JOURNAL OF MATERIALS SCIENCE **28** (1993) 189–192

Electron spin resonance in copper phosphate and copper tellurite glasses containing strontium

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Two series of ternary copper phosphate and copper tellurite glasses containing strontium were prepared and the electron spin resonance spectra of glasses of compositions 65 (P_2O_5) –(35 – x) CuO–xSrO and 65 (TeO_2)–(35 – x) CuO–xSrO where x varied from 0–10 mol% were investigated. From the results and the chemical analyses of the samples it was found that a reduction in the copper (II) signal intensity in the glass samples as the proportion of alkaline earth metal is raised, corresponds to an increase in the reduced valency ratio, C, in the glasses.

1. Introduction

The use of electron spin resonance (ESR) or electron paramagnetic resonance (EPMR) and its introduction into glass science suggested in 1955 by Sands [1], has provided a powerful spectroscopic technique based upon the resonant absorption of microwaves by unpaired electrons tuned by an externally applied magnetic field for determining the coordination environment of a variety of paramagnetic centres for some glass systems. ESR has become a well-established method.

Transition metal ions and rare-earth ions, which are characterized by partially filled d and f shells, can frequently exist in a number of oxidation states and the electronic conduction can occur as an electron transfer or hopping process of unpaired electrons from a transition metal ion in a lower oxidation state to one in a higher oxidation state. One of the most important parameters in explaining this conduction in oxide glasses is the relative proportion of transition metal ions in the different oxidation states. Landsberger and Bray [2] used the ESR method to investigate the reduced ion concentration ratio C = [reduced ion] / [oxidized ion] in P_2O_5–V_2O_5 glasses and found that the ratio decreased with increasing V_2O_5 content. Moridi and Hogarth [3] studied the ESR 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. Edirisinghe and Hogarth [4] also investigated the result of ESR spectra on copper–calcium–phosphate and copper–barium–phosphate glasses and showed that at low concentrations of calcium (or barium) the copper present in the glasses existed largely as Cu^{2+}. An increase in the alkaline-earth metal content with a corresponding decease in the copper content produced a decrease in the Cu^{2+} content with a corresponding increase in the Cu^+ content. Singh [5] reported the broadening of the ESR spectra of tellurium vanadate glasses $35TeO_2$–$(65 - x)\,V_2O_5$–$x Fe_2O_3$ where the molecular fraction, x, was in the range 0.3–1.0 mol % Fe_2O_3, and explained the broadening of the spectra with increasing Fe_2O_3 content on the assumption that the density of Fe^{3+} hopping centres had increased and the electrons were delocalized over various transition metal (TM) ion-hopping centres, as was described by Sanchez *et al.* [6].

2. Experimental procedure

The glass samples in this study have the compositions $65P_2O_5$–$(35 - x)$ CuO–xSrO and $65TeO_2$–$(35 - x)$ CuO–xSrO with x varying from 1–10 mol %. The samples were prepared from appropriate analytical grade component oxides by carefully mixing the required masses of oxides in alumina crucibles and then placing them in a furnace maintained at 350 °C for 1 h to minimize volatilization, The crucible was then transferred to a melting furnace maintained at the temperature of 1300 °C for 3 h. The homogenized melts were subsequently removed, then cast on to a steel plate mould, and allowed to cool in the atmosphere, and were stored in a desiccator.

A Varian E3 ESR spectrometer working in the X-band (9.5 GHz) was used to record the ESR spectra. The glass samples were finely powdered and placed in 3 mm diameter silica sample tubes, packed to a constant length of sample and individually weighed. Throughout the investigation the instrumental conditions were maintained constant except for the gain level setting. Each spectrum was doubly integrated and comparison was made with the spectrum of a sample of crystalline copper sulphate and the cupric

