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INVITED PAPER

LOCAL STRUCTURE AND METAL-METAL INTERACTION IN SOME PHOSPHATE GLASSES

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The local symmetry and the interactions between metallic ions in some soda-phosphate glasses with copper, vanadium, molybdenum and tungsten ions were investigated by ESR spectroscopy. It was evidenced the presence of Cu^{2+}, V^{4+}, Mo^{5+} and W^{5+} ions which are used as spectroscopic ESR probes. The appearance of other valence states of these ions in the studied glasses is possible, too. The obtained ESR data suggest different local symmetry of these ions, which determine specific metal-metal interaction between them.

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1. Introduction

Transition metal ions (Cu^{2+}, V^{4+}, Mo^{5+}, W^{5+}) incorporated in oxide glasses as spectroscopic probes have been investigated in order to characterize the glass local structure and to obtain some specific aspects like the geometry of structural units of the glass network, the character of chemical bonds in glasses as well as the coordination polyhedra (local symmetry) and interaction between paramagnetic transition ions[1-7].

ESR investigation of oxides glasses containing Cu^{2+} or V^{4+} ions have evidenced some differences between the local symmetry and the value of g and A parameters obtained in silicates, borate and phosphate glasses. The characteristic parameters of Cu^{2+} in phosphate glasses are the following: $g_{\parallel} = 2.40 – 2.45$, $g_{\perp} = 2.05 – 208$, $A_{\parallel} = 110 – 130\times10^{-4}$ cm^{-1} $A_{\perp} \leq 20\times10^{-4}$ cm^{-1} and may be explained by a tetrahedral (Td) symmetry at Cu^{2+} site [4].

ESR parameters of V^{4+} ions have also different values for phosphate glasses ($g_{\parallel} \leq 1.93$, $g_{\parallel} > 1.98$, $A_{\parallel} > 176\times10^{-4}$ cm^{-1}, $A_{\parallel} > 64\times10^{-4}$ cm^{-1}) than those obtained in other oxide glasses, where $g_{\parallel} \geq 1.935$ and $A_{\parallel} \leq 170\times10^{-4}$ cm^{-1} . The supposed symmetry of coordination polyhedra is C_{4v} (square-pyradmidal) and octahedrally (O_h)-distorted respectively [1,2].

In order to obtain further information about the local symmetry and interaction between metallic ions in oxide glasses the soda-phosphate glasses with Cu^{2+}, V^{4+}, Mo^{5+} and W^{5+} ions were prepared and investigated by ESR spectroscopy.

ESR measurements were performed at room temperature, in X-band(9.4 GHz), with 100 kHz field modulation with a standard JEOL-JES-3B equipment.

2. Results and discussion

a) $xCuO\cdot(1-x)[2P_2O_5\cdot Na_2O]$ glasses with $0.5 \leq x \leq 30$ mol %

For glasses with $x \leq 5$ mol % the following parameters characteristic of isolated Cu^{2+} ions were obtained: $g_{\parallel} = 2.426$, $g_{\perp} = 2.089$, $A_{\parallel} = 119\times10^{-4}$ cm^{-1} and $A_{\perp} = 21\times10^{-4}$ cm^{-1}. The shape of ESR spectra is modified by increasing the CuO content ($x \geq 10$ mol %). This consists in the appearance of

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a broad line at the g = 2.19 characteristic for clustered ions. The ESR spectra of glasses with x = 30 mol % consist only of a single line with ΔH = 200 G suggesting a strong superexchange interaction between copper ions.

In order to explain the big values of $g_{||}$ (> 2.40) and small values of the hyperfine splittings ($A_{||} \leq 120 \times 10^{-4}$ cm^{-1}), we consider that in phosphate glasses Cu^{2+} ions are coordinated essentially by four oxygen ligands in a tetrahedral (T_d) configuration and not in a tetragonally elongated octahedron (D_{4h}) as has been assumed in previous work [6,7].

