Yamaki 1985) and as ferrites (Nakamura and Ichinose 1987), etc. These glasses owe their semiconducting behaviour to the presence of transition-metal ions in more than one valence state. The electron-phonon interaction in these glasses is strong enough to form small polarons and the electrical conduction process occurs by the hopping of small polarons from the low-valence state to the higher-valence state of the transition-metal ions (Mott 1968, Austin and Mott 1969). Glasses containing vanadium and iron ions have been studied more extensively than glasses containing other transition-metal ions (Sayer and Man-singh 1972, Murawski *et al* 1979, Hansen 1965). The thermal activation energy plays a dominant role in the conduction processes of these glasses. However, in many glass systems the pre-exponential factor also has a great influence on the conductivity (Muraw-ski *et al* 1979).

Drake *et al* (1969) reported the conductivity and switching of calcium phosphate and calcium borate glasses, respectively, containing copper oxide. The conduction processes in these glasses are characterised by a high activation energy (greater than 1.0 eV) which is mainly governed by the electron-hopping mechanism between non-identical copper sites. The activation energy is too high to be explained by polaronic hopping conduction as observed in glasses containing vanadium or iron ions.

The objective of the present work is to investigate the electrical properties of glasses in the system CuO-Bi₂O₃-P₂O₅. It is observed that the electrical conductivity of these glasses is much higher than that of copper phosphate glasses containing equivalent

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Table 1. Glass compositions, densities, concentrations of total and reduced Cu^+ ions, C values and average site spacings of the $\text{CuO-Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses.

Glass composition (mol%)			Density (g cm^{-3})	N (10^{21} cm^{-3})	c_{Cu^+} (10^{21} cm^{-3})	C	R (\AA)
CuO	P_2O_5	Bi_2O_3					
60	20	20	5.12	4.74	4.69	0.99	5.95
70	20	10	6.01	10.4	10.0	0.98	4.58
80	15	5	6.12	23.1	21.9	0.95	3.51

amounts of copper ions. The electrical conduction can be explained by the small-polaron theory. The results are reported in this paper.

2. Experiment

Glass samples of three compositions (table 1) were prepared from reagent grade CuO , Bi_2O_3 and $(\text{NH}_4)_2\text{HPO}_4$. The proportionate mixtures of these chemicals in a 10 g batch were melted at 1000°C in a platinum crucible for 2 h in air. The melt was then quenched by pressing the cast between two brass plates. The amorphous nature of the prepared samples was confirmed by x-ray diffraction studies (Philips PW 1050 instrument). The density of the samples (table 1) was measured using Archimedes' principle.

For electrical measurements, disc-shaped samples of approximate thickness 0.5 mm and approximate diameter 8 mm were cut and polished. Gold electrodes were deposited on both faces of the samples by vacuum evaporation. To stabilise the gold contact the gold-coated samples were heat treated at about 120°C for 2 h. The electrical conductivity of the samples was measured in a cryogenic unit by a Keithley 617 programmable electrometer in the temperature range 80–420 K. The absence of barrier layers at the contacts was ascertained by studying the I - V characteristics which were found to be linear.

The concentration of the total copper ions was determined from atomic absorption spectroscopy (Varian AA 1745 instrument). The concentration of Cu^{2+} ions was obtained from the ESR spectra recorded at room temperature with a Varian E-112 X-band ESR spectrometer. The spectrum of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was used as a standard. The average site spacing was estimated from the concentration of the total copper ions. The estimated concentration c_{Cu^+} of reduced copper, the estimated concentration N of total copper ions, the ratio $C (=c_{\text{Cu}^+}/N)$ of the concentration of the reduced copper ions to concentration of the total copper ions and the average site spacing R are shown in table 1.

3. Results and discussion

The DC conductivities σ of three compositions of the $\text{CuO-Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses are shown in figure 1 as functions of inverse temperature. It is observed that the DC conductivity varies smoothly with inverse temperature, showing a temperature-dependent activation energy W . Such behaviour is typical of small-polaron hopping conduction in transition-metal ion glasses (Mott 1968, Austin and Mott 1969, Sayer and Mansingh 1972). However, above 250 K the conductivity is almost linear with inverse temperature.

