

# Direct and alternating electrical conduction in copper phosphate glasses containing praseodymium and calcium

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Glasses of various compositions were prepared and included  $\text{Pr}_6\text{O}_{11}\text{-CuO-P}_2\text{O}_5$  and  $\text{Pr}_6\text{O}_{11}\text{-CaO-CuO-P}_2\text{O}_5$ . The direct electrical conduction mechanism was generally discussed in terms of small polarons for the whole series of glasses. Alternating electrical conduction was discussed according to the Elliott model and the Meyer-Neldel rule.

## 1. Introduction

The behaviour of direct current (d.c.) electrical conductivity in transition and mixed transition metal oxide glasses has been investigated by many workers [1-4], but relatively little information is available about glasses containing rare earth oxides. Magruder and Kinser [5] studied the electrical properties of praseodymium phosphate glass as a function of oxidation and reduction treatments while Harani and Hogarth [6] reported the electrical conductivity of phosphate glasses containing a considerable amount of praseodymium.

The present treatments of the d.c. electrical conductivity of these glasses are based mainly on the theories of Mott [7] and Austin and Mott [8]. Many authors have suggested thermally activated hopping of electrons or polarons as the mechanism of charge transport in glasses containing metal oxides. The general mechanism of conduction at higher temperatures may be regarded as a process of hopping by small polarons. It was found that the alternating current (a.c.) conductivity,  $\sigma_{\text{a.c.}}$ , generally varies as  $\omega^s$ , where  $\omega$  is the angular frequency of the applied fields and  $s$  is a temperature-dependent index whose value is close to, but less than, unity [9]. The a.c. conduction of the chalcogenide glasses was analysed by Elliott [10] using a model of hopping between charged and uncharged centres and it was of interest to determine whether the values of  $s$  derived on the basis of this model were in accordance with the results of experiments on phosphate glasses.

## 2. Experimental work

Disc-shaped samples were fixed to a special specimen holder and ground to about 2 mm thickness using a grinding machine and different grades of SiC powder with light oil as a lubricant. The samples were then polished using a grade (6-W-42) Hyprez diamond compound paste and Hyprez fluid as a lubricant. After grinding and polishing, the samples were cleaned by acetone and dried. Before the electrode deposition the samples were annealed at 100°C for 1 h to relieve

stress and to remove any volatile contaminants. All composition data of the samples are expressed in units of mol %.

A three-terminal gold electrode system was deposited on each of the glass samples. A Hewlett-Packard impedance analyser (500 Hz to 13 MHz), type 4192ALF, was used to take direct measurements of a.c. conductance and capacitance of the sample, an a.c. signal of 500 mV<sub>rms</sub> being applied across each sample.

## 3. Results and discussion

### 3.1. D.c. measurements

The electrical conductivities of ternary  $(\text{P}_2\text{O}_5)_{50-x}\text{-(CuO)}_{50-x}\text{-(Pr}_6\text{O}_{11})_x$ ,  $(\text{P}_2\text{O}_5)_{65-x}\text{-(CuO)}_{35-x}\text{-(Pr}_6\text{O}_{11})_x$ , and quaternary  $(\text{P}_2\text{O}_5)_{65-x}\text{-(CuO)}_{25-x}\text{-(CaO)}_{10-x}\text{-(Pr}_6\text{O}_{11})_x$  glasses where  $x$  varied from 0 to 5, were measured over the temperature range 293 K to 593 K up to fields of about  $10^4$  V cm<sup>-1</sup>. Ohmic behaviour at low voltages was ascertained from the linearity of the  $V$ - $I$  curves. Figs 1 and 2 show typical  $V$ - $I$  curves for some samples. The d.c. conductivity,  $\sigma$ , is well represented at the higher temperatures by the expression

$$\sigma = \sigma_0 e^{-W/kT} \quad (1)$$

where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\sigma_0$  is a constant and  $W$  is the activation energy. Figs 3, 4 and 5 show plots of conductivity against  $1000/T$  for some of these glass samples. The activation energies were calculated from the slopes of  $\log \sigma$  against  $1000/T$  plots at high temperature. The conductivity was found to decrease for glasses having the higher activation energies. This is consistent with Equation 1 and in agreement with the available results of Moridi and Hogarth [11], Hogarth and Popov [12] and Sayer and Mansingh [9]. Table I shows the results obtained.

