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A study of electron spin resonance of copper phosphate glasses containing tellurium oxide

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Electron paramagnetic resonance in glasses of compositions $(P_2O_5)_{100-x}$–$(CuO)_x$ and $(P_2O_5)_{50}$–$(TeO_2)_{50-x}$–$(CuO)_x$ where x varied from 20 to 40 mol% has been investigated. The distribution of the copper between the two main valency states is determined from measurements of e.s.r. arising from the Cu^{2+} centres. The study of e.s.r. enables the distribution of copper in the glasses between the different valency states to be determined and thus indirectly provides evidence for hopping conduction in the glasses. From the results of e.s.r. and the chemical analysis of the samples it is found that the reduced valency ratio C, i.e. the ratio of the concentration of Cu^+ ions to that of total copper in the glass, increases with increasing CuO content.

1. Introduction

Transition-metal ions characterized by a partially filled d shell can frequently exist in a number of oxidation states and electronic conduction can occur as a result of electron transfer from ions in a lower oxidation state to those in a higher oxidation state.

The relative proportion of transition-metal ions in the different oxidation states has been an important parameter in explaining this electronic conduction in oxide glasses. Landsberger and Bray [1] were the first to use the technique of e.s.r. for determining the $[V^{4+}/V^{5+}]$ ratio in P_2O_5–V_2O_5 glasses. The spin concentration can be determined by double integration of the e.s.r. spectra and comparison with a Varian standard spin sample.

ESR spectra of transition-metal ions in phosphate glasses have been reported by Sayer and Mansingh [2] where strong signals were observed from vanadium, molybdenum and copper oxide glasses with weaker signals being observed from tungsten and some iron glasses.

2. Experimental work

Two different series of CuO–P_2O_5 and CuO–P_2O_5–TeO_2 glasses were prepared. The appropriate amounts of oxides were weighed and mixed together in alumina crucibles using an alumina rod, and then transferred to an electrically heated furnace in an atmosphere of air kept at 1100° C for CuO–P_2O_5 glasses [3] and 900 to 1000° C for CuO–P_2O_5–TeO_2 glasses. The homogenized melts were then cast on to a steel plate mould and allowed to cool in the atmosphere. All samples were stored in a desiccator to avoid absorption of water from the atmosphere.

3. Electron spin resonance measurements

The e.s.r. spectra were recorded on a Varian E.3 e.s.r. spectrometer working at X-band (9.5 GHz), using standard Varian accessories. The glasses were finely powdered and placed in 3 mm silica sample tubes, packed to a constant length of sample and individually weighed. All settings of the instruments were maintained constant throughout the investigation with the exception of the gain level which was varied according to need with individual samples.

Crystalline copper sulphate was used as a standard for comparison and made possible estimates of the absolute cupric ion spin concentration in the samples. Total copper was determined by standard wet chemical analysis.

4. Results and discussion

The glasses investigated were those of initial composition $(P_2O_5)_{100-x}$–$(CuO)_x$ and $(P_2O_5)_{50}$–$(TeO_2)_{50-x}$–$(CuO)_x$ where x varied from 20 to 40 mol %. The glass samples gave strong e.s.r. lines of Lorentzian shape as

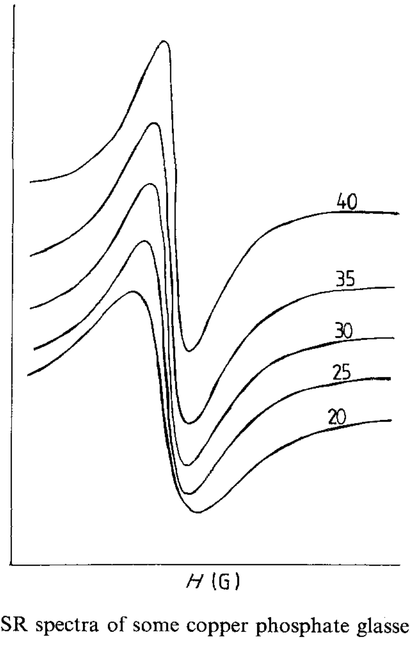

Figure 1 ESR spectra of some copper phosphate glasses.

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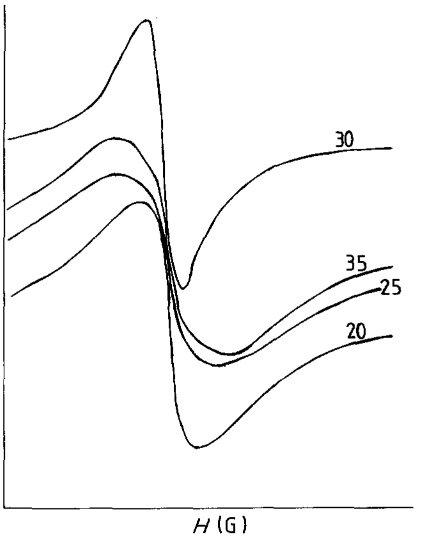

Figure 2 ESR spectra of some copper phosphate glasses containing tellurium.

shown in Figs 1 and 2. No copper hyperfine structure was observable at the concentration of copper used in the glasses and the line shapes agreed with those reported by other workers [4, 5, 6].

