Electrical conduction in copper phosphate glasses containing nickel or cobalt

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A variation in d.c. conductivity and activation energy of 35 mol % CuO – 65 mol % P_2O_5 glasses is observed as CuO is gradually replaced by NiO or CoO. These results are believed to be due to the change in the redox ratio of the two transition metal oxide glasses, which causes an increase and then a decrease of polaron hopping transitions between the ions of the same element and between the ions of the different transition metal elements.

1. Introduction

The electronic conductivity of oxide glasses containing transition metals is governed by the presence of transition metals (TM) in the glass in two different valency states. The conductivity in these glasses arises through electron transfer from a lower to a higher valency state ion.

Many recent investigations have been reported concerning oxide glasses containing two TM oxides simultaneously [1–10]. Sayer and Lynch [3], Caley and Murthy [4], Bogomolova et al. [5] and Chomka et al. [6] all reported an initial decrease and then an increase in conductivity, whereas Bogomolova and Glassova [8] and Singh [9] reported an initial increase and then a decrease in conductivity, when one TM oxide is replaced by other TM oxides in glasses. They have suggested [4, 6, 7, 9] that the increase of conductivity may be due to the hopping of electrons between TM ions of the different elements in addition to the hopping of electrons between TM ions of the same element. The decrease in electrical conductivity was suggested as due to the decrease of the redox ratio [4] and also to the possible formation of bridge bonds composed of one ion from each TM ion with one oxygen ligand, as a result of which hopping is inhibited.

More recently Bruckner [10] reported that the electrical transport properties in mixed TM oxide glasses are closely connected with redox shifts. For double redox pairs there exists a mutual interaction, exclusively during cooling. So the increasing or decreasing of conductivity by partial substitution of one redox pair by another can be observed and will depend widely on the redox of the starting situation and on the efficiency of the dominant type of hopping process of the two redox pairs.

In our electron spin resonance (ESR) results [1] for copper phosphate glasses containing nickel or cobalt, it was suggested that the reduction in the intensity of the ESR signal of the Cu^{2+} ions may be due to an oxidation-reduction mechanism between two valency states of the two different transition metals. In the present work we report the electrical conductivity of the same glasses.

2. Experimental work

Copper phosphate glasses containing nickel or cobalt were prepared as described by Harani et al. [1]. For electrical measurements annealed samples were ground and then polished using conventional abrasives. Gold electrodes were evaporated in a guard-ring configuration. The measurements were conducted using a Keithley 240 high voltage supply and Keithley 610 electrometer. All measurements were made under a vacuum of $\approx 10^{-5}$ torr. The density of the samples was determined by the displacement method.

3. Results and discussion

The density of CuO–P_2O_5 glasses increases when CuO is gradually replaced by NiO, whereas the density decreases when CuO is replaced by CoO, as shown in Table I. Figs 1 and 2 show the density as a function of NiO and CuO contents, respectively. The values of the density of binary CuO–P_2O_5 and CoO–P_2O_5 glasses are in agreement with the results of Sayer and Mansingh [11]. The change in density is probably due to the different molecular weights of NiO and CoO compared with CuO. The fact that it is much easier to make these glasses with a high cobalt content and a low copper content than to prepare glasses with a high nickel content and a low copper content suggests that the bonding of cobalt and nickel is of different character. It may be that the bonding of cobalt involves some element of covalency, whereas the bonding of nickel may be totally ionic. The d.c. conductivities of binary CuO–P_2O_5 and CoO–P_2O_5, and ternary CuO–NiO–P_2O_5 and CuO–CoO–P_2O_5 glasses of the compositions listed in Table I were measured over the temperature range 293 to 573 K. Ohmic behaviour was ascertained from the linearity of the V–I curves. Semilogarithmic plots of conductivity against inverse temperature for the glasses are shown in Figs 3, 4 and 5. The conductivity σ varies very slowly with temperature below 450 K and displays no single activation energy, whereas above 450 K the conductivity behaviour seems to be quite consistent and shows a smooth variation with inverse temperature. The activation energies were calculated from the slopes of log σ against $1/T$ plots. The plots show that the magnitude

