

Computer simulations of electron paramagnetic resonance spectra of $P_2O_5-Li_2WO_4-Li_2O$ glasses

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Abstract

$P_2O_5-Li_2WO_4-Li_2O$ glasses have been synthesized and studied over a wide range of compositions. The glasses were characterized mainly by thermodifferential analysis and electron paramagnetic resonance (EPR). The EPR spectra are characterized by the presence of two signals with very different intensities, associated with the W^V (major signal) and Mo^V (minor signal) paramagnetic centres. The signals have been satisfactorily reproduced by computer simulation, assuming anisotropy in the g values as well as the hyperfine parameters and linewidths. EPR parameters have been extracted and indicate metallic ions located in environments close to square pyramidal.

1. Introduction

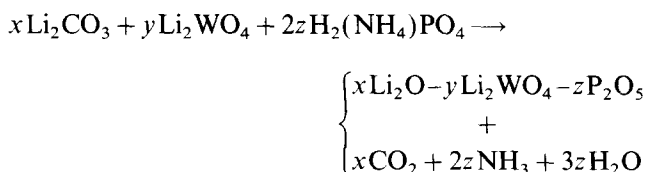
Glasses based on phosphates of several paramagnetic centres have been the subject of study of a number of workers, in order to investigate the semiconducting properties exhibited by some of these systems. The formation of glasses has been observed in binary ($P_2O_5-MO_n$, $M \equiv V, Mo$ or W) as well as ternary ($P_2O_5-MO_n-A_2O$, $M \equiv V, Mo$ or W , $A \equiv Na, K$) systems [1–3].

However, only a few electron paramagnetic resonance (EPR) studies have been realized on tungsten phosphate glasses and none with lithium included in the system. In order to gain insight into the paramagnetism observed in these glasses, we have approached the study of the $P_2O_5-Li_2WO_4-Li_2O$ system by EPR spectroscopy. Owing to the relative complexity of the observed spectra, which exhibit a high degree of anisotropy, we have used computer simulation to deduce the EPR parameters.

2. Experimental details

The glasses studied were prepared from Li_2CO_3 , Li_2WO_4 and $N_2(NH_4)PO_4$ powders by mixing the appropriate amounts in an agate mortar and subsequent

melting in an alumina crucible at 850 °C for a few hours, according to the scheme [4]



Formation of NH_3 during the decomposition of $H_2(NH_4)PO_4$ allowed the partial reduction of W^{IV} to W^V . The melts were quenched to room temperature in air.

Thermodifferential studies were performed by means of a Setaram analyser with a heating rate of 120 °C h⁻¹ and sample masses of 25 mg.

EPR spectra were recorded on a Bruker ER 200D spectrometer, controlled by a microcomputer and equipped with a variable temperature device from 4 to 600 K, working in the X-band ($\nu = 9.5$ GHz).

Computer simulations of the EPR spectra were realized by means of a home-made program. This uses the general expression

$$I_{EPR} = \sum_m \int_{\varphi=0}^{2\pi} \int_{\theta=0}^{\pi} \bar{W}_m(\theta, \varphi) F\left(\frac{H-H_0}{\Delta H}\right) \sin \theta \, d\theta \, d\varphi$$

for calculating the EPR spectrum of a paramagnetic centre in a random environment (powdered or amorphous samples). In this expression, m is the nuclear spin quantum number, \bar{W}_m is the transition probability for every hyperfine signal averaged over all the orientations of the magnetic field, $F[(H - H_0)/\Delta H]$ is the first derivative of the shape function for the elementary absorption curve, H is the static magnetic field, H_0 the resonance magnetic field, ΔH the half-width at half-height of the elementary absorption, and φ and θ are the angles defined by the static magnetic field H and the principal axes of the g tensor.

