JOURNAL OF MATERIALS SCIENCE 24 (1989) 4423–4426

An electron spin resonance study of copper phosphate glasses containing some rare earth oxides

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The electron spin resonance spectra of phosphate glasses containing mixed Cu^{2+}–Er^{3+} and Cu^{2+}–Lu^{3+} oxides have been examined. A reduction in the copper (II) signal intensity in the glasses as the proportion of rare earth oxide is raised corresponds to an increase in the reduced valency ratio C in the glasses. Differences between the behaviour of glasses containing erbium and those containing lutetium are observed and probably arise from magnetic coupling between copper (II) and erbium (III).

1. Introduction

The use of the technique of electron spin resonance (ESR) spectroscopy for the study of paramagnetic centres in glass systems has become a well established method. Both transition metal ions and rare earth (or lanthanide) ions, characterized by partially filled d and f shells in the electronic systems, can frequently exist in a number of oxidation states. Some of these states are paramagnetic and others diamagnetic and electronic conduction is possible as a result of electron transfer or hopping from ions in a lower oxidation state to ones in a higher oxidation state of a particular element.

The relative proportion of the transition metal ions in the different oxidation states has been used in many studies as a parameter which may be related to electronic conduction. The initial resonance study of glassy materials was undertaken by Sands [1] on the soda–lime–silicate glass-based system. Landsberger and Bray [2] used the ESR method in order to investigate the reduced ion concentration ratio C in the P_2O_5-V_2O_5 glass system and Lynch and Sayer [3] undertook studies of the affects of added metal oxides on tungsten oxide–phosphorus pentoxide glasses, observing strong exchange coupling. The application of the ESR technique to a study of copper (II) in the systems CuO–P_2O_5 and CuO–CaO–P_2O_5 was undertaken by Moridi and Hogarth [4] who showed that the relative concentration ratio C, $[Cu^+]/[Cu_{total}]$, increased as the CuO content of the glass was increased. In studies on mixed metal oxide glasses Bogomolova *et al.* [5] suggested that various factors could lead to a decrease in the ESR signal intensity and to signal broadening when a second transition metal oxide was introduced into the glass system.

Moridi and Hogarth [6], Hanson [7], Joffe *et al.* [8], Nester and Kingery [9] and Bogomolova *et al.* [5] found the mechanism of charge transfer by an electron hopping mechanism between oxidation states to be substantiated. More recently, Harani *et al.* [10] studied the systems P_2O_5–CuO–CoO and P_2O_5–CuO–NiO and from ESR and optical data concluded that the loss of the copper (II) signal in these systems was most probably due to an oxidation–reduction mechanism involving electron transfer between the copper ion and the second transition metal ion. Mohammed-Osman *et al.* [11], from a study of similar glasses containing praseodymium oxide, suggested that a redox mechanism at low rare earth ion concentration was enhanced at higher concentrations of Pr(III) by relaxation processes. In this work we have extended the study using erbium (III) oxide as an additive in a range of glasses containing CuO and P_2O_5 and comparing the behaviour with similar glasses containing lutetium (III).

2. Experimental procedure

2.1. Preparation of glasses

All compositions of glasses employed in this investigation are expressed as mol%. Glasses of composition $P_2O_{5(65)}$–$CuO_{(35-x)}$–$Er_2O_{3(x)}$ and $P_2O_{5(65)}$–$CuO_{(35-x)}$–$Lu_2O_{3(x)}$ were prepared from the appropriate analytical grade component oxides by carefully mixing the required masses of oxides in alumina crucibles and subjecting them to the following heat treatment: an initial heating for 1 h at 300° C in order to minimize volatilization and then transfer to a melting furnace at a temperature of 1200° C for a period of 3 h, with occasional stirring to maintain homogeneity. The melts were subsequently removed, poured rapidly on to alumina plates and after cooling in the atmosphere were stored in a desiccator to prevent absorption of moisture.

