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A study of electron spin resonance in copper–phosphate glasses containing praseodymium

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The e.s.r. spectra of glasses of compositions $(P_2O_5)_{65}(CuO)_{35-x}(Pr_6O_{11})$ and $(P_2O_5)_{65}(CuO)_{25}$-$(CaO)_{10-x}(Pr_6O_{11})_x$, where x varied from 0 to 5 mol %, were measured. From the results and the chemical analyses of the samples it is found that the reduced valency ratio C of the copper in the glasses investigated generally increases with increasing Pr_6O_{11} content. In our samples it is believed that enhanced chemical reduction of the cupric (Cu^{2+}) ion is a consequence of its interaction with a reduced ion of the added praseodymium oxide.

1. Introduction

Transition metal ions and rare-earth (lanthanide) ions characterized by partially filled d and f shells 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 ones 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 electron spin resonance (e.s.r.) in a study of the concentration ratio C = [reduced ion]/[oxidized ion] in P_2O_5–V_2O_5 glasses, finding that the ratio decreased with increasing V_2O_5 content. Lynch *et al.* [2] studied the temperature effect on the concentration ratio $[V^{4+}]/[V^{5+}]$ over the temperature range 77 to 300 K, finding the spin density to be temperature-independent. In addition, Lynch and Sayer [3] studied the effect of added metal oxides on the resonance spectra of tungsten–phosphate glasses, observing strong exchange-coupled effects. Moridi and Hogarth [4] first applied e.s.r. to a study of copper ions in binary phosphate and ternary calcium phosphate glasses, and showed that the relative concentration ratio C of monovalent to divalent copper increased as the copper oxide concentration in the glass was increased. In a study of glass systems containing transition metal oxides and mixed transition metal oxides, Bogomolova *et al.* [5] suggested that different factors could be regarded as contributing to loss of the e.s.r. signal intensity and to signal broadening when a second transition metal oxide was introduced into a glass network.

In this study we have examined the effect of added amounts of rare-earth oxides (up to 5 mol %) upon the ratio C of monovalent copper to divalent copper in copper–phosphate glasses.

2. Experimental procedure

2.1. Preparation of glasses

The appropriate weights of analytical-reagent grades of the oxides were carefully mixed in an alumina crucible and placed in a furnace maintained at 400° C for 1 h. This initial heating served to minimize material volatilization. The crucible was then transferred to a melting furnace maintained at a selected temperature of 1350° C for 3 h with frequent stirring. The homogenized

TABLE I Reduced valency state results from titration and e.s.r. for copper–phosphate glasses containing praseodymium

Glass No.	P_2O_5 content (mol %)	CuO content (mol %)	Pr_6O_{11} content (mol %)	Total Cu in 100 g of glass (g)*	Cu^{2+} in 100 g of glass (g)†	Total Cu in 100 g of glass before melting‡	Cu^+ in 100 g of glass (g)	$C = [Cu^+]/[Cu_{total}]$
7	65	35	0	28.00	20.70	18.52	7.30	0.26
8	65	34	1	16.68	10.01	16.68	6.67	0.40
9	65	33	2	14.44	8.50	15.09	5.91	0.41
10	65	32	3	14.00	7.71	13.77	6.29	0.45
11	65	31	4	13.50	7.39	12.49	6.11	0.45
12	65	30	5	12.35	6.10	11.40	6.25	0.51

*From wet chemical analysis.
†From e.s.r. measurements.
‡From original weighing.

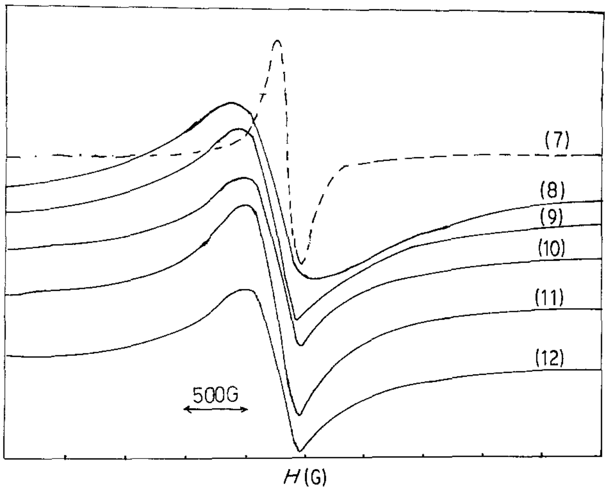

Figure 1 E.s.r. spectra of some copper–phosphate glasses containing praseodymium (Table I). Sample No. 7 is pure $CuO-P_2O_5$ measured at a different gain.