The double integral cannot be evaluated analytically owing to the complexity of the lineshape function and has been numerically computed following the Gauss-Legendre procedure. The symmetry of the g tensor has been considered axial and then

$$g^2 = g_{\parallel}^2 \sin^2\theta + g_{\perp}^2 \cos^2\theta$$

Moreover, in order to account for distributions of parameters related to the random local structural fluctuations in the amorphous compounds, we have considered an anisotropy in the individual linewidths, similar to that for the g -factor [5]:

$$\Delta H^2 = \Delta H_{\parallel}^2 \sin^2\theta + \Delta H_{\perp}^2 \cos^2\theta$$

3. Results

The domain of existence of the LiPW glasses in terms of their nominal composition is indicated in Fig. 1. One can note the existence of a wide glass domain including colourless and coloured zones.

The thermodifferential analysis (DTA) has been used to determine the vitreous nature of the different compositions. The DTA diagram of a sample of composition $55P_2O_5-5Li_2WO_4-40Li_2O$ is shown in Fig. 2, where the glass transition temperature ($T_g = 365^\circ C$) as well as the crystallization ($T_c = 480^\circ C$) and melting ($T_f = 580^\circ C$) temperatures are clearly distinguished.

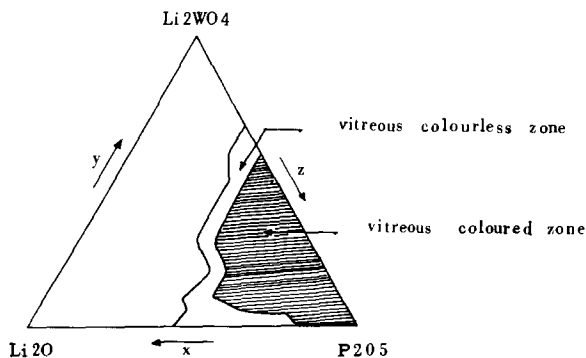


Fig. 1. Glassy domains in the $P_2O_5-Li_2WO_4-Li_2O$ system.

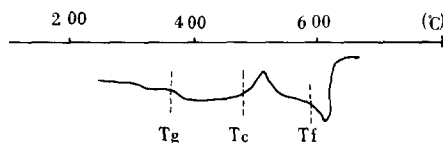


Fig. 2. Thermodifferential analysis of a glass of composition $55P_2O_5-5Li_2WO_4-40Li_2O$.

Typical room temperature EPR spectra for different compositions are seen in Fig. 3. The spectra exhibit two different signals (I and II), the intensity ratio of which is strongly dependent on the composition.

Signal I is relatively broad and does not exhibit hyperfine coupling. It has been simulated with an axially symmetric g tensor and with a spin hamiltonian which considers only the electronic Zeeman term, namely $H_0 = hv/g\beta$. In Fig. 4 are depicted the results of

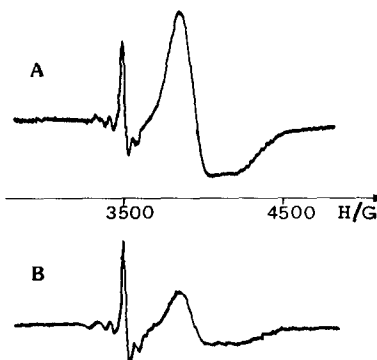


Fig. 3. Typical room temperature EPR spectra for glasses prepared in this work: spectrum A, $50P_2O_5-10Li_2WO_4-40Li_2O$; spectrum B, $80P_2O_5-10Li_2WO_4-10Li_2O$.