For the binary glass system, Fig. 3 shows the variation of both total copper and Cu^{2+} concentration with CuO content for a number of glass samples. For low concentrations of copper, most copper is accommodated in the form of Cu^{2+} ions, but for the higher concentrations of CuO, increased reduction of the copper ions occurs and the Cu^{2+} concentration tends to saturate. On the other hand by replacing TeO_2 by CuO and keeping the content of P_2O_5 constant, the increased CuO content increased both the strength of the e.s.r. signal and the derived spin density as shown in Fig. 4. The increase is associated with the distribution of paramagnetic species in the glass matrix.

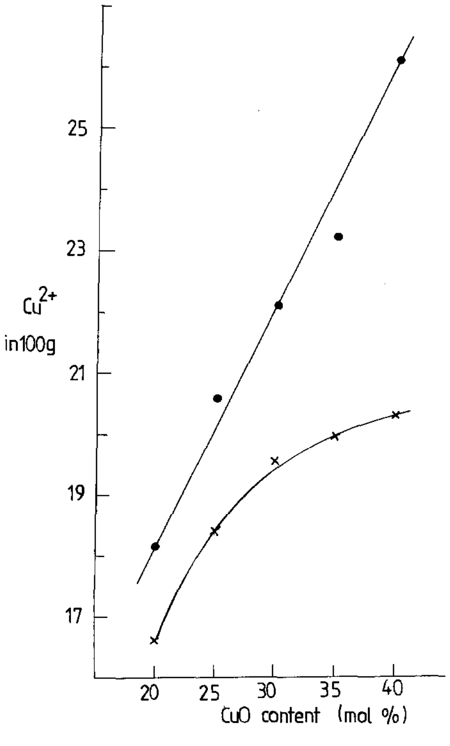

Figure 3 Variation of Cu^{2+} ion concentration (×) determined by ESR with increasing CuO content (●) in a copper phosphate glass.

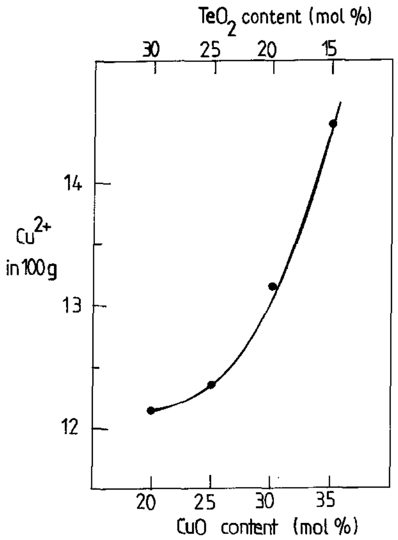

Figure 4 Variation of Cu^{2+} ion concentration determined by ESR with increasing CuO content in a copper phosphate glass containing tellurium.

Variations of the ratio of reduced valency state ion density to that of total copper $C = [Cu^+]/[Cu_{total}]$ with transition-metal oxide concentration are shown in Figs 5 and 6. It is clear that the fraction of the reduced valency states increases with increasing transition-metal oxide content and that the existence of two different oxidation states of copper necessary to support the hopping mechanism of electronic conduction is substantiated. Tables I and II show the derived reduced valency states and the amount of Cu^{2+} in the two systems. Moridi and Hogarth [4] were the first to study e.s.r. in copper phosphate and copper–calcium phosphate glasses and were able to show that the relative concentration of monovalent ions increased as the concentration of CuO in the glass samples increased, certainly upto 35 mol % CuO in the glass. Khawaja and colleagues [7] demonstrated for copper sodium phosphate glasses that the sodium additive in these glasses alters the ratio of concentrations of Cu^+ and Cu^{2+} ions. Bogomolova and co-workers [8, 9] studied V_2O_5–P_2O_5 glasses doped with copper oxide

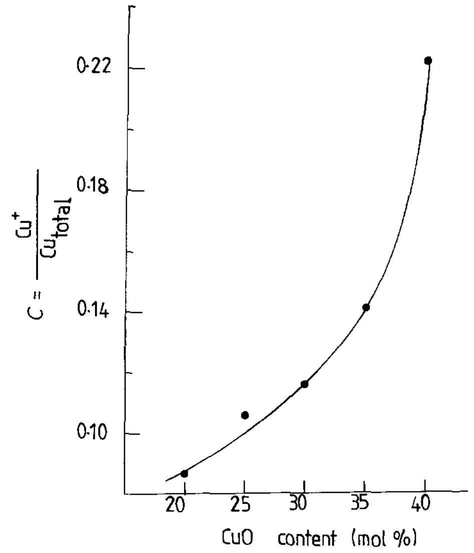

Figure 5 The relationship between CuO content and reduced valency ratio C for a copper phosphate glass.

