

Spectroscopic investigation on some calcium-phosphate glasses

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Phosphate glasses containing transitional metal ions (TMI) are interesting because of their semiconducting and optical properties and because of their potential applications in solid-state lasers and as optical fibres for communication devices. In order to evidence the structural changes induced by CuO and V₂O₅ in the phosphate glass network and their modifier or former role, the following two glass systems were prepared and investigated by EPR and Raman spectroscopy: xCuO(1-x)[P₂O₅.CaO] and xV₂O₅(1-x)[P₂O₅.CaO] with 0 ≤ x ≤ 40 mol%. EPR results obtained for copper doped glasses show $g_{\parallel} > g_{\perp}$ indicating a tetrahedral (T_d) site for Cu²⁺ ions. In the case of vanadium doped glasses, $g_{\parallel} < g_{\perp}$ and indicates that vanadium ions exist in a square pyramidal (C_{4v}) site as VO²⁺ ions. The vibrational bands belonging to the phosphate groups appear clearly in the spectra at low concentration of TMI, but at high concentrations these bands are influenced by those belonging to CuO and V₂O₅ groups; this fact indicates that both oxides act in the phosphate network as modifiers. In the case of vanadium doped glasses, at high concentration of oxide (x > 20 mol%) the bands belonging to the vibration of V₂O₅ groups dominates the spectra while the bands belonging to the phosphate groups are strongly reduced except the specific bands of the short chain phosphate units. From this consideration we can conclude that vanadium prefers to bridge with the oxygen that do not take part in the PO₄ units and in consequence it acts as a network former.

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1. Introduction

Phosphate glasses have been of large interest for a variety of technological applications due to several unique properties such as high thermal expansion coefficient, low viscosity, UV transmission or electrical conduction [1]. Important biological applications for calcium phosphate glasses exist, also, as it was demonstrated that they are biocompatible as bones and dental implants [2,3].

The properties that make phosphate glasses candidates for so many applications are related to their molecular – level structure [4]. The basic building blocks of amorphous phosphates are the P-tetrahedra [4]. They result from the formation of sp³ hybrid orbitals by the P outer electrons (3s 3p³). The fifth electron is promoted to a 3d orbital where strong π – bonding molecular orbitals are formed with oxygen 2p electrons. These tetrahedra link through covalent bridging oxygens to form various phosphate anions. The tetrahedra are classified using the Q_n terminology, where “n” represents the number of bridging oxygen per tetrahedron [5].

The addition of TM oxides to the phosphate glass network leads to a depolymerization of the phosphate chains. It was evidenced that in 40P₂O₅-(60-x)Na₂O-xCuO and 50P₂O₅-(50-x)Na₂O-xCuO glasses the addition of CuO acts as a modifier to depolymerize the phosphate chain and form P-O-Cu linkages [6]. In other glasses containing vanadium oxide xV₂O₅(100-x)NaPO₃ it was evidenced that V₂O₅ acts as a modifier but also as a network former [7].

In fact a very recent problematic related to phosphate glasses doped with TM ions regards the dual role as former and modifier that some TM oxides may have [8].

For evidencing the structural changes induced by CuO and V₂O₅ in the phosphate glass network and their modifier or former role, the following two glass systems were prepared and investigated by EPR and Raman spectroscopy: xCuO(1-x)[P₂O₅.CaO] and xV₂O₅(1-x)[P₂O₅.CaO] with 0 ≤ x ≤ 40 mol%.

2. Experimental

In order to prepare xCuO(1-x)[P₂O₅.CaO] and xV₂O₅(1-x)[P₂O₅.CaO] glasses with 0 ≤ x ≤ 40 mol% we used (NH₄)H₂PO₄, CuO, V₂O₅ and CaO of reagent grade purity. The samples were prepared by weighting suitable amounts of these components, powder mixing and mixture melting in a sintered corundum crucibles at 1250 °C for half an hour. The mixture was put into the furnace directly at this temperature. The melts were poured then on stainless steel plates.

EPR measurements were performed at 9.4 GHz (X-band) at room temperature using a JEOL-JES 3B equipment.

Raman spectra were measured on an Olympus BX-41 Jobin Yvon Horiba with Peltier CCD cooling, using an excitation source of 632.8 nm from a He-Ne laser.

3. Results and discussion

3.1 $xV_2O_5(1-x)[P_2O_5 \cdot CaO]$ glass system

3.1.1 EPR study

EPR spectra for $xV_2O_5(1-x)[P_2O_5 \cdot CaO]$ glasses with $0 \leq x \leq 40$ mol% are given in Fig. 1.

