JOURNAL OF MATERIALS SCIENCE 25 (1990) 1909-1912

A relaxation trend in the electron spin resonance phenomena in copper tellurite glasses containing NiO, CoO and Lu_2O_3

M. SULEMAN MALIK, C. A. HOGARTH AND K. A. K. LOTT*
*Department of Physics, and *Department of Chemistry, Brunel University, Uxbridge, Middlesex, UK*

Copper tellurite glasses containing NiO, CoO and Lu_2O_3 were prepared by the melt-quenching technique. The composition used was $65TeO_2-(35-x)CuO-xTMO$ (mol%), where TMO indicates NiO, CoO, Lu_2O_3, and for NiO- and CoO-doped glasses, x has the values 0, 0.5, 1 to 4, and for Lu_2O_3 doped glasses $x = 0$ to 4. Electron spin resonance (ESR) spectra of all glasses were recorded at room temperature. The results on glasses doped with NiO, CoO and Lu_2O_3 are discussed in terms of oxidation–reduction, cross-relaxation and interelectronic repulsion processes, respectively. Cobalt oxide is found to be more effective in relaxing the ESR spectrum than nickel and lutetium oxides when substituted in copper tellurite glasses.

1. Introduction

Electron spin resonance (ESR) studies are helpful in understanding the interaction between unlike magnetic ions in amorphous solids as well as finding the correlation between the formation of associates of dissimilar transition metal (TM) ions.

The line shapes observed in the ESR spectra give some important ideas concerning the physical state within the sample. Generally, the ESR spectrum is characterized by the following parameters:

1. the intensity of absorption of microwave power;
2. the width and shape of the absorption line; and
3. the value of the g factor and the hyperfine structure.

In paramagnetic resonance there are two major causes of finite line width and these are:

(a) the interaction between the paramagnetic ions and the lattice, and

(b) the interactions between the various ions themselves.

The first reported measurements were those of Zavoisky [1, 2] on the salts of iron group ions at a frequency of a few megahertz and a field of 0.1 T and he obtained a barely resolvable resonance. Sands [3] investigated the soda–lime silicate glass-based system using this technique. Landsberger and Bray [4] were the first to use the technique for determining the $[V^{4+}]/[V^{5+}]$ ratio in vanadium phosphate glasses.

Seigel and Jones [5] first reported their ESR studies of Cu^{2+} ions included in a polymorphic TeO_2 and compared the spectra with that of the tetragonal form of GeO_2. They found hyperfine splitting in the ESR signal and concluded that the Cu^{2+} ions play a similar role in glasses based on TeO_2 (non-Zacharaisen) and in GeO_2 (Zacharaisen) glass. The broadening of the ESR spectra of tellurium vanadate glasses ($35 TeO_2-(65-x)V_2O_5-xFe_2O_3$) with x in the range 0.3 to 1.0 mol % was reported by Singh [6] who described the broadening of the hyperfine spectra with increasing Fe_2O_3 content and suggested that the density of Fe^{3+} hopping centres had increased and also that the electrons were delocalized over various TM ions as had been suggested by Sanchez *et al.* [7]. Singh [8] also reported the absence of an ESR signal in the previous types of heat-treated glasses containing Fe_2O_3 in the range 1 to 5 mol % and attributed this to the phonon-induced superexchange interaction between 3d ions, but he could not observe this phenomenon in unannealed glasses. Sunandana and Rao [9] reported the broadening of the ESR spectra of copper-substituted tellurium vanadate glasses and discussed the results on the basis of electron-exchange between V^{4+} and Cu^{2+} ions which would be expected to lead to the formation of $V^{4+}-Cu^{2+}$ and $Cu^{2+}-Cu^{2+}$ exchange pairs. The loss of ESR signal of copper phosphate glasses doped with NiO and CoO was reported by Harani *et al.* [10]; they discussed their results in terms of an oxidation–reduction mechanism between the valency states of the two different transition metals.