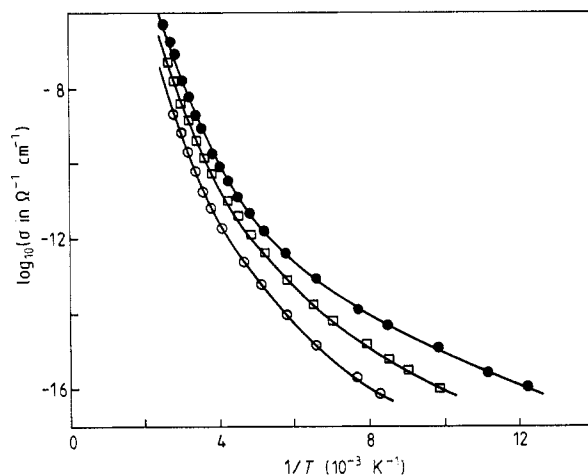


Figure 1. Temperature dependence of DC conductivity for $\text{CuO-Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses: ●, 80 mol% CuO; □, 70 mol% CuO; ○, 60 mol% CuO.

Table 2. Activation energies, pre-exponential factors and decay constants obtained by fitting equation (1) with the experimental data in the system $\text{CuO-Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses.

CuO content (mol%)	W (eV)		$(\sigma T)_0$ ($10^3 \Omega^{-1} \text{cm}^{-1} \text{K}$)	α (\AA^{-1})
	Above 250 K	At 90 K		
60	0.66	0.14	2.92	0.20
70	0.60	0.11	3.05	0.27
80	0.54	0.10	3.16	0.38

The activation energies at 300 and 90 K estimated from figure 1 are shown in table 2. It should be noted that the activation energies for compositions with 60 and 70 mol% CuO have been deduced from the curve fitting of equation (1). It is evident from the latter that the activation energy decreases with the increase in CuO content in the glasses.

A remarkable feature of the present series of glasses is that their conductivity is about three orders of magnitude higher than that of the copper phosphate glasses (Sayer and Mansingh 1972, Duran *et al* 1986) containing similar amounts of copper ions. It appears therefore that the glass-forming oxides may not simply act as non-interacting solvents in the conduction processes as suggested by Ioffe *et al* (1960) for vanadate glasses.

It is also observed that the current intensity in the samples, after application of a fixed voltage, remains constant with time. This implies that the electrical conduction in these glasses is electronic in nature.

Mott (1968) and Austin and Mott (1969) investigated theoretically the hopping conduction in transition-metal ion glasses and obtained the following expression for the DC conductivity in the non-adiabatic approximation:

$$\sigma = \nu_0 [e^2 C(1 - C)/kTR] \exp(-2\alpha R) \exp(-W/kT) \quad \text{for } T > \theta_D/2 \quad (1)$$

where ν_0 is the optical phonon frequency, R the average site spacing, C the ratio of the ion concentration in a low-valence state to the total transition-metal ion concentration, α the wavefunction decay constant, T the absolute temperature, k the Boltzmann constant and W the activation energy for conduction.

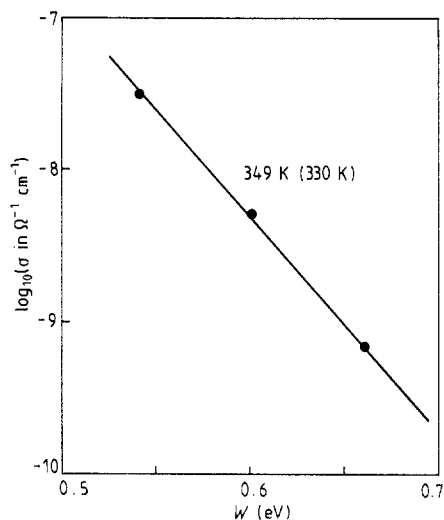


Figure 2. Plot of $\log \sigma$ against W for various glass compositions. The value of 330 K in parentheses is the experimental temperature. The value of 349 K corresponds to the slope.

Assuming a strong electron-phonon interaction, Austin and Mott (1969) showed that

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

$$W \approx W_D \quad \text{for } T < \theta_D/4 \quad (2b)$$

where W_H is the polaron hopping energy and W_D the disorder energy arising from the energy difference of the neighbouring sites. θ_D , defined by $h\nu_0 = k\theta_D$, is the Debye temperature.

A semi-logarithmic plot of the conductivity measured at an arbitrarily chosen temperature (330 K) against the activation energy W at that temperature for all glass compositions is shown in figure 2. It is observed that the plot is a straight line with slope equal to that corresponding to a measurement temperature of 349 K. The general conclusion which may be drawn from figure 2 is that the pre-exponential term in equation (1) inclusive of $\exp(-2\alpha R)$ is virtually constant for all glass compositions. The thermal activation energy for conduction, therefore, appears to dominate the factors that determine the conductivity. In particular, the tunnelling term $\exp(-2\alpha R)$ need not be assumed to vary rapidly with site spacing R in order to explain the variation in the conductivity with transition-metal ion concentration. This observation also suggests small-polaron hopping in the adiabatic regime (Murawski *et al* 1979) in the present glass systems.

