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Electron spin resonance study in P_2O_5–MoO_3 and P_2O_5–MoO_3–CaO glasses

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ESR spectra of the glass systems P_2O_5–MoO_3 and P_2O_5–MoO_3–CaO are presented. The electron spin resonance results showed a strongly exchange-narrowed interaction with the $[Mo^{5+}]/[Mo^{6+}]$ ratio and line shapes independent of temperature over the range 77 to 300 K. This result supports the concept of temperature-dependent mobility of the carriers and an unchanged paramagnetic site over this temperature range. The more important difference between the spectra of the binary and ternary glasses is that in the former with an increase in MoO_3 content the concentration of Mo^{5+} ions decreases but in ternary glasses it is reversed, i.e. the ion concentration of Mo^{5+} increases with increase in MoO_3 content.

1. Introduction

Semiconducting properties of amorphous glasses containing transition metal oxides, in particular those prepared from phosphorus pentoxide have been investigated by a number of workers [1–7]. The origin of the semiconduction is recognized as an electron transfer or hopping process of unpaired d-electrons from a transition metal ion in a low oxidation state M(x+) to one in a higher oxidation state M(y+), with the relative proportion of the reduced and oxidized states forming an important parameter in the explanation of the electrical properties of these glasses [2, 3, 6, 7].

The technique of electron spin resonance (ESR) with its ability to detect paramagnetic centres, is useful in such studies being able to provide the ratio of the concentration of the two species when one is diamagnetic and the other paramagnetic, from a knowledge of the total metal content and the double integral of the ESR spectrum. This method was originally applied by Landsberger and Bray [2] to determine [V(4+)]/[V(5+)] in V_2O_5–P_2O_5 glasses with the result that the ratio was seen to decrease as the V_2O_5 content was increased, and Lynch *et al.* who found that the ratio was invariant over the temperature range 77 to 300 K [3]. In many cases the transition metal has a nuclear spin I; e.g. for V, I = 7/2, and from the spectra, the dependence of the g-tensor and hyperfine tensor on spin density may be determined and estimates of the degree of covalency made [5, 8].

In our experiments, we have compared the use of the binary MoO_3–P_2O_5 system with that of ternary glass systems containing MoO_3, P_2O_5 and CaO, over a range of molybdenum content.

2. Experimental details

The glasses examined were prepared from reagent-grade P_2O_5, CaO and MoO_3 powders by mixing the appropriate proportion in an alumina crucible which was subsequently heated to 1473 K. In order to minimize losses by evaporation, the initial heating of the crucible was restricted to 673 K for 1 h and then heating continued for 3 h at 1473 K, with stirring to ensure homogeneity and attainment of equilibrium. The melts were quenched by pouring on to a steel plate maintained at 633 K. Lower temperatures were liable to result in fracture of the glasses. Annealing at this temperature for a period of 2 h reduced surface stress and removed volatile contaminants. All glasses were prepared under the same standard conditions and then stored under vacuum in a desiccator to prevent absorption of moisture, all the glasses being extremely sensitive to humidity. The range of glass compositions is given in Tables I to III and it may be seen that the binary glass range is restricted to a narrower MoO_3 percentage band (60 to 85%) than the ternary glass system which

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TABLE I Composition and derived concentration of Mo^{5+} for a number of binary glasses

P_2O_5 (%)	MoO_3 (%)	Total Mo in 100 g glass (g)	Mo^{5+} in 100 g glass (g)	Mo^{6+} in 100 g glass (g)	Spin concentration of $Mo^{5+} \times 10^{-21}$ (cm^{-3})	Activation energy $\Delta\epsilon$ (eV)	Relative density of glass
40	60	40.2	35.1	5.1	7.01	0.65	3.17
35	65	43.5	24.3	19.2	6.04	–	3.27
30	70	46.8	11.1	35.7	2.36	0.62	3.37
25	75	50.1	10.7	39.4	2.36	–	3.50
20	80	53.3	7.2	46.1	1.63	0.57	3.60
15	85	56.7	4.5	52.2	1.06	–	3.72

TABLE II Composition and derived concentration of Mo^{5+} for a number of ternary glasses

