

A study of the structural, electrical and optical properties of copper tellurium oxide glasses

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The results of an investigation of some properties of CuO-TeO₂ glasses are reported. X-ray diffraction, differential scanning calorimetry and optical absorption measurements are discussed with respect to the compositions. D.c. conductivity is measured in the temperature range 293 to 453 K and discussed in terms of small polaron theory.

1. Introduction

Several transition metal oxides when heated with glass-forming substances such as P₂O₅, TeO₂ and GeO₂, etc., form glasses on quenching the melt. The loss of oxygen from the melt produces a proportion of lower valency transition metal ions, and electrical conduction in these glasses occurs by electron hopping from an ion in the low valency state (e.g. Cu⁺) transition metal to an ion in the higher valency state (Cu²⁺) [1].

Differential thermal analysis, X-ray diffraction and electrical conductivity for CuO-TeO₂ glasses have been studied by Ivanova *et al.* [2]. They found that for all the compositions examined, the dependence of electrical conductivity, σ , as a function of reciprocal temperature ($1/T$) yields different activation energies at low and high temperatures. Electrical conductivity measurements for glasses of the ternary system CuO-V₂O₅-TeO₂ have been investigated by Dimitriev *et al.* [3]. They noted that the temperature dependence of the conductance is better described by the Arrhenius equation above 100°C and that the calculated activation energy varies within the limits 0.4 to 0.8 eV.

The physical parameters obtained from measurements such as X-ray diffraction, differential scanning calorimetry (DSC), and optical absorption are discussed with respect to the compositions. The conductivity was measured for semiconducting copper tellurium oxide glasses. The present studies show that

the conductivity of CuO-TeO₂ glasses is slightly higher than that of the corresponding CuO-P₂O₅ glasses [4].

2. Experimental work

Six glasses in the CuO-TeO₂ system with 15, 25, 30, 35, 40, and 50 mol % CuO were prepared by melting the oxides in alumina crucibles for 30 min at 700 to 900°C. The electrical measurements were made by standard techniques. Evaporated gold electrodes were found to give ohmic contacts for fields up to at least 10³ V cm⁻¹ and were used in all the electrical measurements. Thin glass films, which are necessary for optical absorption measurements, were obtained by blowing techniques. Specimens in the thickness range 2.5 to 6.25 μ m were obtained as measured using a Sigma comparator. All thin films were unannealed when used for optical measurements. The optical absorption measurements were made on thin blown films at room temperature in the wavelength range 200 to 900 nm.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction is a quite useful technique because it is possible to detect readily crystals in a glassy matrix if the crystals are of dimensions greater than typically 100 nm [5]. The X-ray diffraction pattern of an amorphous material is distinctly different from that of crystalline material and consists of a few broad diffuse haloes

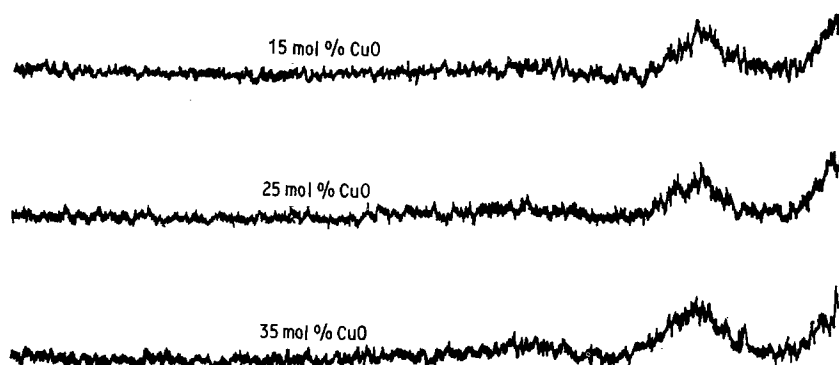


Figure 1 X-ray diffraction patterns of three samples of copper-tellurium oxide glasses.