2.2. Electron spin resonance measurements

The ESR spectra were recorded using a Varian E3 ESR spectrometer working at X-band frequency. The finely ground dry glasses were placed in standard

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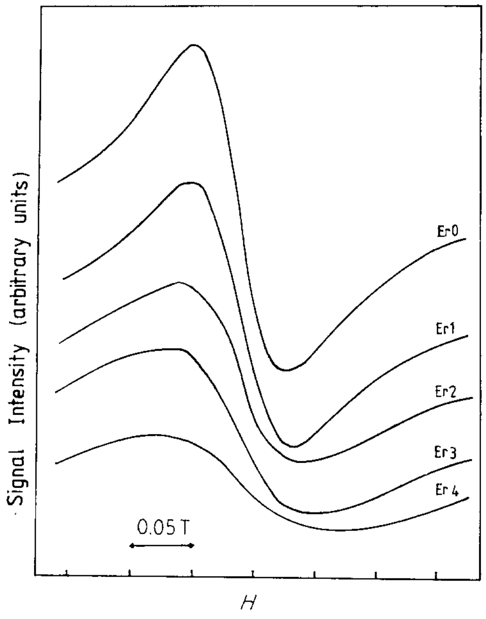

Figure 1 ESR spectra of some copper phosphate glasses containing erbium (Er(O) refers to pure CuO–P_2O_5).

Varian 3 mm quartz sample tubes packed to a depth of 3 cm and each individually weighed. Except for the gain level setting, instrumental conditions were maintained constant for all samples throughout the investigation. Each spectrum was doubly integrated and comparison made with the spectrum of a sample of crystalline Analar hydrated copper (II) sulphate in order to determine the spin concentration of copper (II). The total copper content of the glasses was determined by carrying out standard wet chemical analyses on duplicate samples.

3. Results and discussion

As in the previous study by Mohammed-Osman *et al.* [11] a comparison was made between the behaviour of glasses containing two different rare earth metal oxides, in this instance Lu_2O_3 and Er_2O_3. The ESR spectra recorded for the glasses of composition $P_2O_{5(65)}$–$CuO_{(35-x)}$–$Ln_2O_{3(x)}$ for $x = 0$ to 4 mol% are given in Figs 1 and 2. The concentrations of copper used mean that there is no visible hyperfine structure to the spectra, and the line shapes correspond to those previously recorded by other workers [5, 6, 11]. Increasing values of x resulting in a reduction of the intensity of the Cu(II) ESR signal and the observation of Mohammed-Osman *et al.* [11] that even low concentrations of the added rare earth resulted in considerable reduction in the signal intensity was verified.

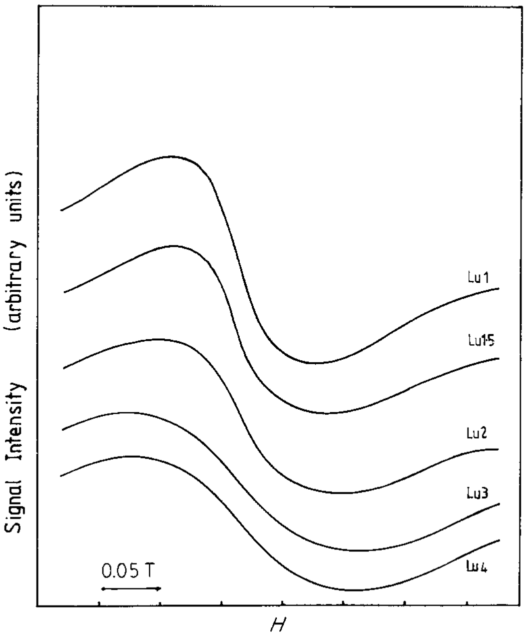

Figure 2 ESR spectra of some copper-phosphate glasses containing lutetium.

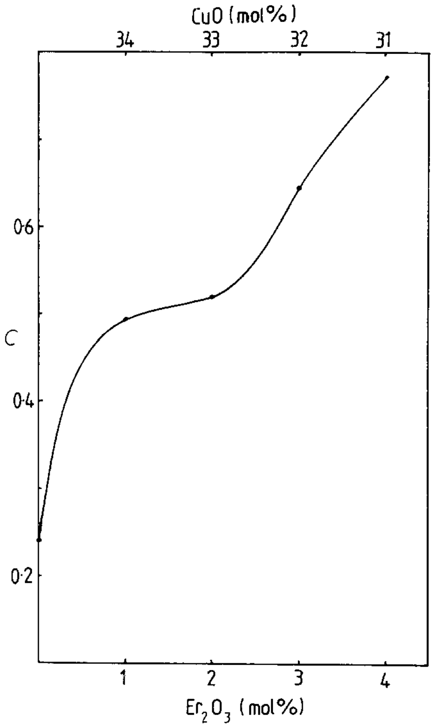

Figure 3 The relationship between Er_2O_3 content and reduced valency ratio C for a copper phosphate glass containing erbium.