Bogomolova *et al.* [11] examined the effect of CoO beginning with 0.25% CoO in barium phosphate glasses and concluded that the intensity of the ESR signal decreases with increase in CoO concentration. They discussed their results in terms of spin diffusion. During their study of vanadium phosphate glasses, Bogomolova *et al.* [12, 13] reported the effect of Co^{2+} on the ESR spectra of Cu^{2+}, V^{4+}, Mn^{4+} and W^{5+} ions in different glassy media and they explained their results in terms of a cross-relaxation process between two spin systems and also by spin-diffusion. Khan *et al.* [14] determined the effect of a fixed quantity of ZnO, NiO and TiO on germanium tellurite glasses and obtained no ESR signal, suggesting that the substituted

0022-2461/90 $03.00 + .12

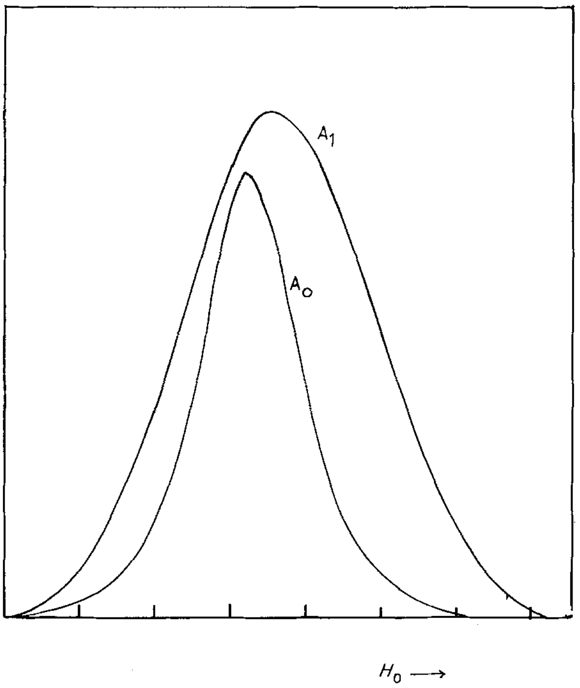

Figure 1 Absorption curves for (i) $65TeO_2$–CuO glass (curve A_0), (ii) $65TeO_2$–34.5CuO–0.5NiO glass (curve A_1).

oxides were behaving diamagnetically in the $50TeO_2$–(50-x)GeO_2–xTMO (mol %) glassy systems. Recently, in our previous communication [15] we have found a decrease in the intensity of the ESR of TeO_2–CuO–$CuCl_2$ with added $CuCl_2$ and have discussed the results in terms of a systematic increase of Cu^+ ion concentration with the increase of $CuCl_2$ and have also considered the probability of spin diffusion.

In this paper, we report the results of our ESR experiments on copper tellurite glasses doped with NiO, CoO and Lu_2O_3.

2. Experimental Work

2.1. Glass preparation

The three series of glasses with composition $65TeO_2$–(35-x)CuO-xTMO (mol %), where TMO = NiO, CoO with $x = 0, 0.5, 1$ to 4 and Lu_2O_3 for which $x = 0$ to 4, were prepared by the melt-quenching technique. All the glasses in batches of 30 g were prepared in alumina crucibles which were initially placed in a furnace preheated at 300° C for 1 h to minimize the tendency to volatilization and then they were transferred to a melting furnace for 2 h at 900 to 950° C in an air atmosphere. The melts were stirred from time to time to improve the homogeneity. After the firing period, the melt was then cast as disc-shaped glasses of 1.2 to 2.0 cm diameter and about 1.28 to 2.10 mm thick. The unannealed samples were ground into fine powders.

2.2 ESR experimental technique

ESR studies were carried out on the unannealed dry powdered glasses contained in a standard Varian 3 mm silica tube at room temperature and at X-band frequency using a Varian E-3 ESR spectrometer. Constant values of amplitude modulation as well as power levels were employed. All measurements were made under constant conditions and the gain setting only was varied as required. The microwave frequency and the magnetic field strength within a scanning range of $\pm$ 0.25 G applied were 9.38×10^9 Hz and 3400 G, respectively. The amounts of glass samples and of the standard $CuSO_4 \cdot 5H_2O$ were weighed carefully and the spin concentrations (X) of Cu^{2+} for each glass were estimated. The total copper (denoted by R) in the glass was determined by wet chemical analysis and the amount of Cu^{2+} in 100 g glass (Z) was calculated using the formula

$$Z = (100\, M_{cu}\, X)/[(W_g/3)N] \qquad (1)$$

where M_{Cu} is the molecular weight of the copper, $W_g/3$ is one-third of the weight of the glass sample, because about one-third of the length of the sample tube is exposed to the field and microwave source. N is the Avogadro number. The density of cuprous [Cu^+] ions was determined by taking the difference of (R–Z). The