TABLE I Exothermal and endothermal temperature transition peaks for some glass samples using DSC in the range 50 to 600°C

CuO (mol %)	Endothermal temp (°C)	Exothermal temp (°C)	$-\Delta H$ (J g ⁻¹)
15	356	410	88.26
	436	472	45.30
25	352	396	14.79
	428	476	54.24

rather than sharp rings. All glass samples were tested and the results showed the absence of crystalline characteristics. Fig. 1 shows typical X-ray diffraction patterns for three compositions, recorded with a Phillips type PW 1050 diffractometer, using a copper tube and nickel filter.

3.2. Thermal analysis

In this investigation the differential scanning calorimetry (DSC) technique was used. An important use of DSC in glasses is to measure the glass transition temperature, T_g . A sample and an inert reference are used and the cell is designed to enable a direct quantitative measurement for the enthalpy changes that occur in a sample as a function of either temperature or time to be made.

The thermal stability of the glasses was studied in a Perkin Elmer DSC 7 equipment for two compositions in the temperature range 313 to 873 K. The heat flow to the sample was measured under thermally controlled conditions. DSC gave much more sensitive results showing that the transitions started at a lower temperature than expected. Fig. 2 shows typical curves of the transitions and Table I gives a summary for the glass endothermal peak values, exothermal peak values and the amount of heat absorbed by the glass in the endothermal transitions.

3.3. Optical absorption

A main feature of the absorption edge of amorphous semiconductors, particularly at the lower values of

TABLE II Chemical composition and derived parameters of CuO-TeO₂ glasses

CuO (mol %)	W (eV)	$E_{cl}(=2W)$ (eV)	E_{opt} (eV)	E_0 (eV)
15	0.8	1.60	-	-
25	0.74	1.48	2.75	0.33
30	0.69	1.38	2.68	0.34
35	0.66	1.32	2.62	0.37
40	0.60	1.20	2.55	0.49
50	0.53	1.06	2.30	0.75

absorption coefficient, is an exponential increase of the absorption coefficient $\alpha(\omega)$ with photon energy ($\hbar\omega$) in accordance with an empirical relation due to Urbach [6]

$$\alpha = \alpha_0 \exp(\hbar\omega/E_0) \quad (1)$$

where α_0 is a constant, E_0 is the Urbach energy which indicates the width of the band tails of the localized states and ω is the angular frequency of the radiation.

Optical absorption measurements were made as a function of photon energy at room temperature. Fig. 3 shows the absorbance in arbitrary units as a function of the wavelength for glass films of different compositions.

The absorption coefficient $\alpha(\omega)$ can be determined near the edge from the formula

$$\alpha(\omega) = \frac{1}{d} \ln \frac{I_0}{I} \quad (2)$$

where d is the thickness of the sample, I_0 and I are the intensities of the incident and transmitted beams, respectively. The most satisfactory results were obtained by plotting the quantity $(\alpha\hbar\omega)^{1/2}$ as a function of $(\hbar\omega)$ as suggested by Davis and Mott [7]. For absorption by indirect transitions the equation takes the form

$$\alpha(\omega) = A(\hbar\omega - E_{opt})^2/\hbar\omega \quad (3)$$

where A is a constant, E_{opt} is the band gap and this

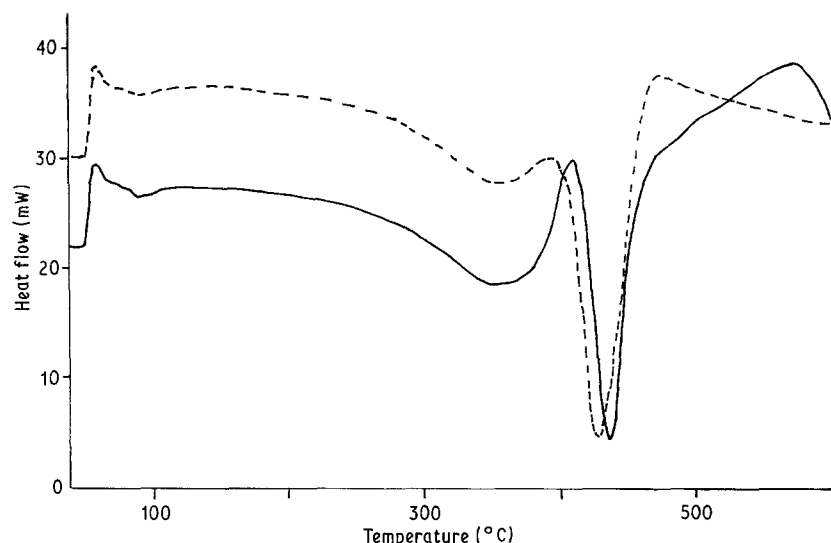


Figure 2 Typical DSC curves for two copper-tellurium oxide glasses. (---) 25 mol % CuO, (—) 15 mol % CuO.