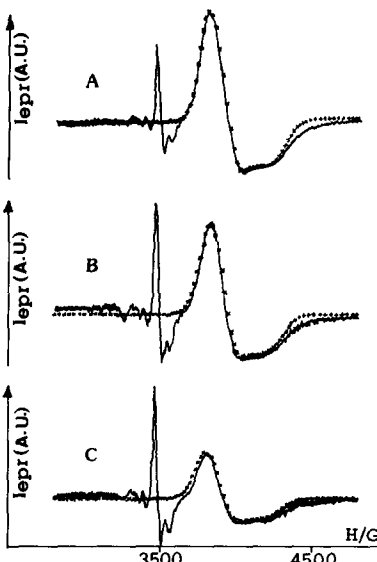


Fig. 4. Computer simulation of signal I (*): spectrum A, $50P_2O_5-10Li_2WO_4-40Li_2O$; spectrum B, $70P_2O_5-10Li_2WO_4-20Li_2O$; spectrum C, $80P_2O_5-10Li_2WO_4-10Li_2O$.

TABLE 1. Electron paramagnetic resonance parameters for signal I from computer simulation for several glasses synthesized in this work

Composition	g_{\parallel}	g_{\perp}	ΔH_{\parallel} (G)	ΔH_{\perp} (G)
$50P_2O_5-10Li_2WO_4-40Li_2O$;	1.5932	1.7351	115	98
$70P_2O_5-10Li_2WO_4-20Li_2O$;	1.5952	1.7732	115	100
$80P_2O_5-10Li_2WO_4-10Li_2O$;	1.5932	1.7398	120	102

TABLE 2. g values for W^v in different compounds

Compound	$g_{\parallel} = g_1$	g_{\perp}		Reference
		g_2	g_3	
$P_2O_5-WO_3-K_2O$ glass	1.55–1.65	1.65–1.75		1
$P_2O_5-WO_3-BaO$ glass	1.884	1.919	1.936	6
WO_3 films	1.823	1.888	1.920	6
$P_2O_5-WO_3$ glass	1.72	1.72	1.72	7
WO_3/Al_2O_3 catalysts	1.60	1.722		8
$P_2O_5-Li_2WO_4-Li_2O$ glass	1.5932–1.6015	1.7321–1.7398		Present work

the simulation of the spectra for three different compositions, considering a gaussian lineshape function, and the corresponding parameters are listed in Table 1. The resulting g_{\parallel} and g_{\perp} values indicate the presence of paramagnetic W^v centres ($S = 1/2$) and are in full agreement with those reported in the literature (Table 2).

On the contrary, signal II is narrow and is composed of an intense feature and a weaker poorly resolved hyperfine structure. These singularities are characteristic of Mo^v ions ($S = 1/2$) owing to the presence of small amounts of molybdenum as an impurity in the lithium tungstate. Figure 5 shows a simulation of this signal taking into account the presence of ^{95}Mo and ^{97}Mo isotopes having a nuclear spin of $5/2$ and a total natural

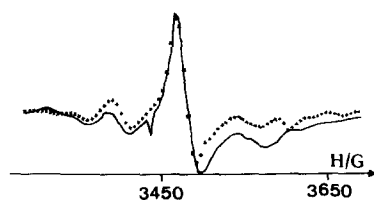


Fig. 5. Computer simulation of signal II (*).

abundance of 25%. The resonance field H_0 has been calculated from the expression $H_0 = hv/g\beta + Am/g\beta$, considering first-order perturbation, where A is the hyperfine coupling constant. The data obtained for a composition $65P_2O_5-5Li_2WO_4-30Li_2O$ are $g_{\parallel} = 1.875$, $g_{\perp} = 1.932$, $A_{\parallel} = 100$ G, $A_{\perp} = 45$ G, $\Delta H_{\parallel} = 25$ G and $\Delta H_{\perp} = 12$ G. The spectra were simulated with a gaussian lineshape and the g and A tensor components are very similar to those described by several researchers (Table 3).

Two series of glassy $P_2O_5-Li_2WO_4-Li_2O$ samples have been studied. For one of them, the Li_2WO_4 concentration was maintained constant and that of Li_2O was varied, whereas for the second the proportion of Li_2WO_4 was variable. The intensity dependence of the EPR signals on the amount of Li_2O is not regular and a measure of the number of paramagnetic centres is necessary in order to extract more information about the role of Li_2O . On the contrary, the intensity of the EPR signal associated with W^v increases when the concentration of Li_2WO_4 is increased, as indicated in Fig. 6. Variable temperature EPR experiments have been carried out with some representative samples.