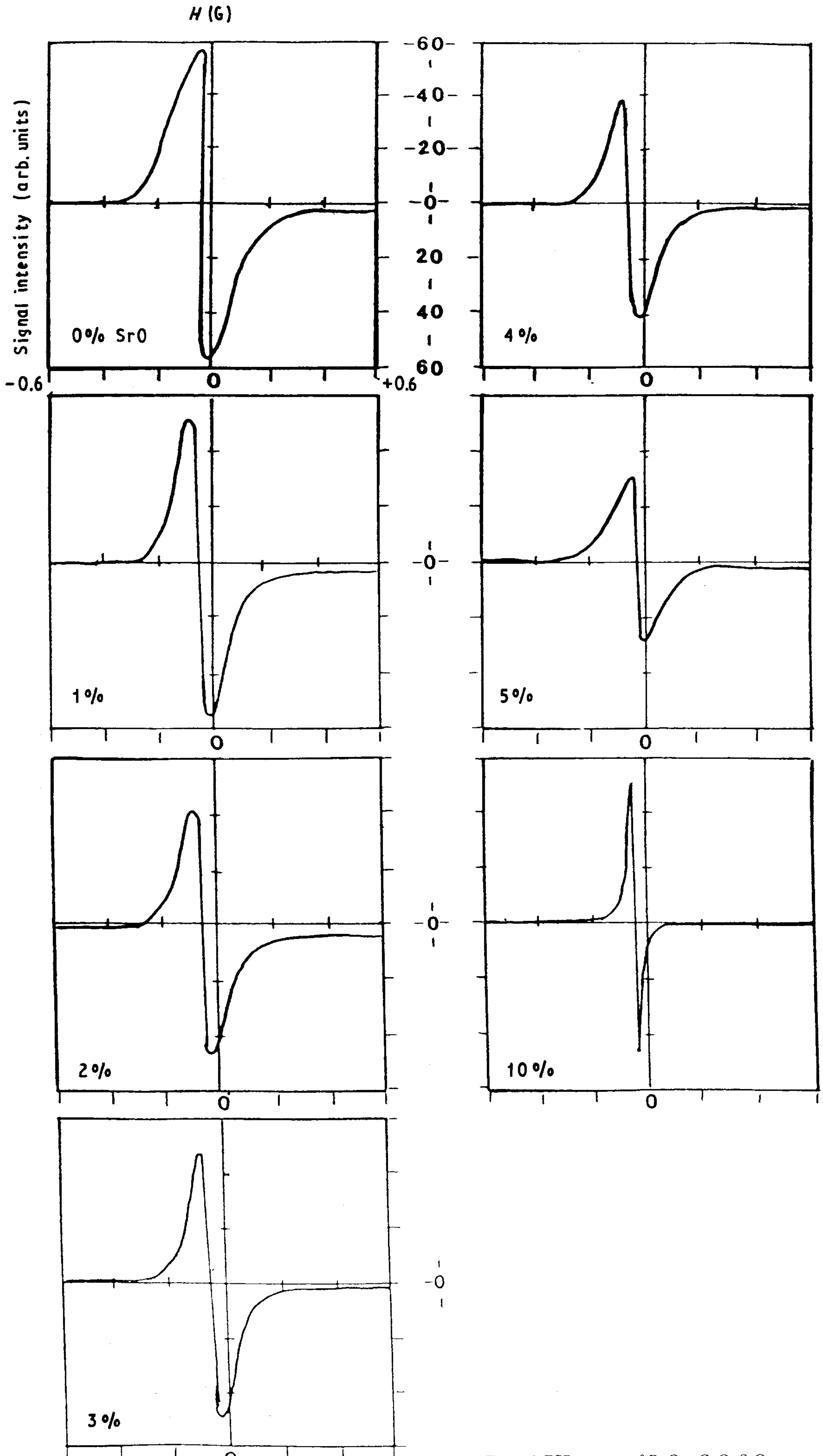

Figure 1 ESR spectra of P_2O_5–CuO–SrO.

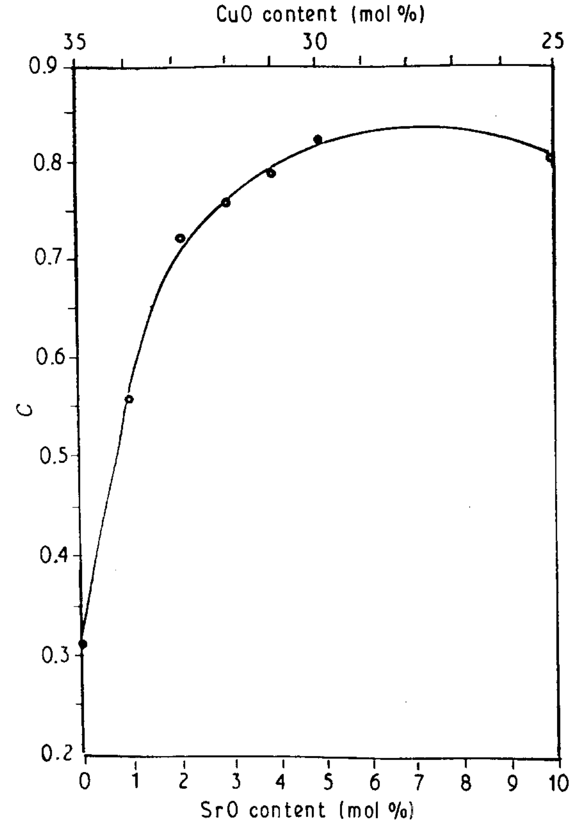

Figure 2 The relationship between valency constant, *C*, for copper phosphate glass, and SrO content (mol %).