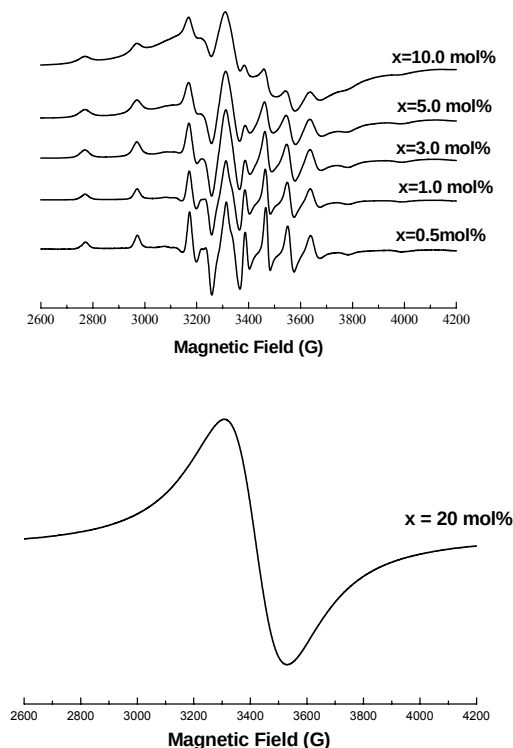


Fig. 1. EPR spectra of $xV_2O_5(1-x)[P_2O_5 \cdot CaO]$ glasses.

The analysis of EPR spectra was made using an axial spin Hamiltonian:

$$B = \beta_0 [g_{\parallel} B_z S_z + g_{\perp} (B_x S_x + B_y S_y)] + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) \quad (1)$$

where β_0 = Bohr magneton, $g_{\parallel}$, $g_{\perp}$ = components of the g tensor, B_x , B_y , B_z = components of the magnetic field, S_x , S_y , S_z = components of the electronic spin operator and I_x , I_y , I_z = components of the nuclear spin operator.

The magnetic field position of the parallel and perpendicular hfs peaks are given by [9]:

$$B_{\parallel}(m) = B_{\parallel}(0) - m A_{\parallel} - A_{\perp}^2 (63/4 - m^2) / 2 B_{\parallel}(0) \quad (2)$$

$$B_{\perp}(m) = B_{\perp}(0) - m A_{\perp} - (A_{\parallel}^2 + A_{\perp}^2) (63/4 - m^2) / 4 B_{\perp}(0) \quad (3)$$

where m = nuclear spin quantum magnetic number, $B_{\parallel}(0) = 4\nu/g_{\parallel}\beta_0$ and $B_{\perp}(0) = 4\nu/g_{\perp}\beta_0$.

Table. 1. EPR parameters of $xV_2O_5(1-x)[P_2O_5 \cdot CaO]$ glass system.

x mol%	$g_{\parallel}$	$A_{\parallel}$ 10^{-4} cm^{-1}	$g_{\perp}$	$A_{\perp}$ 10^{-4} cm^{-1}	K	P 10^{-4} cm^{-1}
0.5	1.94	171.53	2.00	63.22	0.77	130.06
1	1.93	175.47	2.00	59.99	0.73	138.17
3	1.93	185.50	2.004	63.22	0.73	134.90
5	1.94	181.50	2.005	64.50	0.75	141.98

The g and A values obtained in the present work (Table 1) agree with those reported by other authors [10, 11] showing that $g_{\parallel} < g_{\perp} < g_e$ and $A_{\parallel} > A_{\perp}$, relation that corresponds to vanadyl ions in square pyramidal site as C_{4v} symmetry.

Fermi contact interaction term K and dipolar hyperfine coupling parameter P are evaluated by using the expressions developed by Kivelson and Lee [12]:

$$A_{\parallel} = -P [K - 4/7 - \Delta g_{\parallel} - 3/7 \Delta g_{\perp}] \quad (4)$$

$$A_{\perp} = -P [K - 2/7 - 11/14 \Delta g_{\perp}] \quad (5)$$

where $\Delta g_{\parallel} = g_{\parallel} - g_e$, $\Delta g_{\perp} = g_{\perp} - g_e$ and $g_e = 2.0023$.

The values estimated for $K = 0.75$ and $P = 134.9 \times 10^{-4} \text{ cm}^{-1}$ indicates a poor contribution of vanadium 4s orbital to vanadyl bond in this glasses.

3.1.2 RAMAN study

Raman spectra of $xV_2O_5(1-x)[P_2O_5 \cdot CaO]$ with $0 \leq x \leq 40$ mol% are given in Fig. 2.