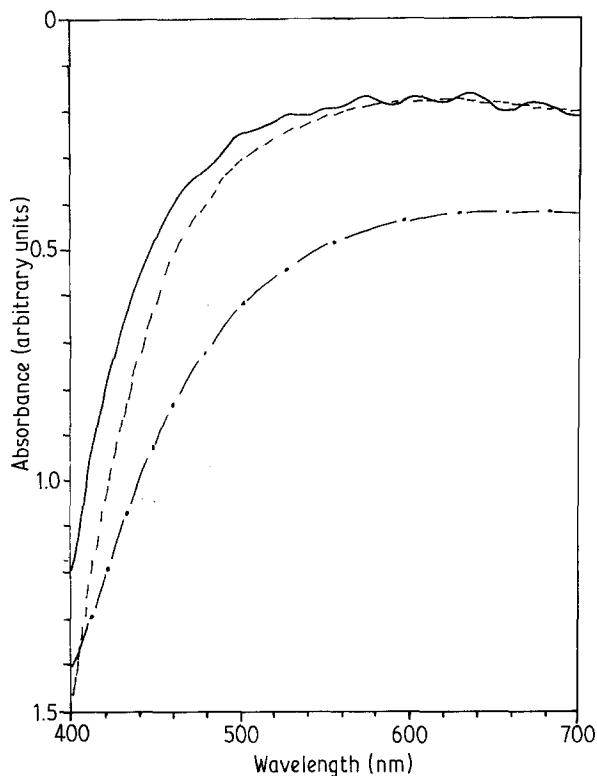


Figure 3 Absorbance as a function of wavelength for three samples of copper-tellurium oxide glasses. (—) 25 mol % CuO, (---) 35 mol % CuO, (-·-·-) 50 mol % CuO.

relation applies to many oxide glasses, particularly at the higher values of absorption coefficient. Figs 4 and 5 show plots of $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ and the equivalent Urbach plot is presented in Figs 6 and 7 in which the absorption coefficients are plotted as functions of $\hbar\omega$

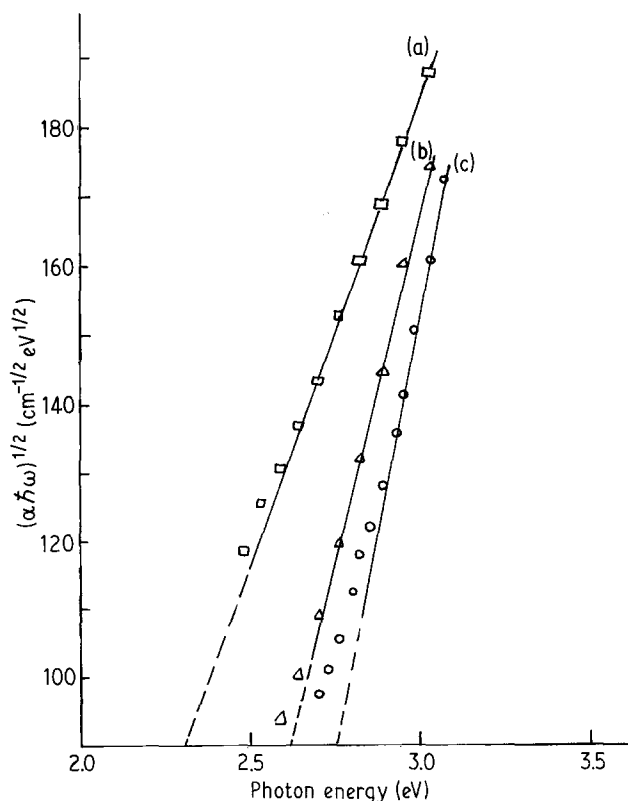


Figure 4 $(\alpha\hbar\omega)^{1/2}$ plotted against $\hbar\omega$ for three samples of copper-tellurium oxide glasses. (a) 50 mol % CuO, 2.5 μm ; (b) 35 mol % CuO, 2.7 μm ; (c) 25 mol % CuO, 2.6 μm .