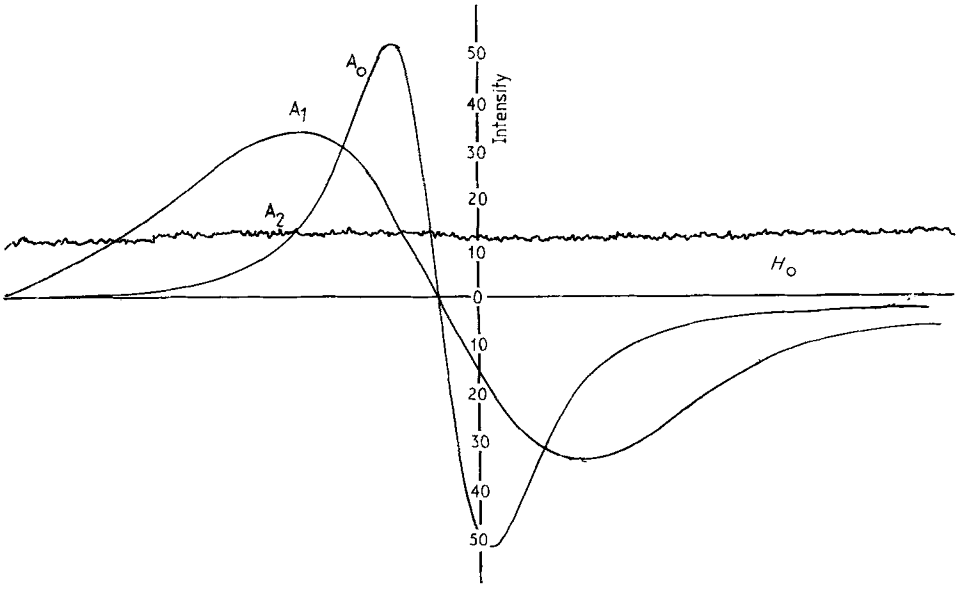

Figure 2 First derivative signal of (i) $65TeO_2$–35CuO with gain 1.25×10^4 (A_0), (ii) $65TeO_2$–34.5CuO–0.5NiO glass with gain 1.25×10^5 (A_1), (iii) $65TeO_2$–34.5CuO–0.5CoO glass with gain 1.25×10^5 (A_2). (All composition in mol %.)

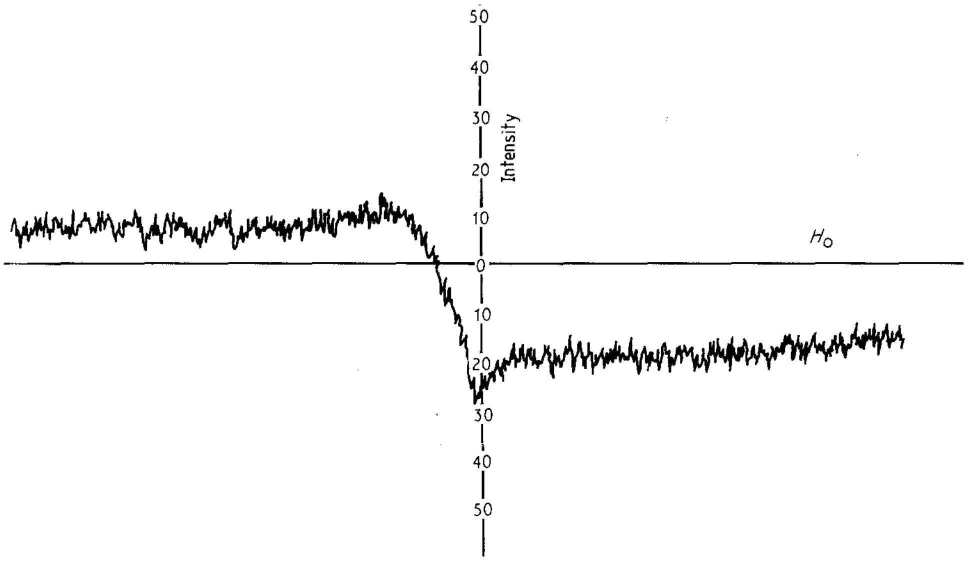

Figure 3 First derivative ESR spectra of TeO_2–CuO glasses containing 1 mol % Lu_2O_3 at gain 4 × 10^5.

reduced valency ratio $C = [Cu^+]/[Cu_{total}]$ was calculated for the respective glasses (see Table I).

The absorption curves (see Fig. 1) for TeO_2–CuO and copper tellurite glasses containing 0.5 mol % NiO were obtained by integrating the first derivative signals in accordance with the procedure described in the literature [16] and the areas under the absorption curves were calculated and were proportional to the number of the spins in the sample.