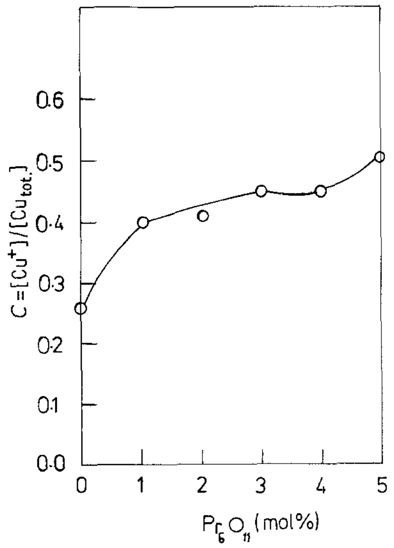

Figure 3 The relationship between Pr_6O_{11} content and reduced valency ratio *C* for a copper–phosphate glass containing praseodymium.

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.

2.2. Electron spin resonance measurements

The e.s.r. spectra were recorded on a Varian E3 e.s.r. spectrometer working in the 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 instrument 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 cupric ion spin concentration determination in the samples. Total copper was determined by standard wet chemical analysis.

3. Results and discussion

The glasses investigated were those of initial composition $(P_2O_5)_{65}(CuO)_{35-x}(Pr_6O_{11})_x$ and $(P_2O_5)_{65}(CuO)_{25}(CaO)_{10-x}(Pr_6O_{11})_x$ where x was varied from 0 to 5 mol %. The spectra obtained are recorded in Figs 1 and 2. No copper hyperfine structure was observable at the concentrations of copper used in the glasses and the line shapes agreed with those reported by other workers [2, 4, 6]. In all cases, the intensity of the copper e.s.r. signal decreased with increased Pr_6O_{11} content; even the use of 1.0 mol % of the rare-earth oxide resulted in significant reduction of the signal.

Plots of the reduced valency ratio *C* for the copper oxidation states (Fig. 3) show a steady increase of *C* with Pr_6O_{11} increase at low concentration of the rare-earth oxide, levelling off at 2 to 3 mol % and then increasing rapidly after 3 mol % up to 5 mol %. These results parallel the observations made on similar systems involving the incorporation of europium(III) oxide, presently being studied by Arzeian [7]. A second set of glasses incorporating the diamagnetic rare-earth oxide Lu_2O_3 and CaO as modifier was also examined. The results plotted in Figs 8 and 9 show a similar trend with regard to the general increase in *C*,

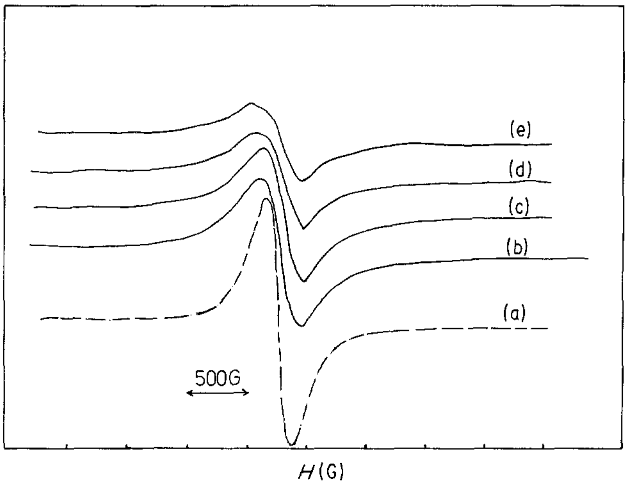

Figure 2 E.s.r. spectra of some copper–phosphate glasses containing calcium and praseodymium (Table II). Sample "a" is pure $CuO-P_2O_5$ measured at a different gain.

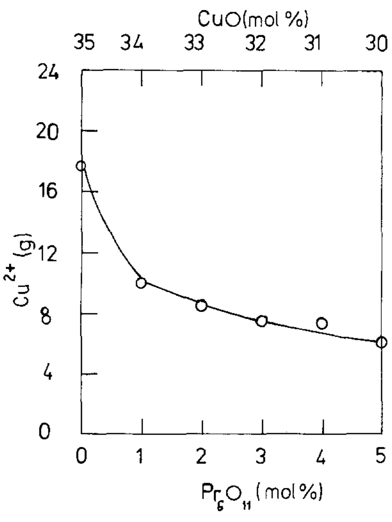

Figure 4 Decrease of Cu^{2+} ion concentration determined by e.s.r. with increasing Pr_6O_{11} content in a copper–phosphate glass containing praseodymium.