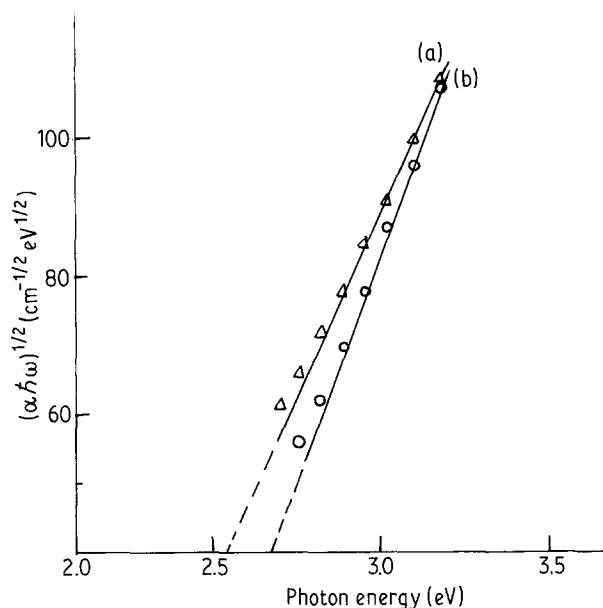


Figure 5 $(\alpha\hbar\omega)^{1/2}$ plotted against $\hbar\omega$ for two samples of copper-tellurium oxide glasses of the same thickness, 6.25 μm . (a) 40 mol % CuO, (b) 30 mol % CuO.

for different compositions of CuO-TeO₂ glasses. The values of E_{opt} determined from Figs 4 and 5 by extrapolating the linear parts of the curves to $(\alpha\hbar\omega)^{1/2} = 0$, and the values of E_0 which are determined from Figs 6 and 7 by using Equation 1 are tabulated in Table II. It is clear from Fig. 8 that the optical gap E_{opt} decreases as the proportion of transition metal oxide CuO is increased, but on the other hand the width of the band tails of the localized states is found to increase with increasing CuO content, as shown in Fig. 9. The value of E_{opt} is considerably larger than twice the electrical activation energy, W .

3.4. D.c. conductivity

The d.c. electrical conductivity of CuO-TeO₂ glasses was measured in the temperature range 293 to 453 K. All measurements were taken more than once. The

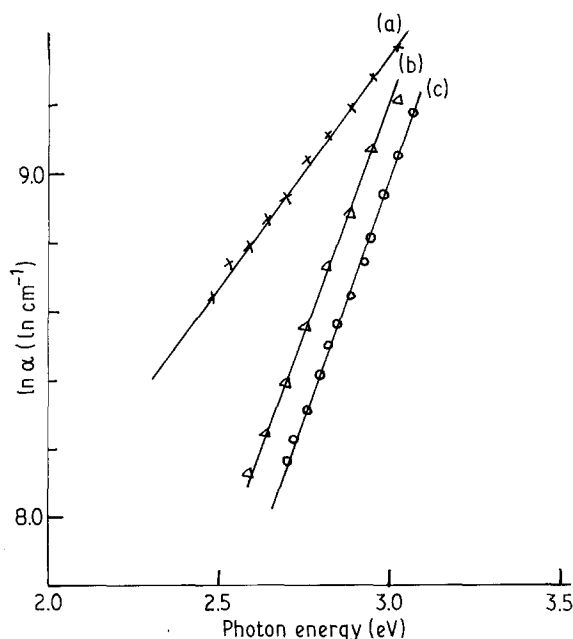


Figure 6 $\text{Ln } \alpha$ plotted against $\hbar\omega$ for the three samples of Fig. 4.