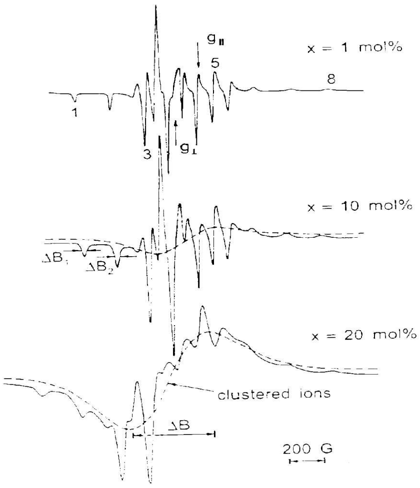

Fig. 1. ESR spectra of $xV_2O_5(100-x)[2P_2O_5 \cdot Na_2O]$ glasses with x ≤ 20 mol %.

This may be attributed to the polymeric structure of soda-phosphate glasses which involves the achievement of weak Cu-O bonds along the O_z axis and a notable distortion of the other four Cu-O bonds from the planar structure (D_{4h}) to the tetrahedral configuration (T_d). Such a distortion of the highly elongated octahedral copper complexes to the tetrahedral structure when the Cu-O bonds along the Oz axis are very weak (or non-existent) have also been reported in the case of Cu^{2+} supported on SiO_2 [8] and Al_2O_3 [9] after a supplementary dehydration.

The absence of a center-of-inversion symmetry introduces a new aspect, which does not occur in octahedral symmetry. This consists in the fact that $3d^8 4p$ configuration can be mixed with the $3d^9$ configuration of Cu^{2+} in T_d symmetry. An alternative viewpoint is to suppose that the paramagnetic "hole" is not in a pure 3d orbital but is in a state which is an admixture of a 3d wave function with a 4p wave function.

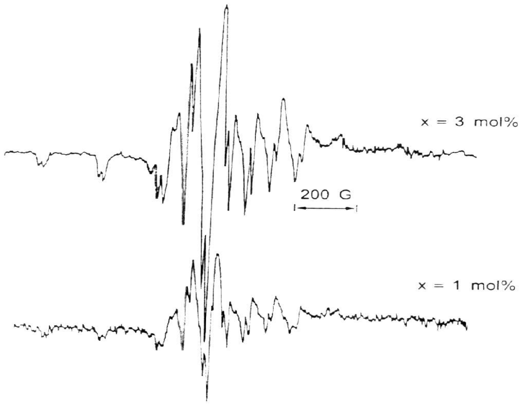

Fig. 2. ESR spectra of $xV_2O_5(100-x)[P_2O_5 \cdot 2Na_2O]$ glasses with x ≤ 3 mol % V_2O_5.

Thus the ground state molecular orbital for paramagnetic “hole” is [10-12]:

$$|xy\rangle = \alpha d_{xy} + \alpha'\phi_L(xy) + \alpha'' p_z .$$

As has been shown, the LCAO-MO scheme developed by Sharnoff [10] or Yokoi and Addison [12] for Cu^{2+} compounds of tetrahedral configurations a small admixture of $4p_z$ orbital in the d_{xy} ground state leads to a greatly reduced hyperfine splitting and to the big values of the copper (II) g-tensor.

Taking into account the relations between ESR parameters ($g_{||}$, $A_{||}$) and MO coefficients given in papers [10-12] we have estimated from experimental data ($A_{||} = -119 \times 10^{-4}$ cm^{-1} and $g_{||} = 2.426$) a value of 0.05 for α''^2, that suggest an admixture of ≈ 5 % of the $4p_z$ character in the $3d_{xy}$ ground state of Cu^{2+} ions in the studied glasses.

b) $xV_2O_5 \cdot (100-x)[2P_2O_5 \cdot Na_2O]$ and xV_2O_5 $(100-x)[P_2O_5 \cdot mNa_2O]$ with m =1.5 and 2

The investigated glasses belong to the systems $xV_2O_5(1-x)[2P_2O_5 \cdot Na_2O]$ with $0 < x \leq 50$ mol % and $xV_2O_5(100-x)[P_2O_5 \cdot mNa_2O]$ with $0 < x \leq 3$ mol % and m = 1.5 and 2.