P_2O_5 (%)	MoO_3 (%)	CaO (%)	Total Mo in 100 g glass (g)	Mo^{5+} in 100 g glass (g)	Mo^{6+} in 100 g glass (g)	Spin concentration of $Mo^{5+} \times 10^{-21}$ (cm^{-3})	Relative density of glass
40	20	40	17.7	12.3	5.4	2.33	3.00
40	30	30	24.6	13.1	11.5	2.63	3.11
40	40	20	30.5	17.8	12.7	3.54	3.15
40	45	15	33.2	22.9	10.3	4.54	3.15
40	50	10	35.7	26.8	8.9	5.34	3.16
40	60	0	40.2	35.1	5.1	7.01	3.17

TABLE III Composition and concentration of Mo^{5+} for a ternary glass showing the effect of annealing

P_2O_5 (%)	MoO_3 (%)	CaO (%)	Annealing temperature (K)	Total Mo in 100 g glass (g)	Mo^{5+} in 100 g glass (g)	Mo^{6+} in 100 g glass (g)	Spin concentration of $Mo^{5+} \times 10^{-21}$ (cm^{-3})	Relative density of glass
40	30	30	293	24.6	11.5	13.1	2.24	3.09
40	30	30	473	24.6	12.1	12.5	2.38	3.10
40	30	30	633	24.6	13.1	11.5	2.63	3.11

was investigated over the range (20 to 60%) MoO_3.

Electron spin resonance experiments were made on powdered glass samples contained in standard Varian silica tubes, using a Varian E.3 ESR spectrometer working at X-band frequency. Constant values of modulation amplitude and power levels were employed such that neither broadening nor saturation were observed. Other instrument settings were maintained at pre-set values with the exception of the receiver gain which was varied to give reasonable spectra for integration purposes. Spin concentrations were estimated by double integration of the ESR spectrum and comparison with the Varian standard spin sample.

3. Results and discussion

A typical powdered glass ESR spectrum obtained in this investigation is given in Fig. 1. In this case it is the reduced species Mo(5+) that is paramagnetic and directly detectable by ESR with a resonance line that is complicated by the fact that this transition metal in its naturally abundant state is composed of seven isotopes, of which some 75% are of even mass number and of zero nuclear spin and the remaining 25% of odd mass number and having a nuclear spin of 5/2. Thus, the powder spectrum shows a main line from the odd electron associated with the even mass number isotopes

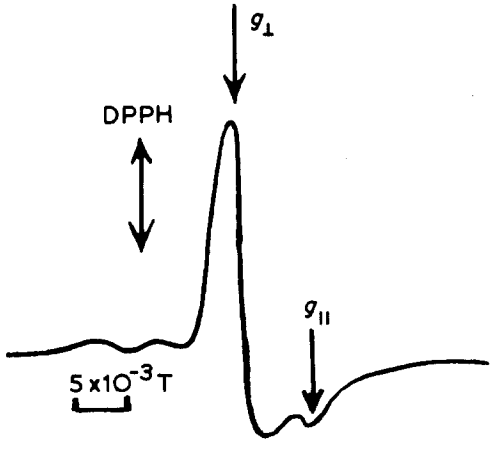

Figure 1 X-band ESR spectrum of Mo^{5+} in phosphate glass ($g_\perp \approx 1.92, g_{||} \approx 1.88$).

and weaker hyperfine components from the odd isotopes, together with perpendicular and parallel components of the g-tensor and A-tensor characteristic of axial symmetry, the values of which agree well with results of detailed spectral analyses by Sperlich [4] and Baugher and Parke [5]. The more important difference between the spectra of the binary and ternary glasses is that the ESR spectra of the former showed characteristic dipole–dipole broadening as the molar proportion of P_2O_5 was increased, making meaningful estimates of the Mo(5+) concentrations difficult. It would appear that the creation of Mo(5+), during the glass formation, by loss of oxygen from MoO_3 and its subsequent stabilization in the glass is favoured by the increase in P_2O_5 content (Fig. 2). A similar observation was made by Nagiev [1] during the investigation of V(4+) in phosphate glasses. In order to overcome this difficulty, which gave results in opposition to those of electrical conduction experiments where $\Delta\epsilon$ the activation energy* of samples decreased with increasing MoO_3 percentage