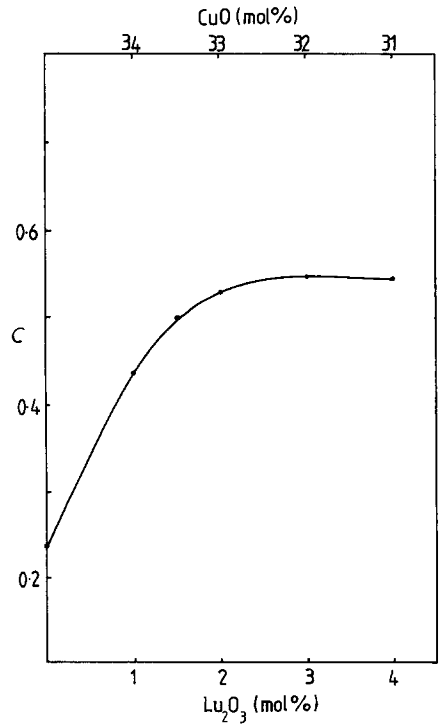

Figure 4 The relationship between Lu_2O_3 content and the reduced valency constant C for a copper phosphate glass containing lutetium.

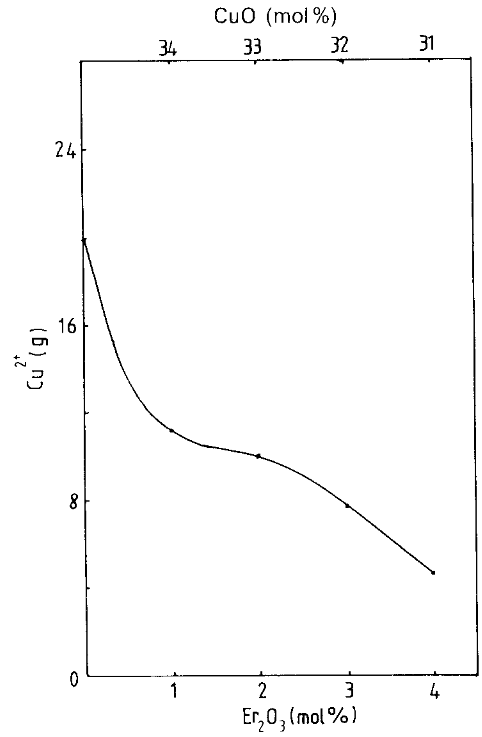

Figure 5 Decrease of Cu^{2+} ion concentration determined by ESR, with increasing Er_2O_3 content in a copper phosphate glass containing erbium.

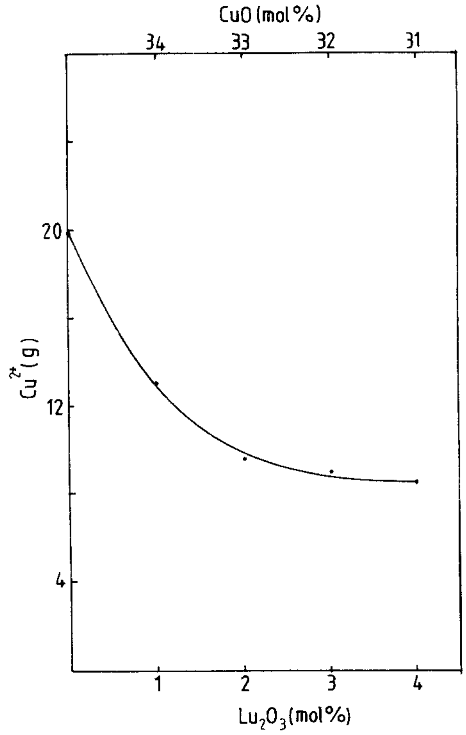

Figure 6 Decrease of Cu^{2+} ion concentration determined by ESR with increasing Lu_2O_3 content in a copper phosphate glass containing lutetium.

TABLE I Some parameters of copper phosphate glasses containing lutetium

No.	Glass sample	P_2O_5 content* (mol%)	CuO content* (mol%)	Lu_2O_3 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)	$C = \frac{[Cu^+]}{[Cu_{total}]}$
1	Lu(0)	65	35	0	26.20	19.93	6.27	0.239
2	Lu(1)	65	34	1	23.24	13.12	10.12	0.435
3	Lu(1.5)	65	33.5	1.5	22.97	11.46	11.41	0.499
4	Lu(2)	65	33	2	20.49	9.58	10.91	0.532
5	Lu(3)	65	32	3	19.86	9.02	10.83	0.545
6	Lu(4)	65	31	4	18.77	8.55	10.22	0.544

*Notional starting content.
†Determined by wet chemical analysis.
‡Determined by ESR.