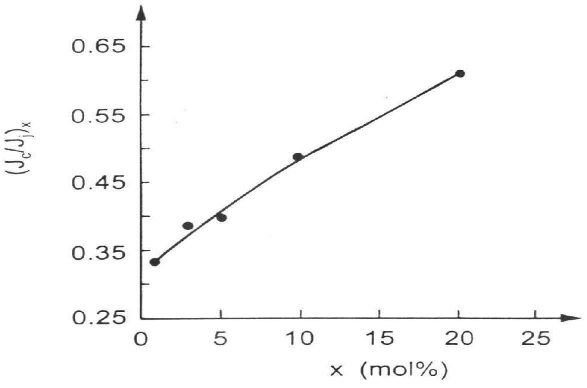

Fig. 3. The composition dependence of the ratio between clusterd and isolated V^{4+} ions in $xV_2O_5(100-x)[2P_2O_5 \cdot Na_2O]$ glasses

The samples were prepared by mixing suitable amounts of $(NH_4)_2HPO_4$ with $Na_2CO_3 \cdot 10H_2O$, and melting these admixtures at 800°C in sintered corundum crucibles by the technique reported previously [3]. After cooling, the host glasses were crushed and the resulting powders mixed with appropriate amount of V_2O_5 before the final melting at 850°C for 1 h. The melted samples were poured onto a stainless-steel plate. The samples structure was studied by X-rays analysis and did not reveal any crystalline phase in the investigated composition range.

The ESR spectra of $xV_2O_5(100-x)[2P_2O_5 \cdot Na_2O]$ glasses with small V_2O_5 content ($x \leq 5$ mol %) show a well resolved hyperfine structure typical for isolated V^{4+} ions present as VO^{2+} species in a ligand field of C_{4v} symmetry (Fig. 1). These resonance lines are better resolved than in the spectra reported for V^{4+} ions in other phosphate glasses by previous workers [13-15]. The characteristic ESR parameters are given in Table 1.

Table 1. ESR parameters of V^{4+} ions in $xV_2O_5(100-x)[2P_2O_5 \cdot Na_2O]$ glasses.

x (mol %)	$g_{\|\|}$ [a]	$g_{\perp}$ [a]	$A_{\|\|}$ [b] (10^{-4} cm^{-1})	$A_{\perp}$ [b] (10^{-4} cm^{-1})
0.5	1.933	1.989	178.5	68.3
1	1.932	1.988	170.6	70.9
3	1.933	1.992	175.1	68.1
5	1.930	1.990	179.6	72.0
10	1.931	1.989	192.9	75.4
20	1.927	1.988	184.6	68.9

[a] Error is ±0.001

[b] Error is ±1.

The shape of the spectra is modified with the increase of vanadium ions content. The changes consist in the appearance (for x > 5 mol %) of a broad line at g = 1.965 characteristic for dipole-dipole coupled ions and the disappearance (for x ≥ 30 mol %) of the vanadyl hyperfine structure. Therefore the spectra obtained for samples with $5 \leq x < 30$ mol % V_2O_5 may be considered as a superposition of two ESR signals, one with a well resolved hyperfine structure typical for isolated VO^{2+} ions, another consisting of a broad line without hyperfine structure, typical for associated ions. This assumption is also supported by the simulation of the experimental spectra by Rieger's [16, 17] program to simulate the ESR spectra of polycrystalline or glassy materials with the spin Hamiltonian solved to second-order perturbation theory. The g and hyperfine (A) tensor principal axes may be non-coincident. The number of associated ions increases with the V_2O_5 content so that for $30 \leq x \leq 50$ mol % the hyperfine structure disappears and only a broad line with variable linewidth versus the V_2O_5 content remains.