Glass sample	P_2O_5 (mol %)	CuO (mol %)	NiO (mol %)	CoO (mol %)	Relative density	Conductivity at 500 K $(\Omega^{-1}cm^{-1})$	Activation energy, W(eV)
a	65	35	—	—	3.03_0	1.3×10^{-10}	1.11
b	65	34	1	—	3.04_2	4.6×10^{-11}	1.18
c	65	33	2	—	3.03_8	—	—
d	65	32	3	—	3.05_0	2.85×10^{-11}	1.22
e	65	31	4	—	3.05_7	—	—
f	65	30	5	—	3.06_1	7.8×10^{-12}	1.32
g	65	25	10	—	3.07_3	2.0×10^{-11}	1.25
h	65	20	15	—	3.08_1	4.0×10^{-12}	1.30
i	65	15	20	—	3.09_5	1.6×10^{-12}	1.32
Co I	65	34	—	1	3.01_8	2.05×10^{-11}	1.28
Co II	65	33	—	2	3.01_5	—	—
Co III	65	32	—	3	3.00_0	—	—
Co IV	65	31	—	4	2.99_0	—	—
Co V	65	30	—	5	2.97_5	2.45×10^{-11}	1.32
Co X	65	25	—	10	2.98_0	1.35×10^{-11}	1.31
Co XV	65	20	—	15	2.96_5	7.6×10^{-12}	1.28
Co XXX	65	15	—	20	2.95_0	7.0×10^{12}	1.28
Co XXX	65	5	—	30	2.94_2	1.7×10^{-11}	1.21
Co XXXV	65	—	—	35	2.92_0	1.43×10^{-11}	1.22

of the conductivity becomes smallest in the glasses having the highest thermal activation energy. This is consistent with the general formula of Mott [12] and agrees with the previous results of Moridi et al. [13], Sayer and Mansingh [11] and Hogarth and Jamel Basha [14].

The conductivity decreases and activation energy increases in the $CuO-P_2O_5$ glass as CuO is gradually replaced by NiO or CoO up to 5 mol %. At 10 mol % of NiO or CoO the conductivity increases and the activation energy decreases to a small value, and then the trend is reversed with further increase of NiO or CoO. When CoO is replaced by CuO in binary cobalt phosphate glass, the conductivity increases and activation energy decreases at 5 mol %, and at 15 mol % CuO the trend is again reversed. The value of activation energy of binary $CuO-P_2O_5$ and $CoO-P_2O_5$ are in agreement with the results of Sayer and Mansingh [11]. The temperature dependence of conductivity shown in Figs 3, 4 and 5 is consistent with a polaron model for conduction in all the glasses. The polaron model predicts that an appreciable departure from a linear log σ against $1/T$ plot should occur below a temperature of $1/2\theta_D$, where the Debye

temperature θ_D is given by $\hbar\omega_0 = k\theta_D$, ω_0 being the phonon frequency and k the Boltzmann constant. The departure from linearity is at a temperature of about 450 K, which suggests that $1/2\theta_D$ may be of the order of 450 K in these glasses.

In order to check the type of conduction for these glasses, the resistances were measured at room temperature and above 450 K by applying a constant voltage of 300 V for 6 h. The graphic representations of resistance against time for some of the glasses are shown in Figs 6 and 7. The resistances were found to be constant with time, when measured above 450 K, but at room temperature there is a short-term initial variation with time; otherwise the resistance is constant over an extended period of time. This could be taken as evidence that there is no measurable polarization effect and that these glasses behave essentially as electronic conductors.

A change in conductivity and activation energy can be explained when CuO is replaced by NiO or CoO. In the case of NiO-doped glasses, a 1 mol % addition of NiO reduces the conductivity by one order of
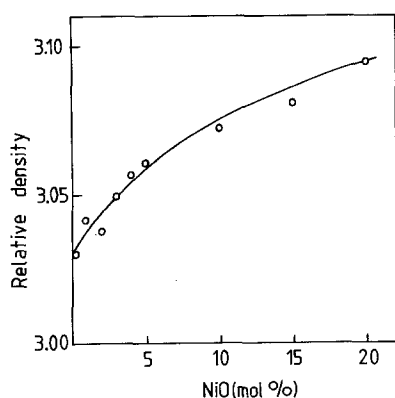

Figure 1 Relative density of copper–nickel–phosphate glasses as a function of NiO content.
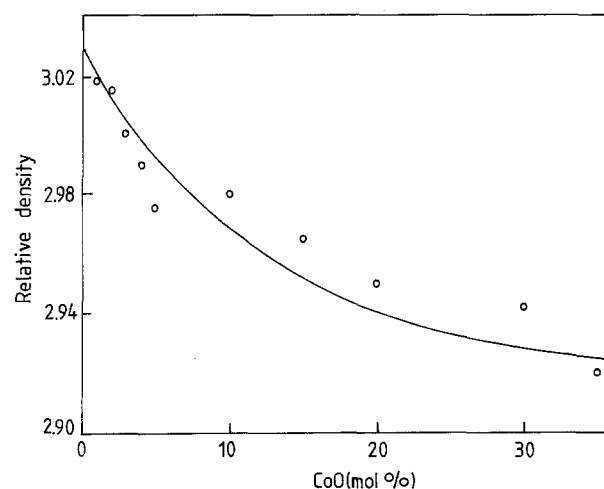