At the lower values of x the plots (Figs 3 and 4) of C the reduced valency ratio for the copper oxidation states against the content of added rare earth oxide (x) are, within experimental error, the same. However, the levelling off that occurs at about 1 to 2% in both cases does not continue in the case of erbium (III) but increases dramatically between 2 and 4 mol% of added erbium (III) oxide. These results are again in accord with those observed by Mohammed-Osman *et al.*, but with one difference, namely that the reduced valency ratio C in the case of erbium (III) is considerably higher at corresponding values of x than in the case of praseodymium.

Investigation of the glass samples annealed at temperatures for periods of 1 h, between 200 and 750° C, showed that at temperatures up to 550° C there was no significant change in the copper (II) concentration but that some slight change could be seen above this temperature. This is again attributed to changes in the glass ordering that takes place at these higher temperatures [4, 11].

As in the previous study [11] the difference in behav-

TABLE II Some parameters of copper phosphate glasses containing erbium

No.	Glass samples	P_2O_5* (mol%)	CuO* (mol%)	Er_2O_3* (mol%)	Total Cu in 100 g of glass†	Cu^{2+} in 100 g of glass‡	Cu^+ in 100 g of glass	$C = \frac{[Cu^+]}{[Cu_{total}]}$
1	Er(0)	65	35	0	26.20	19.93	6.27	0.239
2	Er(1)	65	34	1	23.75	11.96	11.79	0.496
3	Er(2)	65	33	2	22.80	10.97	11.83	0.519
4	Er(3)	65	32	3	21.75	7.65	14.05	0.645
5	Er(4)	65	31	4	20.35	4.76	15.74	0.773

*Notional starting content.
†Determined by wet chemical analysis.
‡Determined by ESR.

iour observed between Lu(III) and Er(III) (Figs 5 and 6; Tables I and II) can probably be attributed to the relaxation processes involving interaction between Cu(II) and Er(III) occurring at the higher rare earth oxide concentrations and the fact that it is more enhanced in the case of erbium compared to praseodymium, is probably due to the greater magnetic susceptibility of Er(III) (μ = 9.6 Bohr magnetons B.M.) compared to Pr(III) (μ = 3.6 B.M.).

References

1. R. H. SANDS, *Phys. Rev.* **99** (1955) 1222.
2. F. R. LANDSBERGER and P. J. BRAY, *Chem. Phys.* **53** (1970) 2757.
3. G. F. LYNCH and M. SAYER, *J. Phys. C* **6** (1973) 3661.
4. G. R. MORIDI and C. A. HOGARTH, Proceedings 7th International Conference on Amorphous and Liquid Semiconductors, edited by W. E. Spear, (CICL, Edinburgh, 1977) p. 688.
5. L. D. BOGOMOLOVA, V. N. LAZUKIN and N. V. PETROVYKH, *Sov. Phys. Dokl* (*USA*) **13** (1969) 679.
6. G. R. MORIDI and C. A. HOGARTH, "The Physics of Non-crystalline Solids" (Proceeding of Fourth International Conferences on Non-Crystalline Solids, Claussthal-Zellenfeld, 1976) edited by G. H. Frischat (Trans Tech. Publications, West Germany, 1977) p. 254.
7. K. W. HANSON, *J. Electrochem. Soc.* **112** (1965) 994.
8. N. A. JOFFE, I. B. PATRINA and I. S. POBEROVSKAYA, *Sov. Phys. Solid Stat.* **2** (1960) 609.
9. H. H. NESTER and W. D. KINGERY, Proceedings of the 7th International Conference on Glass, Brussels, June 1965 (Gordon and Breach, New York, 1965) p. 106.
10. R. HARANI, C. A. HOGARTH and K. A. K. LOTT, *J. Mater Sci.* **19** (1984) 1420.
11. A. E. MOHAMMED-OSMAN, K. A. K. LOTT, C. A. HOGARTH and M. A. HASSAN, *ibid.* **23** (1988) 1098.

Received 23 September 1988
and accepted 24 February 1989