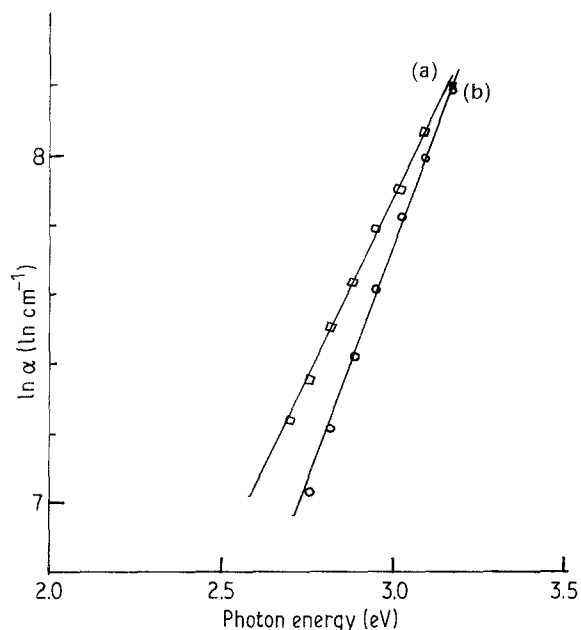


Figure 7 $\ln \alpha$ plotted against $h\nu$ for the two samples of Fig. 5.

d.c. conductivity, $\sigma_{d.c.}$, increases with temperature and also with the increase in the concentration of transition metal oxide CuO in the glass, as shown in Fig. 10. All glasses show a smooth variation of conductivity with $(1000/T) K^{-1}$. The d.c. conductivity is a negative exponential function of inverse temperature and can be expressed by the usual equation

$$\sigma_{d.c.} = \sigma_0 \exp\left(-\frac{W}{kT}\right) \quad (4)$$

where W is the activation energy.

The activation energies were calculated from the slopes of the $\log \sigma_{d.c.}$ against $1/T$ curves and were found to decrease as the concentration of transition metal oxide CuO increases in the glass, as shown in Fig. 11. The values of the activation energy, W , above room temperature are typically 0.61 to 0.8 eV and are

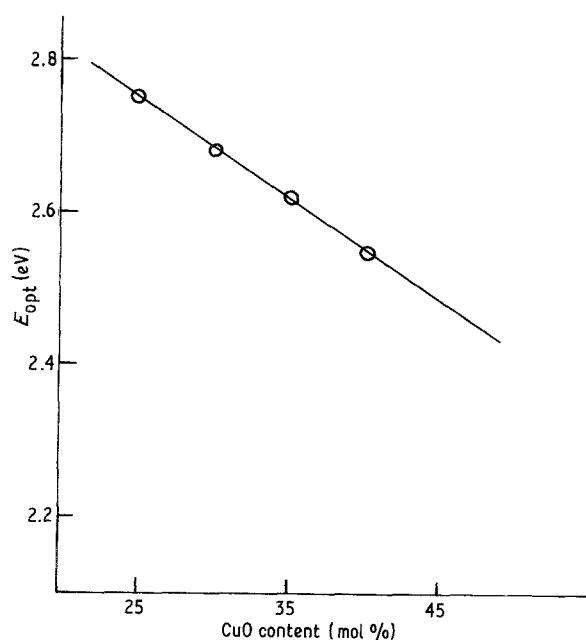


Figure 8 E_{opt} plotted against CuO content for copper-tellurium oxide glasses.

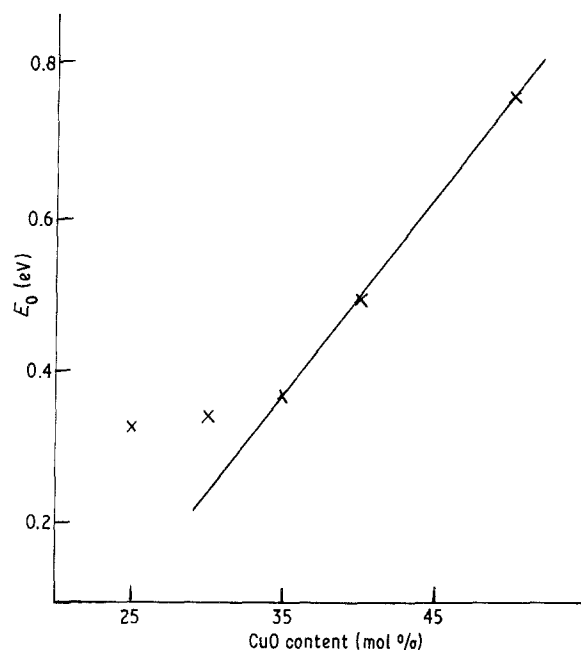


Figure 9 E_0 plotted against CuO content for copper-tellurium oxide glasses.

considerably less than half the calculated values of the optical gap, as shown in Table II.