3. Results and discussion

The first derivative ESR spectra of unannealed TeO_2–CuO, TeO_2–CuO–NiO, TeO_2–CuO–CoO and TeO_2–CuO–Lu_2O_3 glasses recorded at room temperature are shown in Figs 2 and 3, respectively, where no hyperfine splitting was observed due to the large concentration of copper. Fig. 2 shows that the addition of 0.5 mol % NiO has broadened the ESR signal whereas no signal was observed with the same amount of CoO in copper tellurite glasses. NiO and CoO are antiferromagnetic compounds [17, 18] with spins 1 and 3/2 and magnetic moments 4.6 and 5, respectively. The loss of Cu^{2+} signal in the nickel-doped glasses can be attributed to an oxidation–reduction process which is possible according to the following scheme

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

In this reaction, the cupric ion is chemically reduced by interaction with a reduced ion of added TM, namely Ni^+, which together with its corresponding ion in the +2 oxidation state forms a strong reducing couple. The reaction also indicates that the substitution of NiO increases the concentration of diamagnetic Cu^+ ions. From the analysis of the data (Table I), it has been estimated that the addition of 0.5 mol % NiO has reduced the concentration of paramagnetic $[Cu^{2+}]$ ions by 73.6%, the total spin concentrations by 80.6% and at the same time has increased the values of reduced valency ratio by 185.7%, the peak-to-peak width of the resonance by 158.8% and the concentration of Cu^+ ions by 159% over the values for the binary TeO_2–CuO glass. This shows that the said glassy system has been forced to behave diamagnetically by the incorporation of 0.5 mol % NiO. The major error in the measurement of spin concentrations was the distortion of line shape which produced a Lorentzian line shape with extended wings. At 1 to 4 mol % NiO the ESR signals were

TABLE I Compositions and estimated ESR data of copper tellurite glasses containing NiO, CoO and Lu_2O_3. The number of spins in the standard sample used was $(Y) = 1.99 \times 10^{19}$

No.	Composition (mol %)			Shape of ESR signal	R	Z	R–Z	C	X	H_{pp}* (G)	Relative decrease (%) in		Relative increase (%) in		
	TeO_2	CuO	TM oxide								X	Cu^{2+}	H_{pp}	Cu^+	C
1	65	35	–	Lorentz shape	12.7	9.16	3.5	0.28	2.15×10^{20}	20.5	–	–	–	–	–
2	65	34.5	NiO, 0.5	Broad Lorentz	11.6	2.4	9.2	0.8	4.17×10^{19}	53.05	80.6	73.6	158.8	159	185.7
3	65	34.5	CoO, 0.5	No signal	–	–	–	–	–	–	–	–	–	–	–
4	65	34	Lu_2O_3, 1	Distorted signal	–	–	–	–	–	–	–	–	–	–	–

All glasses with TM contents greater than those shown do not show any ESR signal.
*H_{pp} is the peak to peak height of the first derivative ESR spectra of glasses.

broadened beyond the limit of detection and they were attributed to the clustering of the Cu^+ ions with the increase of NiO content and these results were in close agreement with those reported by previous workers [10, 14] in other systems of glasses with NiO contents. Ni^{2+} unlike Co^{2+}, has a long relaxation time and therefore is unlikely to cause the loss of Cu^{2+} signal by the mechanism of cross-relaxation invoked by Bogomolova *et al.* [19] for the Co^{2+}-doped system where the rapidly relaxing Co^{2+} leads to the loss of Cu^{2+} signal.

The loss of Cu^{2+} signal in Co^{2+}-doped copper tellurite glasses can be interpreted in terms of cross-relaxation because of its short relaxation time. The divalent Co (II) ion [20] is an interesting one because the orbital moment is incompletely quenched and the spin-lattice relaxation broadens the Cu^{2+} signal such that the intensity falls below the limits of detection, i.e. a signal in the form of a straight line with some noise-like distortion caused by the spin-orbit interaction was observed and this agrees closely with the observation made earlier by Bogomolova *et al.* [19].

A very surprising ESR spectrum from copper tellurite glasses doped with Lu_2O_3 was observed as shown in Fig. 3. Lutetium (III), the last member of the lanthanide series in the Periodic Table is diamagnetic in nature and has a most stable state 3+ and also its f-shell is completely filled and it is impossible for the inner transition to take place [21]. Lutetium (3+) has $S = O, L = O, J = O\ g = O$ and $\mu = O$ [22].