TABLE 3. Electron paramagnetic resonance parameters for Mo^v in several MoO_3 containing compounds

g_{\parallel}	g_{\perp}	A_{\parallel} (G)	A_{\perp} (G)	Reference
1.89	1.960			8
1.885	1.940	100.2	44	9
1.8726–1.8943	1.9474–1.9437	69–103	38–52	10
1.873–1.902	1.92–1.940			11
1.9013	1.9398			12
1.875	1.932	100	45	Present work

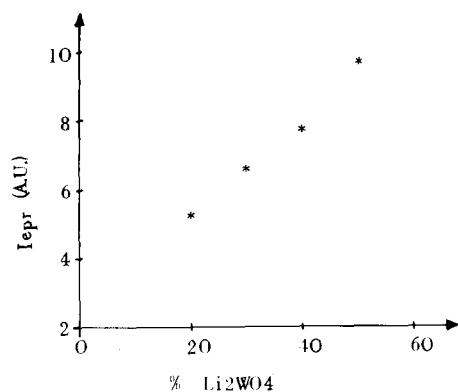


Fig. 6. Variation in the intensity of the W^V EPR signal with the amount of Li_2WO_4 .

Although the exact spin concentration has not been measured, it is evident that the amplitudes of both signals I and II decrease when the temperature is increased, which indicates a nearly constant spin density. It should also be noted that the EPR intensity varies reversibly with temperature, the samples exhibiting identical spectra to those observed initially.

4. Discussion

The identification of the paramagnetic centres which are responsible for the observed signals in the glasses has essentially been made on the basis of the spin hamiltonian parameters obtained by means of EPR spectra simulation.

The experimental spectra and mainly the signal of W^V ions have been satisfactorily reproduced by numerical calculations (Fig. 4). The small differences between the linewidths of the experimental and calculated spectra could be related to the presence of the ^{183}W isotope, with nuclear spin $I = 1/2$ and a natural abundance of 14.5%. The interaction between the electronic spin and the nuclear spin in this isotope increases the experimental linewidths. This kind of behaviour has been observed in enriched ^{183}W glasses (90%) by Raveau and coworkers [1].

The spectra have been simulated by assuming linewidth anisotropy. This indicates that the main reason for the signal's enlargement is related to the random fluctuations of the local environment of W^V . The linewidth contribution of other interactions, namely

dipolar interactions or spin-lattice relaxation, is weak. The exchange coupling interactions have been neglected owing to the magnetically dilute nature of the systems and the presumably scarce presence of clusters.

Interestingly enough, the concentration of the W^V ions increases with increase in Li_2WO_4 content in the glasses. A similar phenomenon was observed previously in $P_2O_5-MoO_3-CaO$ glasses [2], with respect to the amount of Mo^V . The greater possibility of forming more stable tungstate species in glasses with more Li_2O (and so with less Li_2WO_4) implies destabilization of W^V species and could be at the origin of this observation.

On the contrary, integration of signal II with respect to signal I indicates that the amount of Mo^V in the samples is very low.

From the EPR spectra it can be stated that the local environments of both paramagnetic centres, Mo^V and W^V , must be very similar. The g values are consistent with a coordination geometry corresponding to a distorted octahedron. As observed in most amorphous or crystalline Mo^V and W^V compounds, the metallic ions must be displaced from the centre of the octahedron [9, 13], giving rise to actual WO_5 square pyramids. In some cases, such as in the $P_2O_5-WO_3-K_2O$ system, the pyramid is characterized by a very short $W-O$ axial distance (1.6 Å) so that it has been described as tungstyl WO^{3+} ions [1].

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