The most important bands observed in our glasses are: $\sim 350 \text{ cm}^{-1}$ a band assigned to the bending vibration of the phosphate polyhedra; $\sim 710 \text{ cm}^{-1}$ a band assigned to the symmetric stretching vibration of P-O-P bonds; $\sim 1180 \text{ cm}^{-1}$ due to the symmetric stretching vibration in the PO_2 groups; $\sim 1280 \text{ cm}^{-1}$ due to the vibration of the P=O bonds [13-16].

It is known that V_2O_5 have usually a network modifier effect [17] which consist in a depolymerization of the long phosphate chains and in a local reorganization of the structural units in which only the short range phosphate units or ring structure appear. Recently it was suggested that for high concentration of V_2O_5 it can also act as a network former and it is possible to evolve from a phosphate to a pure vanadate network in which PO_4 tetrahedra are isolated [7]. In this respect we can observe that in our glasses for low concentration of V_2O_5 ($x < 10$ mol%) Raman spectra are dominated by the bands belonging to the phosphate chains and for high concentration of V_2O_5 the spectra are dominated by the bands belonging to vanadium oxide.

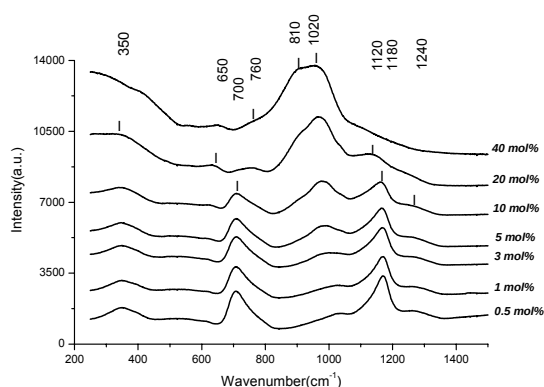


Fig. 2. Raman spectra of $xV_2O_5(1-x)[P_2O_5 \cdot CaO]$ glasses.

For high content of V_2O_5 ($x > 7$ mol%) other bands occur in the spectra : a band at ~ 650 cm^{-1} due to the vibration of P-O-P in-chain, a band at ~ 700 cm^{-1} assigned to P-O-P asymmetric stretching vibration, a shoulder at ~ 900 cm^{-1} due to V-O stretching vibration and a band at ~ 980 cm^{-1} attributed to V=O vibration in the tetragonal pyramid of V_2O_5 . These last two bands are clearly observed in the spectra of the glasses with $x \geq 10$ mol %.

An important remark regards the decrease in intensity of the 710 cm^{-1} band due to the breaking of the P-O-P phosphate chains [15] and to the appearance of short phosphate units or ring structures [14, 17]. The increase in intensity of the band at ~ 650 cm^{-1} is related with the shorter chains or ring structures of phosphate units [14,17]. In the same time a second P-O-P symmetric stretching vibration band due to the PO_4 isolated polyhedra appears at 760 cm^{-1} as the content of PO_4 groups increase when the phosphate chains are breaking [17].

For high content of V_2O_5 ($x \geq 20$ mol%) at ~ 810 cm^{-1} a new band appear, band that other papers [13] ascribe to O-V-O and V-O-V groups but also to very short phosphate chain units [15]. Furthermore the increasing intensity of the band at ~ 1002 cm^{-1} ascribe to short V=O vibration within the VO_5 tetragonal pyramid [18] underline the breaking of the phosphate chains and tendency of V_2O_5 to be a former of the network as these two last bands dominates the spectra at $x = 40$ mol%. It is clearly observed that the bands at 1180 cm^{-1} and 1280 cm^{-1} attributed to PO_2 groups and P=O bonds decrease in intensity up to disappearance because of the formation of $\overline{M} - O \equiv P$ bonds which makes weaker the initial P=O bond. The appearance of V-O-P bonds leads in the same time to the broadening of the 350 cm^{-1} band [16,19].

3.2 $xCuO(1-x)[P_2O_5 \cdot CaO]$ glass system

3.2.1 EPR study

EPR spectra of $xCuO(1-x)[P_2O_5 \cdot CaO]$ glasses with $0 \leq x \leq 40$ mol% are given in Fig. 3.

The shape of these spectra for $x \leq 10$ mol% are typical for Cu^{2+} isolated ions having four well resolved bands in the parallel absorption band. The hfs is not resolved at all in the perpendicular band. With the increase of CuO content ($x \geq 20$ mol%) the spectra becomes a broad line with $\Delta B \sim 300$ Gs typical for clustered ions.