The conductivity decreases and activation energy increases in the praseodymium copper phosphate glasses as CuO is replaced by  $\text{Pr}_6\text{O}_{11}$  or as CaO is replaced by  $\text{Pr}_6\text{O}_{11}$  in praseodymium calcium copper phosphate glasses as shown in Fig. 6. Our results

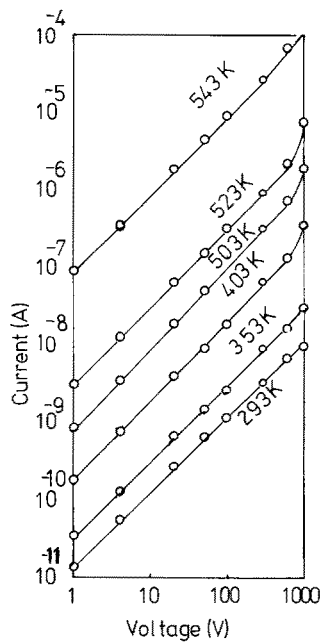


Figure 1 Current as a function of voltage for a  $P_2O_5-CuO-Pr_6O_{11}$  glass sample 1 at different temperatures.

agreed with those reported by Komiyama [13], that conductivity decreases with the increase of rare earth oxide content in glass.

Figs 3, 4 and 5 show that the conductivity depends on rise in temperature. If this is taken as evidence of polaronic conduction in these glass samples the polaron model predicts that an appreciable departure from a linear  $\log \sigma$  against  $1000/T$  plot should occur below a temperature of  $\frac{1}{2}\theta_D$ , where the Debye temperature,  $\theta_D$ , is given by  $\hbar\omega_0 = k\theta_D$ ,  $\omega_0$  being the phonon frequency. The departure from linearity is at temperatures in the range 540 to 450 K which suggests that  $\theta_D$  may lie between 900 and 1000 K for these glasses, depending on the glass composition.

In the low-temperature range ( $T < \frac{1}{4}\theta_D$ ), charge carrier transport should be an acoustical phonon-assisted hopping process having an activation energy  $\sim W_D$ , whereas in the high temperature range

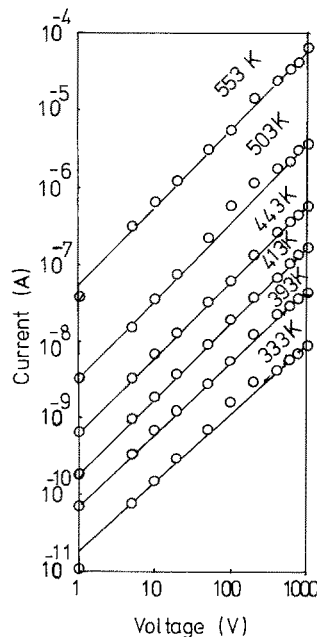


Figure 2 Current as a function of voltage for a  $P_2O_5-CuO-Pr_6O_{11}$  glass sample 2 at different temperatures.

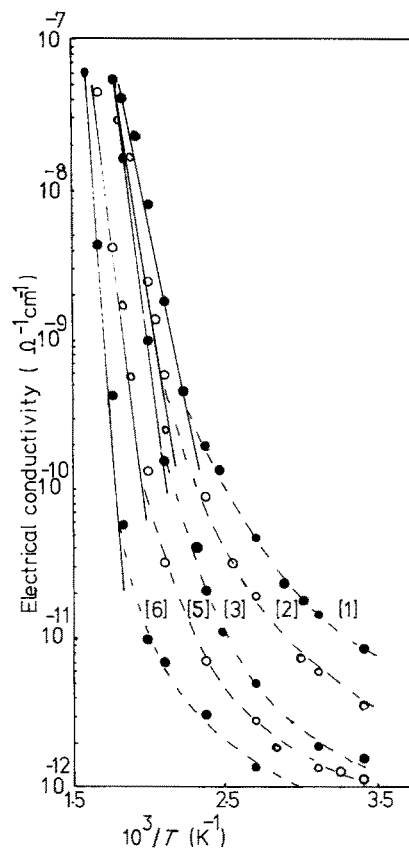


Figure 3 Electrical conductivity as a function of inverse temperature for praseodymium copper phosphate glass samples annealed at  $400^\circ C$ .