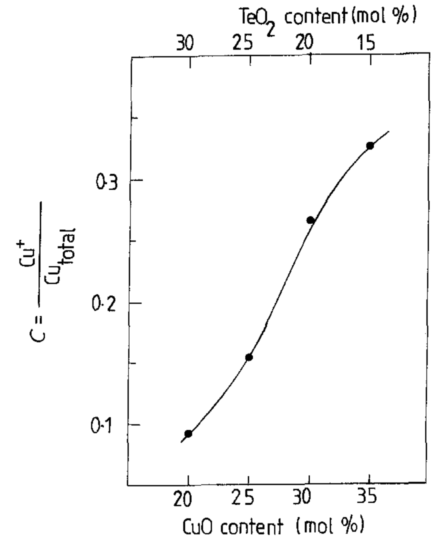

Figure 6 The relationship between CuO content and reduced valency ratio *C* for a copper phosphate glass containing tellurium.

and also investigated the effect of Co^+ on the e.s.r. spectra of Cu^{2+}, V^{4+}, Mn^{2+} and W^{5+} ions in different glassy media, explaining the results in terms of cross-relaxation processes between the two spin systems and also by spin diffusion. It has been reported by Hogarth and Popov [10] that a maximum in the electrical conductivity of CuO–$CuCl_2$–P_2O_5 glasses is observed for samples in which the concentration $[Cu^+]$ and $[Cu^{2+}]$ are of the same order of magnitude and that this ratio can be modified by the incorporation of chlorine in the glass. Similar results have been reported by Kutub and colleagues [11] on the V_2O_5–VCl_3 system. Harani and co-workers [5] concluded that the loss of Cu^{2+} signal in phosphate glasses containing CuO and NiO and also CuO and CoO is due to an oxidation reduction mechanism between two valency states of the two different transition elements of the following type.

$$Cu^{2+} + Ni^+ \rightleftarrows Cu^+ + Ni^{2+}$$

Electron paramagnetic resonance and optical spectra of Cu^{2+} ions doped into polymorphic TeO_2 have been investigated by Siegel and Jones [12]. They found that the Cu^{2+} ions were more covalently bonded in the TeO_2 glass than in the TeO_2 crystal, and less covalently bonded in both forms of TeO_2 than in the corresponding GeO_2 polymorphs. Ardelean and co-workers [13] studied e.s.r. and magnetic properties of XCuO. $(1 - X)[19TeO_2 \cdot PbO]$ glasses. They concluded that the properties are a function of the CuO content and for $X \geqslant 10$ mol % CuO, antiferromagnetic behaviour is observed. The antiferromagnetic coupling takes place between Cu^{2+} ions situated in axially distorted octahedral co-ordinations, which are randomly distributed in the glass matrix. Sunandana and Bhatnagar [14] examined the e.s.r. of the binary semiconducting glasses 55 mol % V_2O_5–45 mol % MO_2 (M = Ge, Se, Te) in the temperature range 298 to 498 K. They showed that the covalency of the V–O bonds increases in the order $SeO_2 < TeO_2 < GeO_2$ and the electronic conduction in these glasses involves a thermally activated hopping of $3d^1$ electrons of V^{4+} by way of a progressive delocalization over several vanadium nuclei.

TABLE I Reduced valency states results from chemical analysis and ESR for copper phosphate glasses

CuO content (mol %)	Total Cu in 100 g of glass (g)*	Cu^{2+} in 100 g of glass (g)†	Cu^+ in 100 g of glass (g)	$C = Cu^+/Cu_{tot}$
20	18.2	16.62	1.58	0.087
25	20.60	18.41	2.19	0.106
30	22.10	19.54	2.56	0.116
35	23.20	19.93	3.27	0.141
40	26.10	20.30	5.80	0.222

*From wet chemical analysis.
†From e.s.r. measurements.

TABLE II Reduced valency states results from chemical analysis and ESR for copper phosphate glasses containing tellurium oxide

CuO content (mol %)	Total Cu in 100 g of glass (g)*	Cu^{2+} in 100 g of glass (g)†	Cu^+ in 100 g of glass (g)	$C = Cu^+/Cu_{tot}$
20	13.40	12.16	1.24	0.093
25	14.59	12.35	2.24	0.154
30	17.87	13.15	4.72	0.264
35	21.49	14.48	7.01	0.326
40	25.0	–	–	–

*From wet chemical analysis.
†From e.s.r. measurements.

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