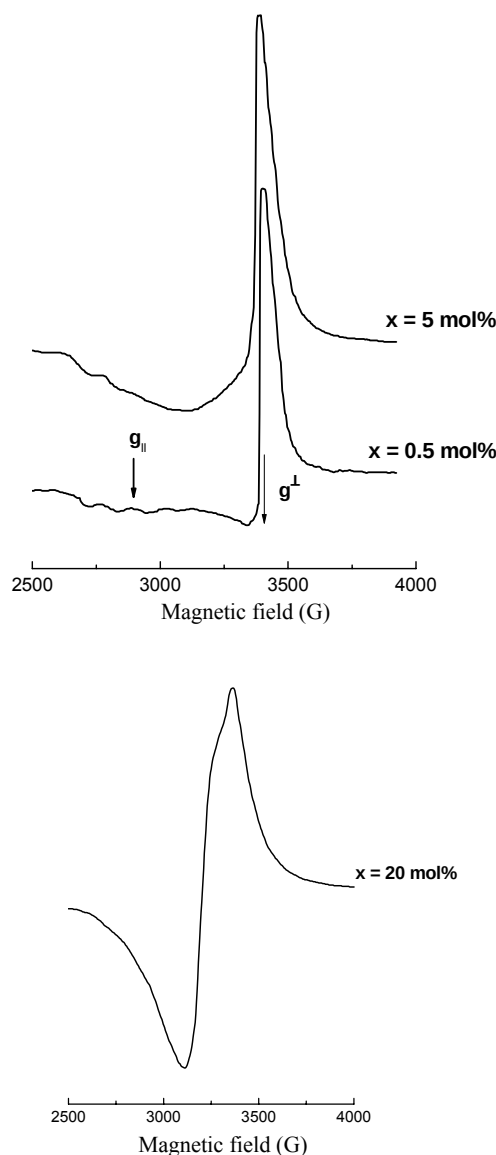


Fig. 3. EPR spectra of $xCuO(1-x)[P_2O_5 \cdot CaO]$ glasses.

Characteristic EPR parameters of these glasses are given in Table 2. The values of $g_{\parallel}$ and $A_{\parallel}$ parameters suggest that Cu^{2+} ions are in a tetrahedral site T_d [9,20,21]. In this supposition the paramagnetic “hole” is not in a pure 3d orbital, but in a state containing an admixture of 3d wave function with 4p wave function [9]. Thus the ground state for the paramagnetic “hole” is the following molecular orbital:

$$|xy\rangle = a d_{xy} + a' \Phi_L(xy) + a'' p_z \quad (6)$$

where d_{xy} and p_z orbitals belong to Cu^{2+} ion and $\Phi_L(xy)$ correspond to the ligand contribution.

The relation between EPR parameters ($g_{\parallel}$ and $A_{\parallel}$) and MO coefficients [9] is given by the relations:

$$g_{\parallel} = 2.0023 - 8\lambda_d \alpha^2 \beta^2 / \Delta_{x^2-y^2} \quad (7)$$

$$A_{\parallel} = \theta + P_d [-4\alpha^2/7 + 8\lambda_d \alpha^2 \beta^2 / \Delta_{x^2-y^2} + 6\lambda_d \alpha^2 \delta^2 / \Delta_{xz}] + P_p [4(\alpha'')^2/5 + 6\lambda_p (\alpha'')^2 (\delta'')^2 / 7\Delta_{xz}] \quad (8)$$

where: Δ_{xz} and $\Delta_{x^2-y^2}$ denote the optical d-d transitions between $|xy\rangle - |xz\rangle$, $|yz\rangle$ states and $|xy\rangle - |x^2-y^2\rangle$ respectively; λ_d and λ_p are the spin-orbit coupling parameters for 3d and 4p electrons; K is the isotropic Fermi contact term and P_p , P_d are the dipolar hyperfine parameters.