The small-polaron model (Austin and Mott 1969) predicts that an appreciable departure from a linear plot of $\log \sigma$ against $1/T$ should occur below a temperature of $\theta_D/2$. Figure 1 also shows that a temperature-dependent activation energy is observed only below a temperature of 250 K. Thus the small-polaron model provides an estimate for $\theta_D/2$ of about 250 K and hence an estimate of the optical phonon frequency ν_0 of about 1.04×10^{13} Hz for the CuO-Bi₂O₃-P₂O₅ glasses. It is worthwhile to note here that the infrared spectra of the different compositions of these glasses are very similar, suggesting that the optical phonon distribution does not differ appreciably between the different compositions of these glasses (Ghosh and Chakravorty 1989). From the infrared spectra, the characteristic phonon frequency has been estimated to be of the order of 1.60×10^{13} Hz corresponding to an observed infrared band at about 550 cm^{-1} . Therefore

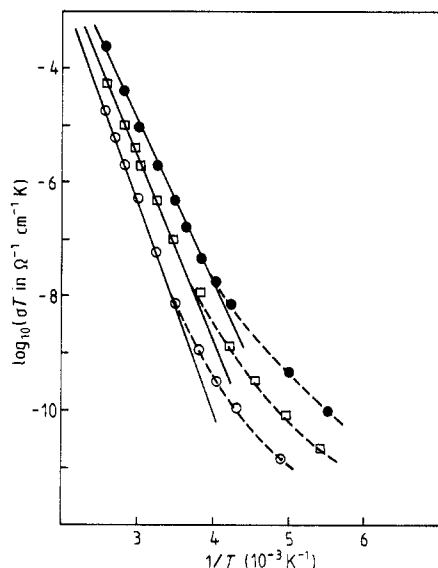


Figure 3. Plot of $\log(\sigma T)$ against $1/T$ for various glass compositions: ●, 80 mol% CuO; □, 70 mol% CuO; ○, 60 mol% CuO; —, least-squares fit of equation (1).

the value of the phonon frequency estimated from the small-polaron theory is close to the phonon frequency estimated from infrared studies.

It is interesting to estimate the decay constant α from the high-temperature electrical data using equation (1). For this purpose a plot of $\log(\sigma T)$ against $1/T$ is shown in figure 3 for various glass compositions. The full lines in figure 3 are obtained by the least-squares fitting procedure. The values of the pre-exponential factor in equation (1) obtained by this fitting procedure are shown in table 2. The values of α are obtained from the pre-exponential factor using known values of the parameters listed in table 1. It is evident from table 2 that the values of α calculated for the various glass compositions indicate strong localisation in these glasses (Mott and Davis 1979). The values of α also fall within the range given by Austin and Garbett (1973) for the transition-metal ion glasses. Two methods of calculating the polaron binding energy W_p have been suggested. The most general expression has been given by Holstein (1959):

$$W_p = (2N)^{-1} \sum_q |\gamma_q|^2 h\nu_q \quad (3)$$

where $|\gamma_q|^2$ is the electron-phonon coupling constant and ν_q is the frequency of optical phonons of wavenumber q and N is the site concentration. Austin and Mott (1969) have derived a more direct expression:

$$W_p = \frac{1}{2}(e^2/\epsilon_p r_p) \quad (4)$$

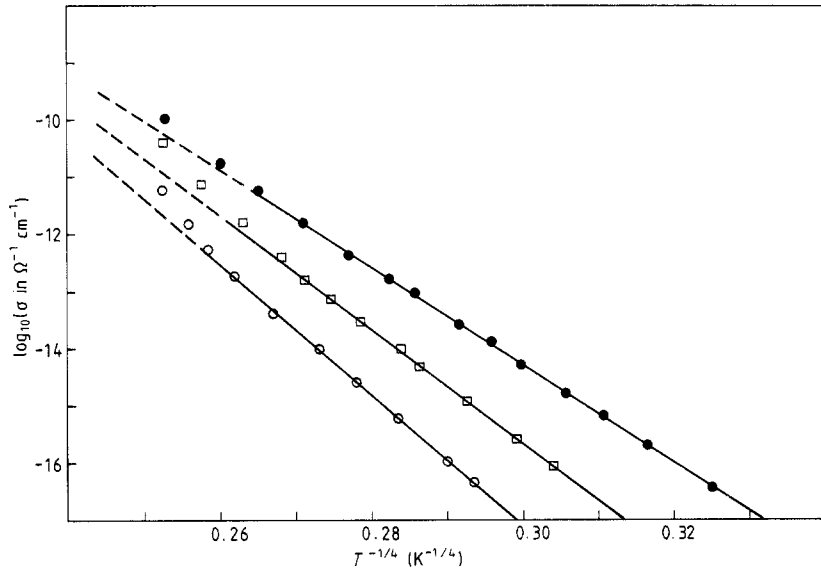
where r_p is the polaron radius and ϵ_p is an effective dielectric constant given by $1/\epsilon_p = 1/\epsilon_\infty - 1/\epsilon_s$, ϵ_∞ and ϵ_s being the high-frequency and static dielectric constants, respectively. Bogomolov *et al* (1967) have shown that an expression of the form of equation (4) can be derived from equation (3) for a non-dispersive system of frequency ν_0 . The polaron radius is given by

$$r_p = \frac{1}{2}(\pi/6)^{1/3} R. \quad (5)$$

The value of the polaron radius calculated from equation (5) using the average site spacing (table 1) as an estimate for R is shown in table 3. An experimental estimate (Austin and Mott 1969) may be obtained from equation (4) taking $W \approx W_H = \frac{1}{2}W_p$. The

Table 3. Hopping energies, effective dielectric constants and polaron radii obtained from equations (4) and (5) for the CuO–Bi₂O₃–P₂O₅ glass systems.

CuO content (mol%)	W_H (eV)	ϵ_p	r_p (Å)	
			Calculated from equation (5)	Calculated from equation (4)
60	0.66	2.31	2.38	2.29
70	0.60	3.37	1.83	1.78
80	0.54	4.80	1.40	1.39

**Figure 4.** Plot of $\log \sigma$ against $T^{-1/4}$ for various glass compositions: ●, 80 mol% CuO; □, 70 mol% CuO; ○, 60 mol% CuO; —, least-squares fit of equation (6).

values obtained are shown in table 3. The values of ϵ_p used with the calculation are obtained from the Cole–Cole plot of the real and imaginary parts of the dielectric constants (Ghosh and Chakravorty 1989). Table 3 shows that the theoretical and experimental estimates of r_p are in satisfactory agreement. Although the possible effects of disorder have been neglected in the above calculations, the small value of the polaron radii suggests that the polarons are highly localised.

At low temperatures, where the polaron binding energy is small and the static disorder energy of the system plays a dominant role in the conduction mechanism, Mott (1968) has suggested a variable-range hopping process. The conductivity for the variable-range hopping is given by

$$\sigma = A \exp(-B/T^{1/4}) \quad (6)$$

where A and B are constants, and B is given by

$$B = 2.1[\alpha^3/kN(E_F)]^{1/4} \quad (7)$$

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

A plot of $\log \sigma$ against $T^{-1/4}$ for the glasses is shown in figure 4 which suggests that the variable-range hopping mechanism may be valid in these systems below 150 K.

Table 4. Decay constants and densities of states of different glasses at the Fermi level obtained from the variable-range hopping analysis.

CuO content (mol%)	α (\AA^{-1})	$N(E_F)$ ($10^{19} \text{ eV}^{-1} \text{ cm}^{-3}$)
60	0.23	1.56
70	0.27	4.20
80	0.29	9.91

Equation (6) is fitted in figure 4 to the experimental data using α and $N(E_F)$ as variable parameters. The values of α and $N(E_F)$ obtained by the least-squares fit are shown in table 4. The values of $N(E_F)$ and α are reasonable for the localised states (Mott and Davis 1979). The values of α are also close to the values estimated (table 2) from the high-temperature electrical data.