The d.c. electrical conductivity and the shape of the current-voltage characteristics were sensitive to temperature. The glasses show ohmic behaviour at low fields, as shown in Fig. 12. As can be seen from Fig. 13, the resistance of CuO-TeO₂ glasses is independent of time. This could be taken as evidence that the polarization effect in these glasses is minimal or absent and the electrical conduction would in this case be due to transport of electrons rather than ions.

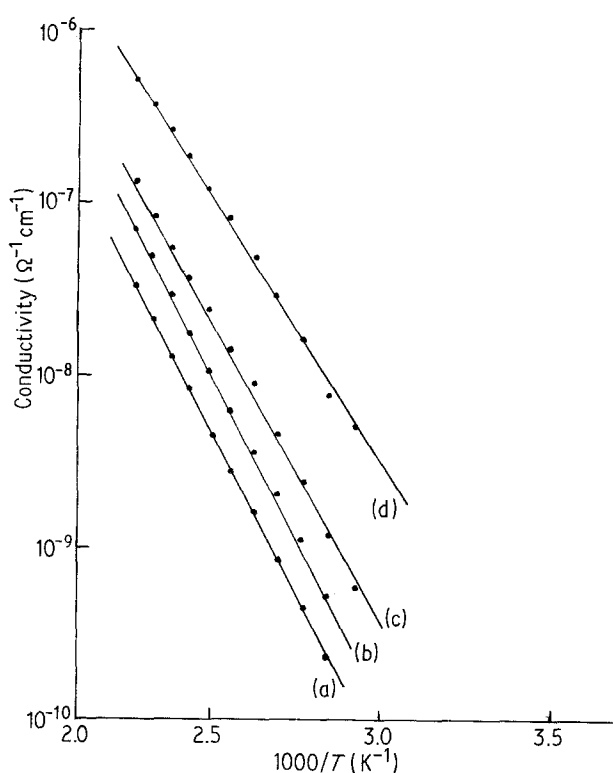


Figure 10 Conductivity as a function of inverse temperature for four samples of copper-tellurium oxide glass. (a) 15 mol% CuO, (b) 25 mol% CuO, (c) 30 mol% CuO, (d) 40 mol% CuO.

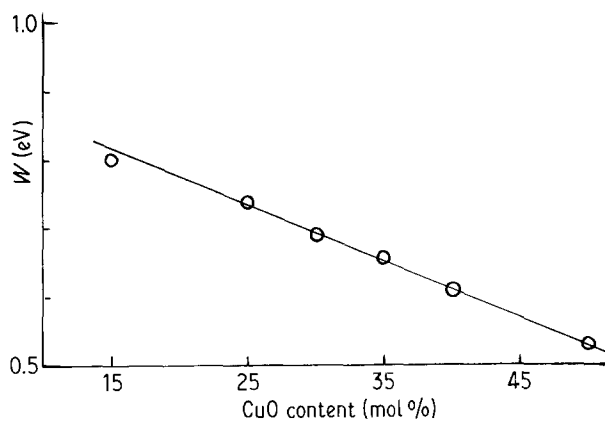


Figure 11 Variation of activation energy, W , with CuO content of copper-tellurium oxide glass.

4. Discussion

It is of interest to discuss the following points.

(i) The shift of the ultraviolet absorption band to longer wavelength with the increasing CuO content.

(ii) The variation of E_{opt} with electrical activation energy.

(iii) The kind of conduction mechanism which is likely to be involved in these materials.