Table 2. EPR parameters for $x\text{CuO}(1-x)[\text{P}_2\text{O}_5\cdot\text{CaO}]$ glass system.

x mol%	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel} 10^{-4} \text{ cm}^{-1}$	α^2	$(\alpha'')^2$
0.5	2.389	2.039	131.14	0.73	0.04
1	2.406	2.045	131.14	0.77	0.04
3	2.397	2.041	120.46	0.75	0.05
5	2.418	2.040	118.05	0.79	0.05

The small values obtained for $A_{\parallel}$ arises from the contribution of the p-type wave function which has a canceling effect of the d-type wave function, for it always appears with an opposite sign. Thus, a small admixture of $4p_z$ orbital in the $3d_{xy}$ ground state leads to a considerable diminishing of the hyperfine splitting [9]. Taking into account the values of EPR parameters we consider that for the investigated glasses $\Delta_{x^2-y^2} = 11500 \text{ cm}^{-1}$ and $\beta^2 = 0.9$. From eq. 8 and $A_{\parallel}$ values the $(\alpha'')^2$ coefficient was also estimated (Table 2). This suggest that in the studied phosphate glasses an admixture of about 4% of the $4p_z$ character in the $3d_{xy}$ ground state of Cu^{2+} ion exist.

The covalency parameter α^2 for the in-plane σ -bonding ($\alpha^2 \sim 0.75$) indicates a moderate covalency and it is relatively insensitive to the composition [11].

The results obtained by us are in good agreement with those reported in other papers [22-25].

3.2.2 Raman study

Raman spectra of $x\text{CuO}(1-x)[\text{P}_2\text{O}_5\cdot\text{CaO}]$ with $0 \leq x \leq 40 \text{ mol}\%$ are given in Fig. 4.

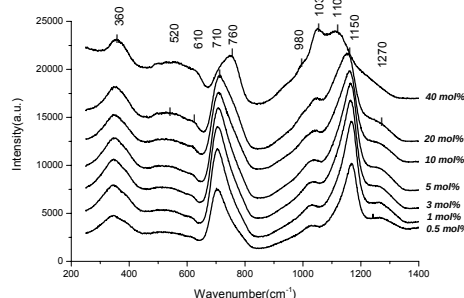


Fig. 4. Raman spectra of $x\text{CuO}(1-x)[\text{P}_2\text{O}_5\cdot\text{CaO}]$ glasses.

The main bands observed in the spectra are: $\sim 350 \text{ cm}^{-1}$, $\sim 520 \text{ cm}^{-1}$, $\sim 610 \text{ cm}^{-1}$, $\sim 710 \text{ cm}^{-1}$, $\sim 980 \text{ cm}^{-1}$, $\sim 1030 \text{ cm}^{-1}$, $\sim 1150 \text{ cm}^{-1}$ and $\sim 1270 \text{ cm}^{-1}$.

The evolution of these bands is influenced by the CuO content. The band at $\sim 350 \text{ cm}^{-1}$ is due to the network bending vibrations and also to Cu-O-P vibrations [16, 26]. This band is constant with the content of the modifying oxide; this shows that PO_4 chains still exist in the structure of the glass at high content of CuO comparing with the same band obtained in the case of $x\text{V}_2\text{O}_5(1-x)[\text{P}_2\text{O}_5\cdot\text{CaO}]$ glasses which at high content of V_2O_5 disappeared as PO_4 chains were broken.

The bands at $\sim 520 \text{ cm}^{-1}$ and $\sim 610 \text{ cm}^{-1}$ belong to a complex of vibrations due to P-O-P, Cu-O and P-O-Cu chains [13]; their increasing intensity suggest a partial depolymerization of the phosphate chains.

The band at $\sim 710 \text{ cm}^{-1}$ is attributed to P-O-P in-chains stretching vibrations. The band has a shift at 760 cm^{-1} for $x > 20 \text{ mol}\%$, due to a change in the in-chain P-O-P bond angle because of CuO effect [15].

The bands at $\sim 980 \text{ cm}^{-1}$ and $\sim 1030 \text{ cm}^{-1}$ belongs to the vibration of PO_3 and PO_2 groups [22]. Both bands increase in intensity as the phosphate chains breaks and the number of PO_2 and PO_3 increase for $x > 20 \text{ mol}\%$.

The bands at 1150 cm^{-1} and 1270 cm^{-1} belong to PO_2 symmetric and asymmetric stretching vibrations [27]. The decrease in intensity of these two bands with the increase of CuO content is characteristic of phosphate glasses and consistent with the depolymerization of the three dimensional network [15, 27].

4. Conclusions

EPR analysis indicates a C_{4v} symmetry for vanadyl ions and a T_d symmetry for copper ions in the studied glasses.

For high content of V_2O_5 ($x > 10 \text{ mol}\%$) and CuO ($x \geq 20 \text{ mol}\%$) clustered ions were evidenced from the shape of the EPR spectra.

The addition of TM oxides in both studied glass systems leads to the depolymerization of the phosphate network; as a consequence both V_2O_5 and CuO act as network modifiers but for high concentration of V_2O_5 it seems to act also as a network former.

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