The nature of hopping conduction can be ascertained from Holstein's condition (Holstein 1959, Emin and Holstein 1969). The polaron band width J should satisfy the inequality

$$J \geq (2kTW_H/\pi)^{1/4}(h\nu_o/\pi)^{1/2} \quad (8)$$

where the greater than sign ($>$) is for hopping in the adiabatic regime and the less than sign ($<$) for hopping in the non-adiabatic case. The condition for the existence of a small polaron is $J < W_H/3$. On the assumption that $W_H = W$ the limiting values of J calculated from the right-hand side of (8) at 400 K are in the range 0.038–0.040 eV depending on the composition. In the above calculation, our estimate of ν_o from the electrical data has been used. Since $W_H/3 \approx 0.20$ eV, the condition for the formation of a small polaron is satisfied. An unambiguous conclusion as to whether the polaron hopping is in the adiabatic or in the non-adiabatic regime requires an estimate of J . An upper limit of J can be deduced by assuming that the entire concentration dependence of activation energy is due to the variation in J . For the present glasses this corresponds to a change in W from 0.54 to 0.66 eV (table 2), a possible variation in J being 0.12 eV. However, since W is likely to change with composition, the true value is probably smaller than this. J can also be estimated from the following expression (Mott and Davis 1979):

$$J \approx e^3 [N(E_F)/\epsilon_p^3]^{1/2}. \quad (9)$$

Using the values of ϵ_p and $N(E_F)$ from table 4, equation (9) gives $J \approx 0.06$ eV. Thus the adiabatic hopping theory may be most appropriate for describing polaronic conduction in the $\text{CuO-Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses.

Recently, Triberis and Friedman (1985) and Triberis (1985, 1988), on the basis of the microscopic generalised molecular crystal model (Triberis and Friedman 1981) applicable to small-polaron hopping motion in a disordered system, have used percolation theory to evaluate the conductivity of a disordered material at high and low temperatures. Taking correlation into account, Triberis and Friedman (1985) have obtained an expression for the conductivity similar to Mott's expression for variable-range hopping conductivity:

$$\sigma = \sigma_0 \exp(-T_0/T)^{1/4} \quad (10)$$

where the constants σ_0 and T_0 have different values at high and low temperatures. However, if the correlation is neglected, the temperature dependence of the conductivity reduces to (Triberis and Friedman 1981)

$$\sigma = \sigma_0 \exp(-T_0/T)^{2/5}. \quad (11)$$

Attempts have been made to analyse the conductivity data of the present work in the

light of the model of Triberis and Friedman, but the temperature dependence of the conductivity as predicted by equation (10) or equation (11) has not been observed.

4. Conclusion

The small-polaron theory can adequately explain the temperature dependence of the electrical conductivity of the $\text{CuO-Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses. At high temperatures the adiabatic hopping theory is most appropriate for describing the polaronic conduction in these glasses, while conduction takes place by the variable-range hopping mechanism at low temperatures. The fitting of experimental data to the theoretical models provides reasonable values of the optical phonon frequency, the wavefunction decay constant and the density of states at the Fermi level.

References

- Austin I G and Mott N F 1969 *Adv. Phys.* **18** 41
Austin I G and Garbett E S 1973 *Electronic and Structural Properties of Amorphous Semiconductors* ed. P G Le Comber and J Mort (New York: Academic) p 393
Bogomolov V N, Kudinov E K and Frisov Y A 1967 *Sov. Phys.-Solid State* **9** 3175
Drake C F, Scanlan I F and Engel A 1969 *Phys. Status Solidi* **32** 193
Duran A, Jurado J K and Navarro J M E 1986 *J. Non-Cryst. Solids* **79** 333
Emin D and Holstein T 1969 *Ann. Phys., NY* **53** 439
Ghosh A and Chakravorty D 1989 unpublished
Hansen K W 1965 *J. Electrochem. Soc.* **112** 10
Hirashima H, Watanabe Y and Yoshida T 1987 *J. Non-Cryst. Solids* **95-96** 825
Holstein T 1959 *Ann. Phys., NY* **8** 349
Ioffe V A, Patriva I B and Poberivskaya I S 1960 *Sov. Phys.-Solid State* **2** 609
Mott N F 1968 *J. Non-Cryst. Solids* **1** 1
Mott N F and Davis E A 1979 *Electronic Processes in Non-Crystalline Materials* (Oxford: Clarendon)
Murawski L, Chung C H and Mackenzie J D 1979 *J. Non-Cryst. Solids* **32** 91
Nakamura S and Ichinose N 1987 *J. Non-Cryst. Solids* **95-96** 849
Sakurai Y and Yamaki J 1985 *J. Electrochem. Soc.* **132** 512
Sayer M and Mansingh A 1972 *Phys. Rev. B* **6** 4629
Triberis G P 1985 *J. Non-Cryst. Solids* **74** 1
— 1988 *J. Non-Cryst. Solids* **104** 135
Triberis G P and Friedman L R 1981 *J. Phys. C: Solid State Phys.* **14** 4631
— 1985 *J. Phys. C: Solid State Phys.* **18** 2281