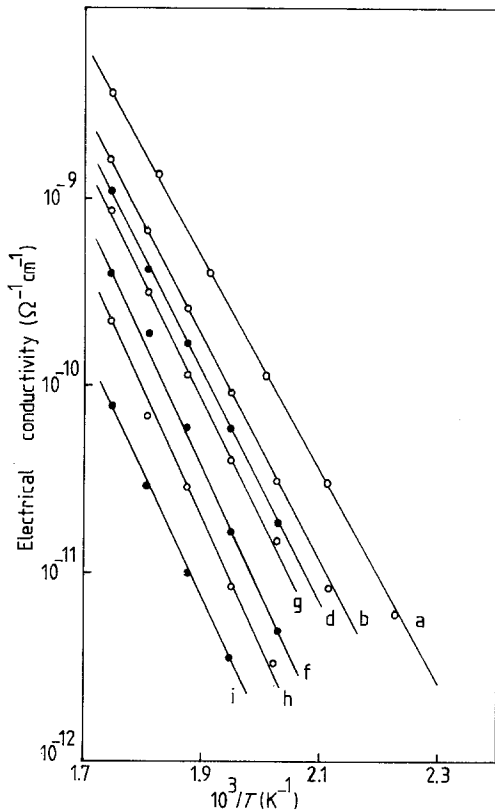Figure 2 Relative density of copper–cobalt–phosphate glasses as a function of CoO content.

Figure 3 Electrical conductivity as a function of inverse temperature for copper–phosphate and copper–nickel–phosphate glasses (notation as in Table I).
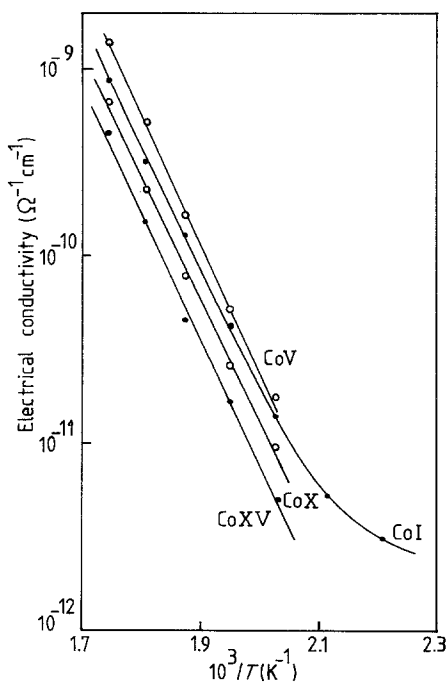

Figure 4 Electrical conductivity as a function of inverse temperature for some copper–cobalt–phosphate glasses (notation as in Table I).
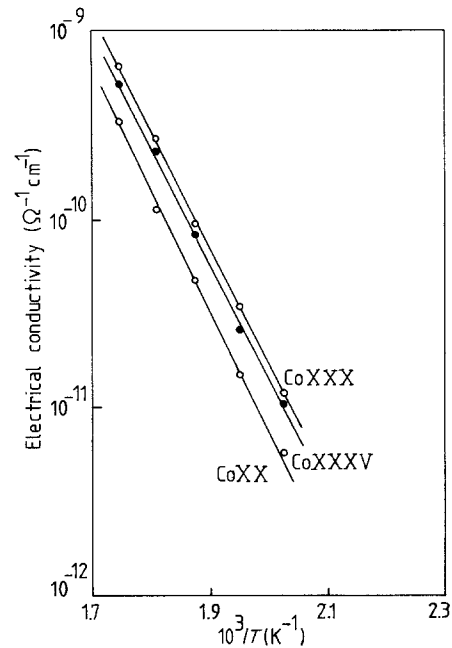

Figure 5 Electrical conductivity as a function of inverse temperature for some copper–cobalt–phosphate glasses (notation as in Table I).