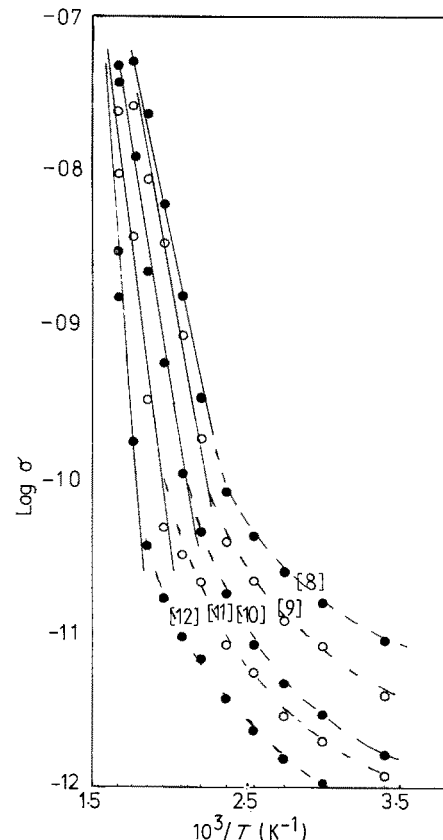


Figure 4 Electrical conductivity as a function of the reciprocal of temperature for a series of praseodymium copper phosphate glass samples annealed at  $400^\circ C$ .

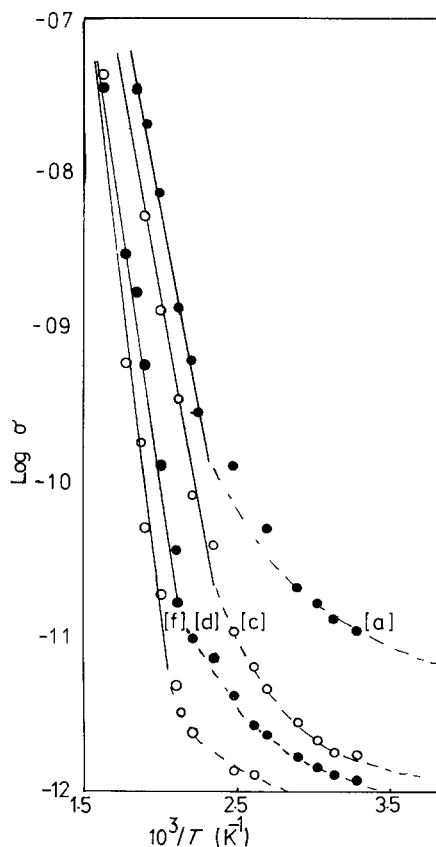


Figure 5 Electrical conductivity as a function of inverse temperature for praseodymium-calcium-copper-phosphate glass samples annealed at 400°C.

$T > \frac{1}{2}\theta_D$ , an optical multiphonon process takes place and the activation energy should be  $(W_H + \frac{1}{2}W_D)$ , where  $W_H$  is the hopping energy and  $W_D$  is the energy difference between localized states arising from the disorder.

Many authors [2, 9, 14] including Bogomolov *et al.* [15], have made the assumption that the small polaron radius,  $r_p$ , can be calculated from the relation  $r_p = \frac{1}{2}(\pi/6N)^{1/3}$ , where  $N$  is the concentration of praseodymium ions in the glass. The total praseodymium ion