Amorphous TeO_2 contains Te^{4+} cations in six-fold octahedral coordination to oxygen [5]. Two electrons are given out from the following solid state reaction and their spins are slightly affected by the combined effect of the applied field and the microwave power. They are also minutely repelled by the field set up by the interelectronic repulsion effects of $4f^{14}$ electrons.

According to the following reaction, which is believed to represent what is occurring, no unpaired electrons exist in this glassy network

$$TeO_2 \rightarrow Te^{6+} + 2O^{-2} + e^- + e$$

$$Cu^{2+} + e^- \rightarrow Cu^+$$

$$Cu^+ \rightarrow Cu^{2+} + e^-$$

$$e^- + e^- \rightarrow 2e^- \text{ (electron pair)}$$

The interaction of the different energy levels of the spins of these free electrons are slightly separated and due to the effect of the magnetic field and that of the microwave frequency, they undergo some kind of spin distortion or spin deviation rather than splitting. Another possible reason for the distorted signal may be the fluctuation of the thermally induced spin waves and their interactions with the phonons or with the field of the neighbouring ions. The above arguments favour the idea that the effect of lanthanide can never be totally ignored [23]. If the effects of the lanthanide are included, and because of the completely filled f-shell, any inner transition is impossible [21] and thus the stable state is maintained in such glasses containing lutetium.

Overall, cobalt oxide was found to be more effective in relaxing the ESR signal completely than the other oxides present in the glassy networks under investigation.

References

1. E. ZAVOISKY, *J. Phys. USSR* **9** (1945) 211.
2. *Idem, ibid.* **9** (1945) 245.
3. R. H. SAND, *Phys. Rev.* **99** (1955) 1222.
4. F. R. LANDSBERGER and P. J. BRAY, *J. Chem. Phys.* **53** (1970) 2757.
5. I. SEIGEL and E. P. JONES, *ibid.* **57** (1972) 2368.
6. R. SINGH, *J. Phys. D Appl. Phys.* **17** (1984) 57.
7. C. SANCHEZ, M. HENERY, I. C. GRENET and J. LIVAGE, *J. Phys. C Solid State Phys.* **15** (1982) 7133.
8. R. SINGH, *J. Phys. D Appl. Phys.* **17** (1984) L. 163.
9. C. S. SUNANDANA and K. S. RAO, *Phys. Status. Solidi (a)* **90** (1985) 681.
10. RAVISHANKAR HARANI, C. A. HOGARTH and K. A. K. LOTT, *J. Mater. Sci.* **19** (1984) 1420.
11. L. D. BOGOMOLOVA, T. F. DOLGOLENKO, V. N. LAZUKIN and N. V. PETROVYKH, *Sov. Phys. Doklady* **18** (1973) 61.
12. L. D. BOGOMOLOVA, T. F. DOLGOLENKO, V. N. LAZUKI and I. V. FILATOV, *Sov. Phys. Solid State* **15** (1974) 2477.
13. L. D. BOGOMOLOVA, V. N. LAZUKIN and N. V. PETROYKH, *Sov. Phys. Dokl (USA)* **13** (1969) 679.
14. M. N. KHAN, M. A. HASSAN and C. A. HOGARTH, *Phys. Status Solidi. (a)* **106** (1988) 191.
15. M. SULEMAN MALIK, C. A. HOGARTH and K. A. K. LOTT, *J. Mater. Sci. Lett.* **8** (1989) 1344.
16. B. RANBY and J. F. RABEK, "ESR Spectroscopy in Polymer Research" (Springer Verlag, Berlin, New York, 1977) pp. 14–41.
17. P. A. COX, "Electronics Structure and Chemistry of Solids" (Oxford University Press, 1987) p. 157.
18. N. F. MOTT, *Pre. Progr. Phys.* **47** (1984) 909.
19. L. D. BOGOMOLOVA, T. F. DOLGOLENKO, V. N. LAZUKIN and N. V. PETROVYKH, *Sov. Phys. Dokl (USA)* **14** (1970) 760.
20. M. H. L. PRYCE, *Nature* **164** (1949) 116.
21. H. L. SMITH and A. J. COHEN, *Phys. Chem. Glasses* **4** (1963) 173.
22. N. CUSACK, "The Electrical and Magnetic Properties of Solids", 5th Edn Longmans Green, London, 1987) p. 293.
23. B. N. FIGGIS, "Introduction to the Ligand Field" (Wiley, London, 1966) p. 327.

Received 24 February
and accepted 30 August 1989