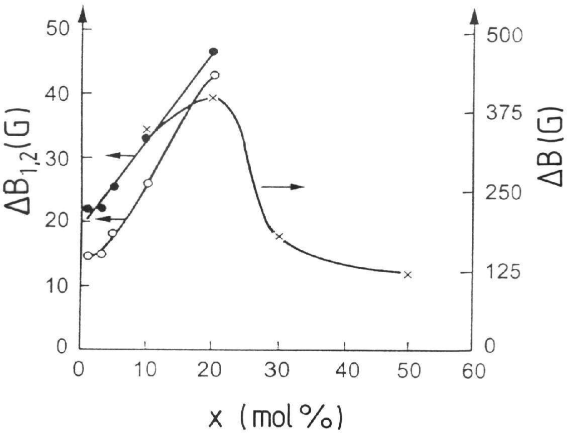

Fig. 4. The linewidth of the first and second hfs peaks from the parallel absorption band (ΔB_1, ΔB_2) and of the broad line (ΔB) V_2O_5 content for vs. $xV_2O_5(100\text{-}x)[2P_2O_5{\cdot}Na_2O]$ glasses. Closed circles show ΔB_1; open circles show ΔB_2; crosses show ΔB.

The above presented results are obtained for glasses having the soda-phosphate matrix characterized by a ratio between the network former and network modifier oxides of 2:1. For the $xV_2O_5(100\text{-}x)[P_2O_5{\cdot}mNa_2O]$ glasses where m = 1.5 and 2 the ESR spectra show two hfs sets in the parallel absorption band ($g_{\parallel}$) and three hfs sets in the perpendicular absorption band ($g_{\perp}$) (Fig. 2). The characteristic ESR parameters of the two nonequivalent hfs sets are given in Table 2.

Table 2. ESR parameters of two nonequivalent hfs of VO^{2+} centers in $xV_2O_5(100\text{-}x)$ $[P_2O_5{\cdot}mNa_2O]$ glass systems.

M	x (mol %)	$g_{\parallel}$[a]	$g_{\perp}$[a]	$A_{\parallel}$[b] (10^{-4} cm^{-1})	$A_{\perp}$[b] (10^{-4} cm^{-1})	hfs
1.5	1	1.954	2.005	171.1	59.9	A
		1.943	1.999	179.7	64.4	B
2	1	1.948	2.004	163.4	65.7	A
		1.937	1.995	174.3	61.0	B
2	3	1.945	2.002	160.6	67.5	A
		1.939	1.992	170.2	61.8	B

[a] Error is ±0.001
[b] Error is ±1.

As a measure of the ratio between clustered and isolated ions from a sample containing x mol % V_2O_5 $(J_c/J_i)_x$, we have considered the expression [18]:

$$\left(\frac{J_c}{J_i}\right)_x = \frac{J_{3x} - J_{1x}}{\alpha J_{1x}},$$

where J_{1x} and J_{3x} are the heights of the first and the third peak from the parallel band and α = 4.29 is the value of J_3/J_1 ratio for the sample with x = 0.5 mol % V_2O_5. We have considered that in glasses containing x < 5 mol % al the V^{4+} ions are manifested only as isolated species. Fig. 3 shows the variation of J_c/J_i ratio versus V_2O_5 content. For x > 20 mol % the J_c/J_i ratio cannot be evaluated because the hyperfine structure disappears. The composition dependence of the linewidths of the first (ΔB_1) and the second (ΔB_2) hfs peaks from the parallel absorption and also of the broad line (ΔB) characteristic of associated ions are given in Fig. 4. All the linewidths increase with V_2O_5 content until x = 20 mol % suggesting that the dipole-dipole interactions prevail among V^{4+} ions even in the case of clustered ions. The typical linewidth (ΔB) of these species decreases with the increasing of V_2O_5 content over x ≥ 20 mol % showing that in this composition range the superexchange interactions become dominant between resonance centers [2].