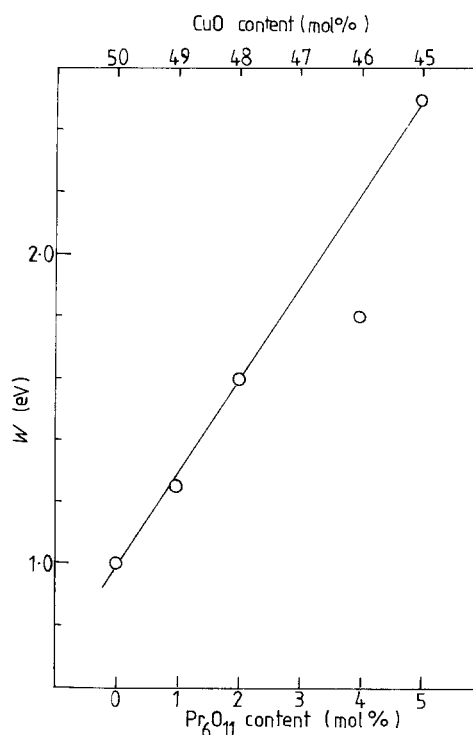


Figure 6 D.c. conductivity activation energy as a function of  $\text{Pr}_6\text{O}_{11}$  content.

concentration was estimated using the Nester and Kingery [16] relation

$$N = \frac{\rho_g P_r N_A}{AW} \times 100$$

where  $\rho_g$  is the glass density,  $N_A$  is Avogadro's number,  $AW$  is the atomic weight of praseodymium (in g), and  $P_r$  is the weight per cent of praseodymium in the glass matrix. The average Pr-Pr spacing in the glasses was calculated as

$$R = (1/N)^{1/3}$$

Table I shows that the values of  $r_p$  and  $R$  are consistent with the presence of a strong electron-phonon

TABLE I Some physical parameters of praseodymium phosphate glasses containing copper and calcium

Glass samples	$x$ (mol %)	$x$ ( $10^{21} \text{ cm}^{-3}$ )	$R$ (nm)	$r_p$ (nm)	Relative density	Pr concentration	$W$ (eV)
$(\text{P}_2\text{O}_5)_{50}-(\text{CuO})_{50-x}-(\text{Pr}_6\text{O}_{11})_x$							
1	0	—	—	—	3.11	0	1.00
2	1	0.97	1.011	0.407	3.21	7.1	1.25
3	2	1.90	0.808	0.326	3.39	13.1	1.60
4	3	2.84	0.706	0.285	3.63	18.3	—
5	4	3.69	0.647	0.261	3.78	22.9	1.80
6	5	4.37	0.612	0.247	3.81	26.9	2.50
$(\text{P}_2\text{O}_5)_{65}-(\text{CuO})_{35-x}-(\text{Pr}_6\text{O}_{11})_x$							
7	0	—	—	—	2.95	0	1.11
8	1	0.85	1.056	0.425	3.06	6.5	1.00
9	2	1.90	0.807	0.325	3.09	14.7	1.25
10	3	3.00	0.693	0.280	3.23	17.1	1.62
11	4	3.03	0.691	0.279	3.31	21.4	1.81
12	5	3.77	0.643	0.259	3.49	25.3	2.50
$(\text{P}_2\text{O}_5)_{65}-(\text{CuO})_{25-x}-(\text{CaO})_{10-x}-(\text{Pr}_6\text{O}_{11})_x$							
a	0	—	—	—	2.79	0	1.00
b	1	0.86	1.066	0.429	2.93	6.6	—
c	2	1.57	0.860	0.347	2.98	12.3	1.05
d	3	2.28	0.760	0.306	3.09	17.3	1.33
f	5	6.37	0.539	0.217	3.24	46.0	1.67

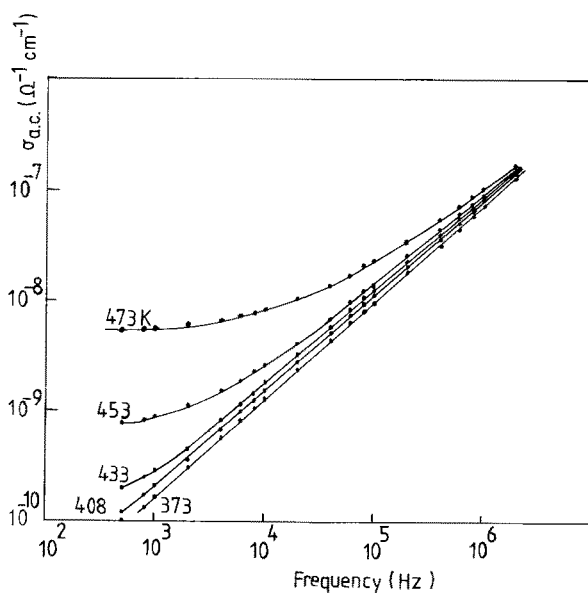


Figure 7 Variation of a.c. conductivity with frequency for a  $P_2O_5$ - $CuO$ - $Pr_6O_{11}$  glass sample (no. 3 in Table II) at five different temperatures.

interaction and the formation of small polarons in these glasses.