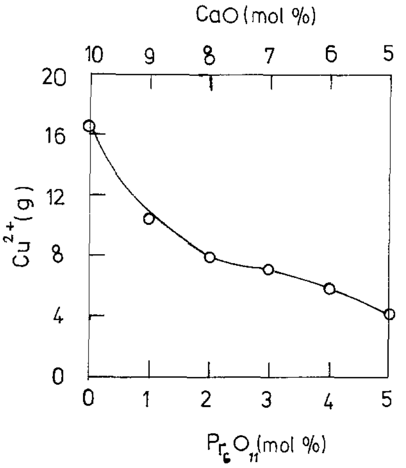

Figure 5 Decrease of Cu^{2+} ion concentration determined by e.s.r. with increasing Pr_6O_{11} content in a copper–phosphate glass containing praseodymium and calcium.

but without the same marked increase above 3 mol % of the rare-earth ion.

Investigations of glass samples annealed at different temperatures in the range 300 to 800° C for periods of 1 h and determination of the copper(II) concentration showed there to be no significant variation of the latter with temperatures up to 500° C, but that at 800° C some change did take place. A similar effect was observed by Moridi and Hogarth [4] in the copper–calcium phosphate glasses and was attributed to changes in the glass ordering which took place at high temperature; this was subsequently confirmed from studies of X-ray diffraction, scanning and transmission electron microscopy, and differential thermal analysis. A study of the effect of melting times on the glasses over a period of 1 to 3 h at constant temperature showed minimal increase in the copper(II) content that is ascribable to losses from the glasses due to volatilization. Low-temperature e.s.r. studies at 77 K on these glass samples indicated the copper concentration to be the same within experimental error, implying that the free carrier concentration in the glass does not vary with temperature and that the average paramagnetic site is unchanged over the temperature range 77 to 300 K. Optical studies of the

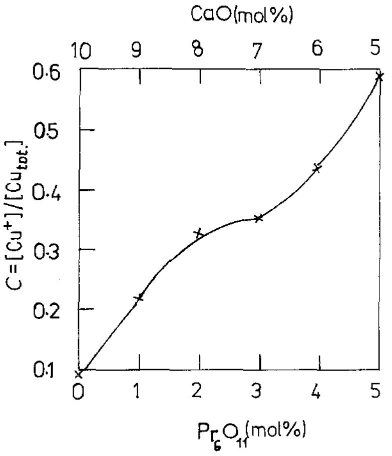

Figure 6 The relation between Pr_6O_{11} content and the reduced valency constant *C* for a copper–phosphate glass containing praseodymium and calcium.

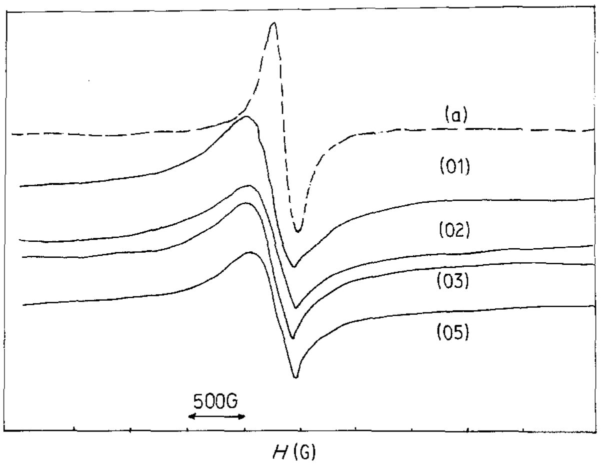

Figure 7 E.s.r. spectra of some copper–phosphate glasses containing lutetium and calcium (Table III).

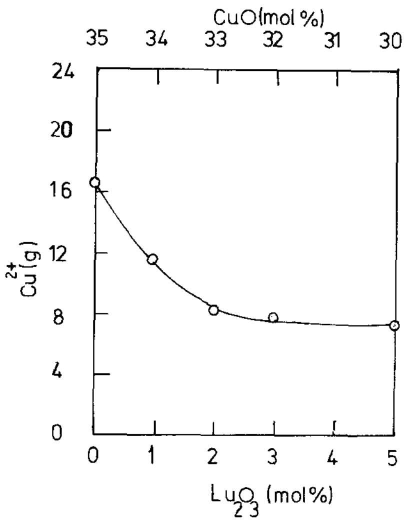

Figure 8 Decrease of Cu^{2+} ion concentration determined by e.s.r. with increasing Lu_2O_3 content in a copper–phosphate glass containing lutetium and calcium.