The bonding coefficient of the in-plane V-O $\sigma(\beta_1^2)$ - and $\pi(\beta_2^2)$-bonds and of π-bond with the vanadyl oxygen were evaluated by LCAO-MO model developed by Kivelson and Lee [19]. We considered the spin-orbit coupling constant λ = 170 cm^{-1} and the energy transition of 16700 and 10500 cm^{-1}, respectively [19,20].

We have also estimated the Fermi contact ($K \cong 0.85$) and dipolar ($P \cong 125\times10^{-4}$ cm^{-1}) terms. The values of $\beta_1^2 \cong 0.97$ and $\beta_2^2 \cong 0.92$ indicate a very weak covalency for the in-plane σ- and π-bonds while the $\varepsilon_\pi^2 \cong 0.60$ value indicates a strong covalency for the out of plane V=O bond. These results are consistent with the square-pyramidal coordination (C_{4v}) ions in phosphate glasses, while the bond of the sixth oxygen atom coordinated in the transposition with respect to the “yl” oxygen is negligible.

The results obtained for $xV_2O_5(100-x)[P_2O_5\cdot mNa_2O]$ glasses with m = 1.5 and 2 are different from those reported by Hosono et al. [1] which predicted that in soda-phosphate glasses the VO^{2+} ions lead to a single hyperfine structure due to the ionic potential Z/R (Z – valence, R – ionic radius). Our result show that the appearance of nonequivalent VO^{2+} centers depends on the network former and network modifier oxides ratio and not only on the ionic potential.

c) $xMoO_2\cdot(100-x)[2P_2O_5\cdot Na_2O]$ glasses with 0.5 ≤ x ≤ 40 mol %

The ESR spectra of glasses with x ≤ 5 mol % show a hyperfine structure with six lines in both parallel ($g_{\parallel}$) and perpendicular ($g_{\perp}$) bands (Fig. 5a). These may be attributed to the ^{95}Mo (15.7 %) and ^{97}Mo (9.4 %) isotopes which have the nuclear spin I = 5/2. The intense absorption line belongs to the ^{96}Mo isotope which has the nuclear spin I = 1. The ESR parameters of glasses with 0.5 ≤ x ≤ 40 mol % are given in Table 3. These data suggest that Mo^{5+} ions are essentially coordinated in the studied glasses by five oxygen ligands in a square-pyramidal form(C_{4v} symmetry) with a Mo=O double bond. This local vicinity is also confirmed by optical spectra which show two absorption band at 14000 cm^{-1} and 26500 cm^{-1}. These may be attributed to the $|B_2\rangle - |E\rangle$ and $|B_2\rangle - |B_1\rangle$ transitions characteristic for d^1 configuration in C_{4v} symmetry.

Table 3. ESR parameters of Mo^{5+} ions in P_2O_5-Na_2O glasses.

x (mol %)	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (10^{-4} cm^{-1})	$A_{\perp}$ (10^{-4} cm^{-1})
0.5	1.882	1.931	87.5	40.4
2	1.879	1.927	90.0	40.3
5	1.889	1.942	87.8	40.6
10	1.885	1.934	87.6	40.4
20	1.891	1.934	-	-
40	1.889	1.935	-	-

The shape of the ESR spectra is modified with the increase of the MoO_2 content (Fig. 5). This consists in the partial disappearance of the hyperfine structure and the appearance of a broad line at $g \cong 1.91$ value characteristic for dipole-dipole coupled Mo^{5+} ions. The number of clustered ions increases with the increase of MoO_2 content. This fact influence the shape of ESR spectra by widening the signal form, the $g_\perp$ absorption and by symmetrizing the spectrum.