ion spin concentrations were determined. Total copper was determined by wet chemical analysis.

3. Results and discussion

The ESR spectra of glass samples having the compositions $65P_2O_5$–$(35-x)$CuO–xSrO where $x = 0$–10 mol % are shown in Fig. 1 and no hyperfine structure was observed. Increasing values of x resulted in a reduction of intensity of the Cu^{2+} ESR signal in all the samples of this glassy system. Fig. 2 shows the relationship between SrO content and the reduced valency ratio, *C*, for the copper phosphate glass and indicates a steady increase of *C* with SrO increase, a levelling off at 3–4 mol % SrO and then a decrease after 5 mol % up to 10 mol %. The variation of Cu^+ is seen to rise from around 8 mol % for no SrO content

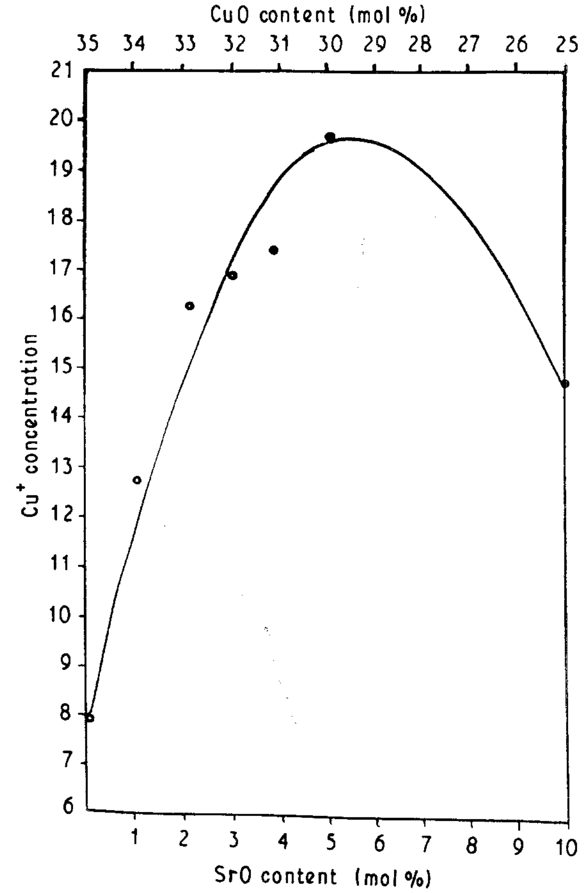

Figure 3 The variation of $[Cu^+]$ in copper phosphate glass with SrO content (mol %).

TABLE I Some parameters of copper phosphate glasses containing SrO

P_2O_5 content (mol %)	CuO content (mol %)	SrO content (mol %)	Total copper in 100 g glass (g)	Cu^{2+} in 100 g glass (g)	Cu^+ in 100 g glass (g)	*C*
65	35	0	25.57	17.61	7.96	0.31
65	34	1	23.17	10.18	12.99	0.56
65	33	2	22.33	5.92	16.41	0.73
65	32	3	22.09	5.21	16.88	0.76
65	31	4	22.00	4.78	17.22	0.79
65	30	5	24.07	4.12	19.95	0.83
65	25	10	18.44	3.49	14.95	0.81

TABLE II Some parameters of copper tellurite glasses containing SrO

TeO_2 content (mol %)	CuO content (mol %)	SrO content (mol %)	Total copper in 100 g glass (g)	Cu^{2+} in 100 g glass (g)	Cu^+ in 100 g of glass (g)	*C*
65	35	0	14.89	3.60	11.29	0.75
65	34	1	14.50	0.16	14.34	0.98
65	33	2	14.43	–	–	–