Figure 6 Resistance as a function of time for some copper–nickel–phosphate glasses. Notation as in Table I; RT = room temperature.

magnitude and this continues to decrease slowly up to 5 mol % of NiO. The introduction of NiO into the copper phosphate glasses decreases the concentration of Cu^{2+} ions as reported earlier [1]. The drop in the electrical conductivity may be due to the increasing number of $Ni^+ \rightarrow Ni^{2+}$, $Cu^{2+} \rightarrow Ni^+$ and $Cu^+ \rightarrow Ni^{2+}$ transitions which cannot compensate for the drop of conductivity which is due to the decreasing number of $Cu^+ \rightarrow Cu^{2+}$ transitions. The increase in conductivity (which does not reach the initial value of

binary $CuO–P_2O_5$ glass) at 10 mol % of NiO may be due to the increasing number of hopping processes which take place not only as $Cu^+ \rightarrow Cu^{2+}$ and $Ni^+ \rightarrow Ni^{2+}$, but also between centres $Cu^{2+} \rightarrow Ni^+$ and $Cu^+ \rightarrow Ni^{2+}$. The existence of hopping between TM ions of different elements has been suggested by the results of studies of internal friction [6]. Again a decrease in conductivity can be explained if there is a possibility of formation of associates composed of one ion from each TM ion with one oxygen ligand, i.e. Cu–O–Ni, as a result of which hopping is inhibited.

Similarly, when CuO is replaced by CoO the decrease in conductivity may be due to the increasing number of $Co^+ \rightarrow Co^{2+}$, $Cu^+ \rightarrow Co^{2+}$ and $Co^+ \rightarrow Cu^{2+}$ transitions which cannot compensate for the decreasing number of $Cu^+ \rightarrow Cu^{2+}$ transitions. Our ESR results [1] show that the Cu^{2+} ion concentration decreases with the increase of CoO content. Nevertheless a small increase in conductivity at 10 mol % CoO may be due to the increase in transitions between sites
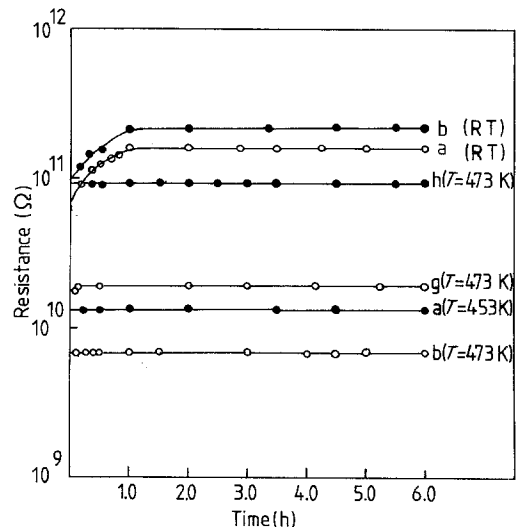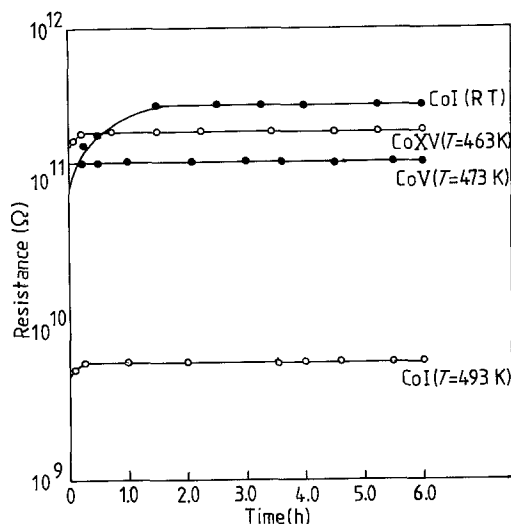
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Figure 7 Resistance as a function of time for some copper–cobalt–phosphate glasses. Notation as in Table I; RT = room temperature.

of different TM oxides (i.e. $Cu^+ \rightarrow Co^{2+}$ and $Cu^{2+} \rightarrow Co^+$) together with the transitions between sites of the same TM ions (i.e. $Cu^+ \rightarrow Cu^{2+}$ and $Co^+ \rightarrow Co^{2+}$). Any further decrease in conductivity may be due to the formation of bridge bonds Cu–O–Co as a result of which hopping is inhibited.

In binary cobalt phosphate glass (Co XXXV, Table I) when 5 mol % of CoO is replaced by CuO, the conductivity increases and this can be explained in terms of the total hopping which takes place between TM ions of the different elements, and the hopping between the ions of the same TM element must be greater than the transition in binary cobalt phosphate glass as $Co^+ \rightarrow Co^{2+}$.

The variation of conductivity in glasses containing mixed TM oxides may be closely related with a change in the redox ratio and the possible formation of bridge-bonds composed of one ion from each TM ion with one oxygen ligand when the content of two TM oxides approaches the same value in the glass. As reported by

Bruckner [10], when one TM oxide is replaced by another an increase or decrease in conductivity can be obtained, depending widely on the redox ratio of the starting material and on the effeciency of the dominant type of hopping process of the two redox pairs of the TM oxides.

Acknowledgement

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