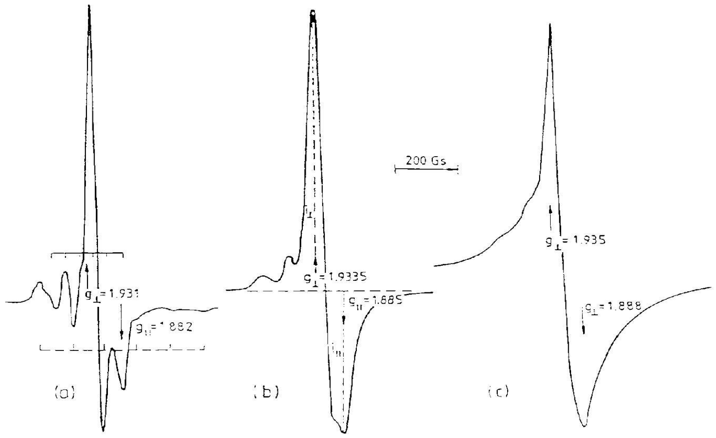

Fig. 5. ESR spectra of Mo^{5+} ions in soda-phosphate glasses with x = 0.5 mol % (a), x = 10 mol % (b) and x = 40 mol % (c).

The increase of the linewidth of the signal from the $g_\perp$ absorption ($\delta B_\perp$) vs. MoO_2 content as a result of the increase of the intensity of the broad line characteristic for associated Mo^{5+} ions is shown in Fig. 6. The composition dependence of asymmetry parameter ($\eta = i_\perp/i_\parallel$) is shown here, too.

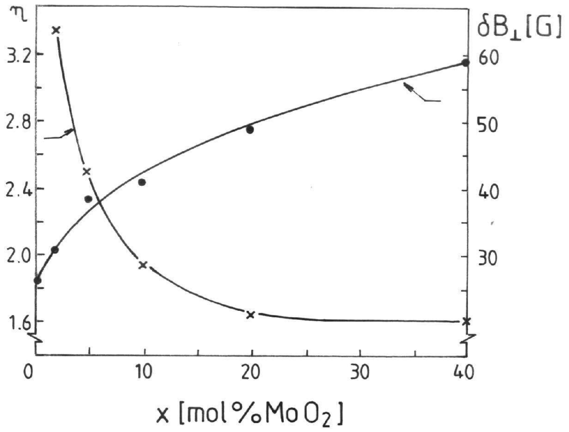

Fig. 6. Asymmetry parameter (η) and linewidth ($\delta B_\perp$) variations vs. MoO_2(x mol%) in soda phosphate glasses

For the assessment of the metal-ligand bonding coefficients in these oxo-molybdenum (MoO^{3+}) compounds, a similar LCAO-MO scheme with that from the case of vanadyl complexes was used.

The bonding coefficients (β_2, β_1, ε) and Fermi contact term (K) obtained by the method reported in [21-23] show a weak covalency for the in plane π bonding ($\beta_2 \cong 0.95$) while the β_1 values(~ 0.72) indicate a high degree of covalency for in plane σ bonding. A strong covalency is also indicated by ε values (~ 0.80) for the out of plane Mo=O bond. This is consistent with the square-pyramidal coordination (C_{4v}) of Mo^{5+} ions in phosphate glasses, the bonding of the sixth oxygen atom coordinated in the transposition with respect to the "yl" oxygen being negligible.

W^{5+} ions adopt in these glasses a rhombic local symmetry and are isolated dispersed even at x = 50 % mol WO_3.

3. Conclusions

ESR results evidenced the presence of the Cu^{2+}, V^{4+}, Mo^{5+} and W^{5+} ions in soda phosphate oxide glasses. These ions are very good as spectroscopic probes in order to characterize the local structure and metal-metal interactions in the studied glasses. The changes in the shape of the ESR spectra and their characteristic parameters determined by the nature and the concentration of transition ions give subtle information about different local structures and specific interaction between metallic ions.

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