### 3.2. A.c. measurements

The a.c. conductivity of all the samples investigated increases with frequency. A typical result for 49 mol %  $CuO$ -50 mol %  $P_2O_5$ -1 mol %  $Pr_6O_{11}$  is shown in Figs 7 and 8, where  $\log \sigma$  against  $1/T$  is plotted for frequencies up to 4 MHz. In general, the main feature of such a.c. measurements is that the observed frequency dependence in the measured range can be expressed as  $\sigma_{a.c.} = \sigma_{tot} - \sigma_{d.c.} = A\omega^s$  where  $A$  is a constant which increases slightly with temperature, and  $0.5 < s < 1.0$ . This observation is similar to those reported by Lynch and Sayer [17] for vanadium phosphate glasses and by Mansingh *et al.* [18] for tungsten trioxide films. This type of behaviour is well known in amorphous systems and has been attributed to the distribution of relaxation times arising from the disorder [19].

Fig. 9 shows a linear decrease in the capacitance with increasing frequency and this could be associated with the increasing leakage current with frequency. It

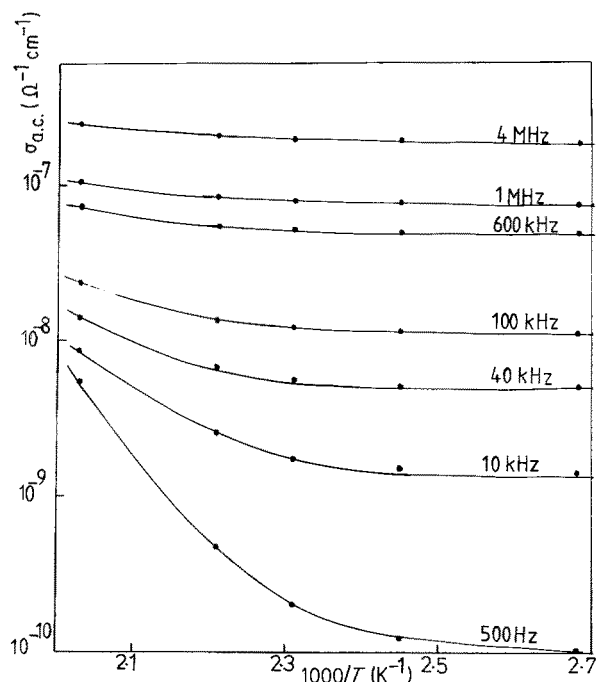
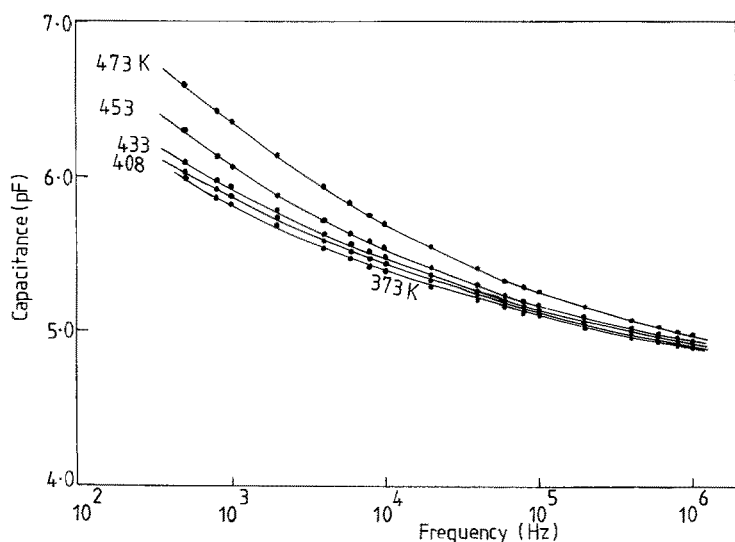


Figure 8 A.c. conductivity as a function of inverse temperature at different frequencies.

is found that the capacitance generally increased with temperature as shown in Fig. 10.