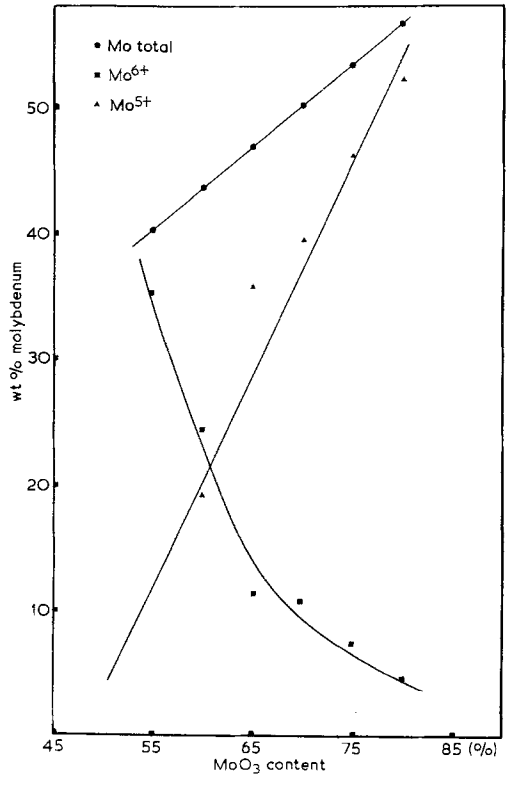

Figure 2 Wt% Mo total, Mo^{5+} and Mo^{6+} in P_2O_5–MoO_3 glasses as functions of MoO_3 content.

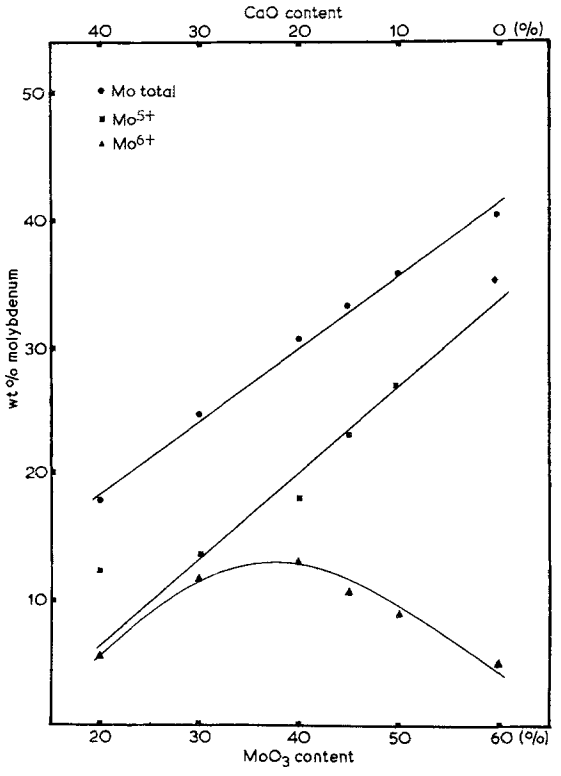

Figure 3 Wt% Mo total, Mo^{5+} and Mo^{6+} in P_2O_5–MoO_3–CaO glasses as functions of MoO_3 content.

(Table I) it was decided to investigate the ternary glass system where the molar proportion of P_2O_5 was fixed at a value at which a reasonable concentration of Mo(5+) would be obtained in the binary glass with a high molybdenum trioxide content, and to make up the composition to 100% by use of an ESR inactive oxide, namely CaO (Table II). In this way it was anticipated that there would be a greater possibility of forming more stable molybdate species in glasses with the higher CaO content and less Mo(5+) formed from MoO_3 decomposition with the rise in concentration of Mo(5+) corresponding to a decrease in the CaO content. This would appear to be the case as in Fig. 3.

In addition, it was found that annealing the glasses at higher temperatures rather than lower produces slightly greater concentrations of reduced spin centre (see Table III). It has been recorded previously that the concentration of reduced M(x+) ions is not significantly affected by temperature in the binary glasses [3, 6] and that the temperature dependence of electrical conduc-

*The activation energy, $\Delta\epsilon$, is defined from the variation of electrical conduction with temperature T of the form $\sigma = \sigma_0 \exp(-\Delta\epsilon/kT)$.

tivity arises from a change in the effective carrier mobility and that semiconduction in these binary oxide glasses does not follow the normal law for conduction as a function of temperature. The results from the ternary glasses show a similar patter of behaviour in that the spin concentration is not affected by temperature.

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