(i) Stevels [8] suggests that the movement of the ultraviolet absorption band to longer wavelengths corresponds to a transition from the non-bridging oxygens which bind an excited electron less tightly than a bridging oxygen. As can be seen from Fig. 3 the shift of the ultraviolet absorption band to longer wavelengths with increasing CuO content could be explained in the same way. Thus the result of Fig. 8 showing the variation of E_{opt} with composition can be explained by suggesting that the non-bridging oxygen

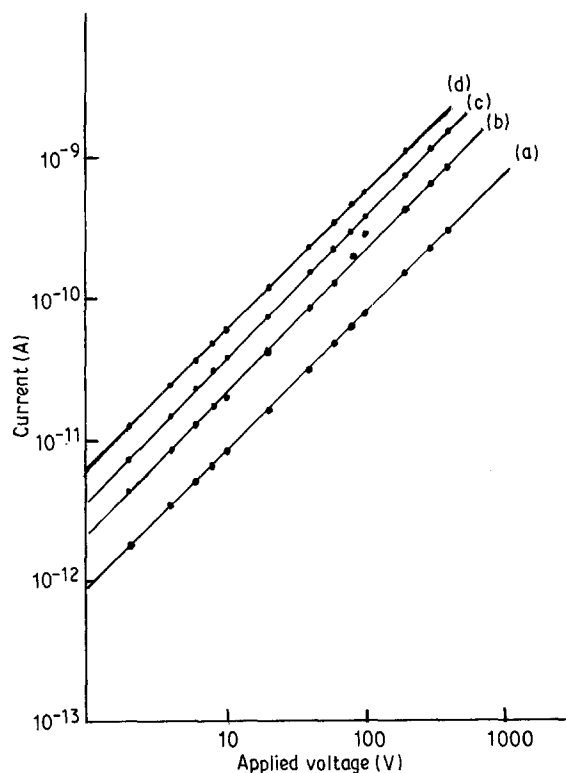


Figure 12 V - I characteristics at room temperature of the four samples of Fig. 10.

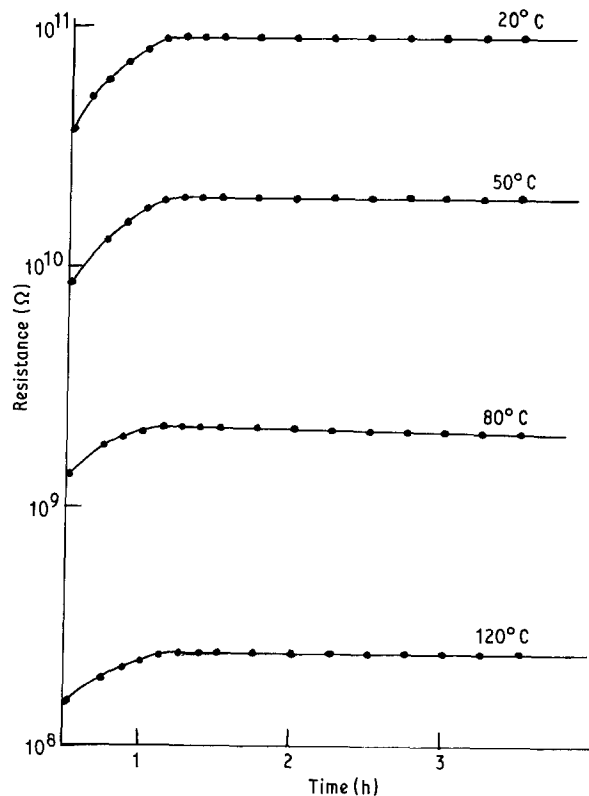


Figure 13 Variation of resistance with time for a 30 mol % CuO sample at different temperatures.

ion content increases with increasing CuO content, shifting the band edge to lower energies and thus consequently leading to a decrease in E_{opt} .

(ii) As can be seen from Table II, the so-called optical gap (E_{opt}) is three to four times larger than the high-temperature activation energy. This is consistent with the results of many workers on oxide and chalcogenide glasses which show that the electrical energy gap, sometimes regarded as twice the activation energy, W , is less than the value of the optical gap on the same glass. The results suggest that the electronic activation is not across the whole mobility gap but is possibly from one or more trapping levels to the conduction band or from bonding states to a trapping level.

(iii) The log σ against reciprocal temperature plot displays linear behaviour which is typical of the small polaron hopping mechanism exhibited by 3d and 4d transition metal oxide glasses.

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Received 7 July
and accepted 9 October 1987