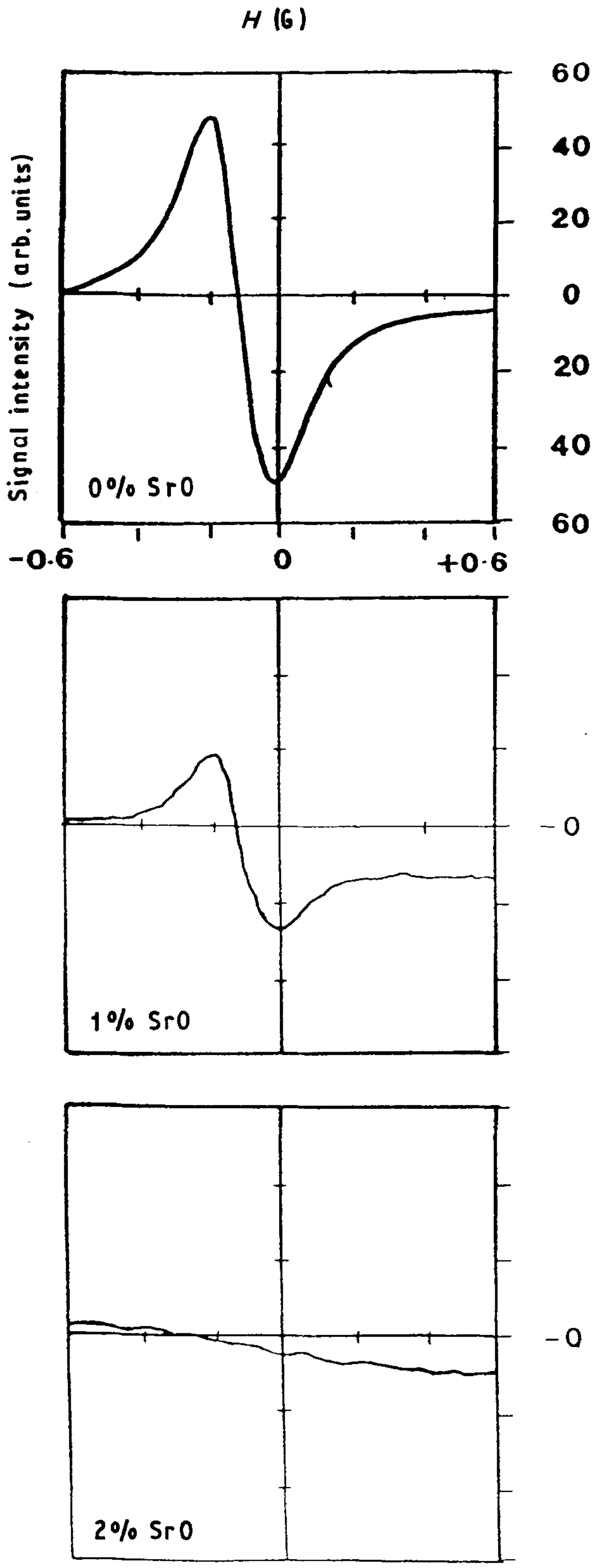

Figure 4 ESR spectra of TeO_2-CuO-SrO.

to a maximum at around 5 mol %, after which it appears to decrease. As shown in Fig. 3 these results are similar to the results which Arzeian [7] observed on a system involving europium (III) oxide and shows a similar trend with regard to the general increase in *C*. From the data recorded in Table I it is clear that the ratio of Cu^+ to total copper increases with increasing alkaline-earth metal and that the existence of two different oxidation states of copper might be consistent with a hopping mechanism of electronic conduction. Harani *et al.* [8] described the loss of ESR signal as being due to the decrease in the concentration of Cu^{2+} ions in phosphate glasses, as the result of an oxidation–reduction mechanism between two valency states of two transition metals.

Fig. 4 shows the first derivative ESR spectra of TeO_2–CuO and copper tellurite glasses containing 1 mol % SrO. The addition of 1 mol % SrO has broadened the ESR signal beyond the limit of detection and only a signal in the form of a straight line with some noise-like distortion was observed. As Table II shows, the substitution of SrO increases the concentration of diamagnetic Cu^+ ions and, at the same time, has increased the values of reduced valency *C*. This could show that the paramagnetic centres in the said glassy system have been substantially reduced by the incorporation of 1 mol % SrO. All the various processes of spin–spin interactions and spin–lattice interactions and cross-relaxation are likely to have contributed to the line-broadening of the ESR spectra and it is not possible to isolate the particular mechanism in this study.

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Received 22 January
and accepted 17 February 1992