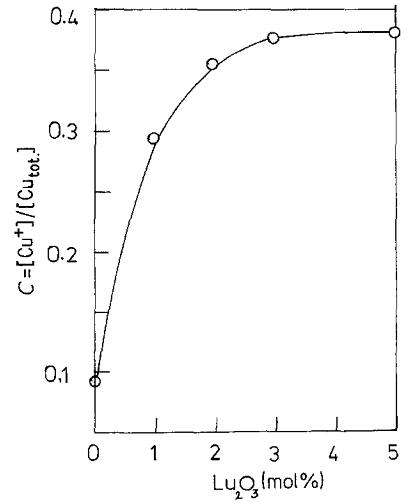

Figure 9 The relation between the Lu_2O_3 content and the reduced valency ratio *C* for a copper–phosphate glass containing lutetium and calcium.

TABLE II Reduced valency state results from titration and e.s.r. for copper–phosphate glasses containing calcium and praseodymium

Glass No.	P_2O_5 content (mol %)	CuO content (mol %)	CaO content (mol %)	Pr_6O_{11} content (mol %)	Total Cu in 100 g of glass (g)*	Cu^{2+} in 100 g of glass (g)†	Total Cu in 100 g of glass before melting‡	Cu^+ in 100 g of glass (g)	$C = [Cu^+]/[Cu_{total}]$
a	65	25	10	0	18.12	16.49	13.49	1.63	0.09
b	65	25	9	1	13.33	10.43	12.47	2.90	0.22
c	65	25	8	2	11.79	7.93	11.59	3.86	0.33
d	65	25	7	3	11.03	7.18	10.83	3.85	0.35
e	65	25	6	4	10.48	5.85	10.16	4.63	0.44
f	65	25	5	5	10.25	4.25	9.57	6.00	0.59

*From wet chemical analysis.
†From e.s.r. measurements.
‡From original weighing.

TABLE III Reduced valency state results from titration and e.s.r. for copper–phosphate glasses containing calcium and lutetium

Glass No.	P_2O_5 content (mol %)	CuO content (mol %)	CaO content (mol %)	Lu_2O_3 content (mol %)	Total Cu in 100 g of glass (g)*	Cu^{2+} in 100 g of glass (g)†	Total Cu in 100 g of glass before melting‡	Cu^+ in 100 g of glass (g)	$C = [Cu^+]/[Cu_{total}]$
01	65	25	9	1	16.48	11.70	13.11	4.80	0.290
02	65	25	8	2	12.76	8.35	12.75	4.41	0.356
03	65	25	7	3	12.69	7.96	12.41	4.80	0.378
05	65	25	5	5	11.95	7.40	11.78	4.55	0.381
a	65	25	10	0	18.12	16.49	13.49	1.63	0.090

*From wet chemical analysis.
†From e.s.r. measurements.
‡From original weighing.

glasses showed a gradual loss of strength of the absorption band at 830 cm^{-1} (attributed to Cu^{2+} in an octahedral environment but with tetragonal distortion) as the concentration of Pr_6O_{11} was increased.

Various reasons have been forwarded to explain the reduction of the signal from the paramagnetic ion in these types of glass, such as paramagnetic ions coupled by strong exchange interaction [5], spin–spin interaction between neighbouring paramagnetic ions of different elements [8] and processes involving inter-element redox phenomena [6].

At low concentrations of Pr(III) the last of these three may well be the dominant mechanism, with an equilibrium of the type

$$Cu^{2+} + Pr^{3+} \rightleftharpoons Cu^{+} + Pr^{4+}$$

playing an important role. At higher concentrations of the rare-earth paramagnetic oxide, the enhanced loss of the copper signal may well be due to relaxation processes involving interaction between Cu(II) and Pr(III) which is not observed when the diamagnetic Lu(III) is incorporated into the glass.

From the data recorded, it is clear that the ratio of copper (I) to total copper increases with increasing rare earth (III) ion concentration, and that the existence of two different oxidation states of copper necessary to support the hopping mechanism of electronic conduction is substantiated. The temperature-independence of the spin concentration suggests that the carrier concentration remains constant and that the temperature dependence of electrical conductivity [2] is due to a change in the carrier mobility which is activated and increased by raising the temperature.

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