There are many theoretical treatments of the frequency dependence of conductivity given among others, by Mott [20], Austin and Mott [21], Davis and Mott [22] and Elliott [10]. At frequencies less than 1 MHz, the conductivity obeyed the power law which was interpreted by Mott and Davis [23] in terms of hopping of carriers between pairs of isolated sites close to the Fermi level and with a random distribution of separation distances  $R$ . The carriers involved are not necessarily electrons but may well be polarons as suggested by Moridi and Hogarth [24] following studies of d.c. conduction, and as discussed earlier in Section 3.

According to Elliott's [10] model (hopping over a potential barrier), the index  $s$  can be evaluated by use of the expression

$$s = 1 - \frac{6kT}{W_m} \quad (2)$$

where  $W_m$  is taken as the band gap.

Figure 9 Variation of capacitance with frequency for the sample in Fig. 7, at different temperatures.

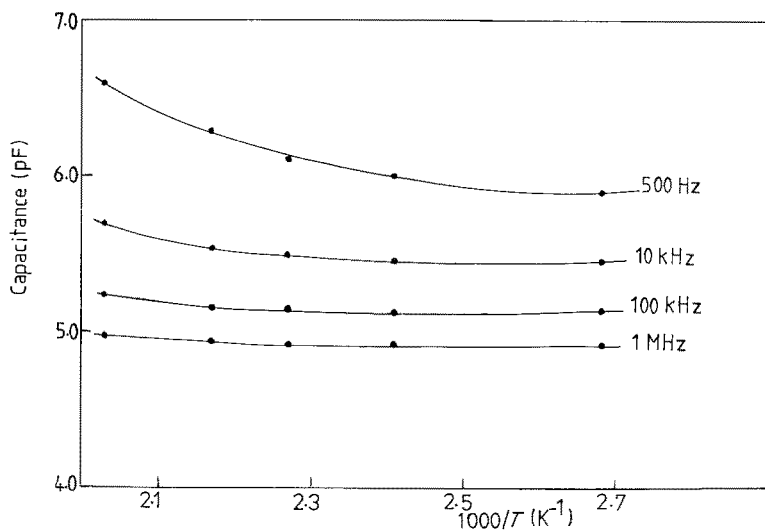


Figure 10 Temperature variation of capacitance for the sample in Fig. 7 measured at different frequencies.

TABLE II The measured and calculated values of the index  $s$  for some glass compositions

Glass compositions (mol %)	$s$ (measured)*	$s$ (calculated)	
		Equation 2	Equation 5
$(P_2O_5)_{65}-(CuO)_{32}-(Pr_6O_{11})_3$	0.92	0.96	0.97
$(P_2O_5)_{65}-(CuO)_{34}-(Pr_6O_{11})_1$	0.93	0.96	0.95
$(P_2O_5)_{50}-(CuO)_{49}-(Pr_6O_{11})_1$	0.88	0.96	0.96

\*Varies with temperature

Dyre [25] applied a phenomenological model for the Meyer-Neldel rule and predicted that

$$\sigma(\omega) = \sigma(\theta) \frac{i\omega\tau}{\ln(1 + i\omega\tau)} \quad (3)$$

where  $\tau$  is the relaxation time between hops and this formula implies an a.c. conductivity which is very close to a power law  $\sim \omega^s$  where  $s$  at low temperature is given by Dyre [26]

$$s = 1 - (T/T_1) \quad (4)$$

As we take  $kT_1 = \frac{1}{2}\Delta E$ , where  $\Delta E$  is the d.c. conductivity activation energy, then we may write

$$s = 1 - \frac{2kT}{\Delta E} \quad (5)$$

Table II shows the measured and calculated values of  $s$  according to Equations 2 and 5 with fair agreement between theory and experiment.

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