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EPR and Raman investigation of some fluoro-calcium phosphate glasses containing copper ions

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The $xCuO(1-x)[P_2O_5 \bullet CaF_2]$ glass system with $0 \le x \le 40\%$ mol was prepared and investigated by means of EPR and Raman spectroscopy in order to evidence the structural changes induced by the content of copper oxide and its modifier role. EPR analysis indicates a change of the coordination polyhedra of Cu^{2+} ions from a tetragonal to a tetrahedral local symmetry in the studied glasses. For high content of CuO ($x \ge 10$ mo l%) the presence of clustered copper ions was evidenced from the spectra. Raman spectra of the studied glasses contain the typical bands attributed to the phosphate glasses. It can be observed that the band at ~980 cm^{-1} attributed to symmetric stretching vibrations in PO_4 and ~1030 cm^{-1} due to symmetric stretching vibrations in PO_3 groups slowly increase in intensity as the phosphate chain breaks and so a larger number of PO_3 and PO_4 are formed. The band at 1280 cm^{-1} belonging to the symmetric stretching vibrations in P = O double bonds decrease in intensity with increasing the CuO content and this fact is consistent with the depolymerization of the three dimension phosphate network.

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1. Introduction

Phosphate glasses doped with transition metal ions have attracted interest because of their potential applications. The addition of modifier cations in the phosphate network results in glasses which possess a large variety of properties for potential applications as bioactive materials, sensor applications, glass-to-metal sealing, optoelectronic devices, laser host glasses and solid state ionic conductors [1-3]. The various properties of the glasses are determined by the type of modifier cations and the degree of depolymerization of the phosphate network [4,5].

EPR and optical absorbtion techniques have been used to obtain information about the nature of the ground state of paramagnetic ions in the glasses and their local site symmetries [6]. Phosphate glasses containing copper oxide have received much attention due to the existence of copper ions in both Cu^+ and Cu^{2+} valence state [7] but also to their ability to accommodate to high concentration of transition metal ions and remain amorphous [8].

Raman studies of phosphate glasses have shown that the modifier cations (Cu^{2+}, V^{4+}, Mo^{5+}, Fe^{3+}) produce a drastic depolymerization of the phosphate network and form P-O-metal bonds which have been suggested that give an improvement in the chemical durability of the phosphate glasses [1].

Similar studies were carried out on the phosphate matrix $[P_2O_5 \bullet CaF_2]$ or $[P_2O_5 \bullet CaO]$, but containing vanadium or a combination of vanadium and copper ions [4, 9]. Raman results on the mentioned glass systems pointed out that vanadium oxide acts not only as a network modifier but also as a network former for high content of V_2O_5 ($x > 20$ mol%)

This paper presents the results of EPR and Raman spectroscopy for $CuO-P_2O_5-CaF_2$ glass system. The interest lies on the nature of the ground state of the paramagnetic ions, their local symmetry and also on their modifier role in the paramagnetic network.

2. Experimental

In order to prepare $xCuO(1-x)[P_2O_5 \bullet CaF_2]$ glasses with $0 \le x \le 40$ mol% we used $(NH_4)H_2PO_4$, CuO, and CaF_2 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 ºC for half an hour. The mixture was put into the furnace directly at this temperature. The melts were poured then on stainless steel plates.

XRD spectra of the studied glasses have shown that all the samples are vitreous samples and they do not present any crystalline phase (Fig.1).

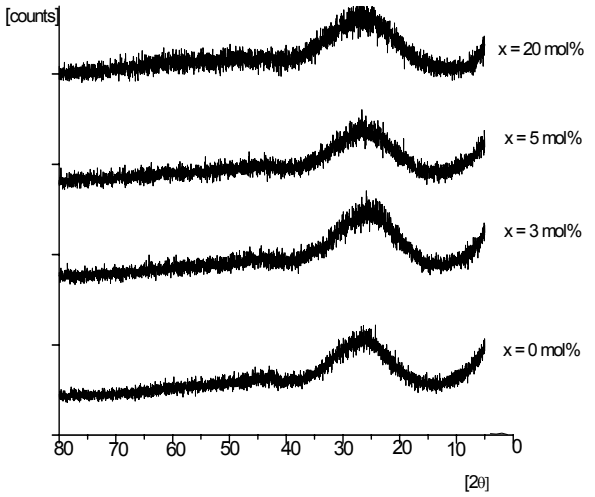

Fig.1. XRD spectra of some xCuO (1-x)[P_2O_5·CaF_2] glasses.

EPR measurements were performed at 9.4 GHz (X-band) at room temperature using an ADANI type spectrometer.

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

3.1 EPR spectra

EPR spectra of some xCuO(1-x)[P_2O_5.CaF_2] glasses with $0 \leq x \leq 40$ mol% are given in Fig. 2.

The EPR spectra of Cu^{2+} ions exhibits hyperfine structure (HFS) having a quartet of hyperfine lines in the parallel increases ($x \geq 5$ mol%) the HFS components begin to broaden due to spin-spin interactions; then the HFS disappears and the EPR spectra tend to take an isotropic form ($x \geq 10$ mol%). At further increase in band. When the concentration of Cu^{2+} ions the Cu^{2+} concentration the spectra consist from a symmetric line ($\Delta B \sim 315$ G) due to the presence of isotropic exchange interaction between paramagnetic ions [2,10].

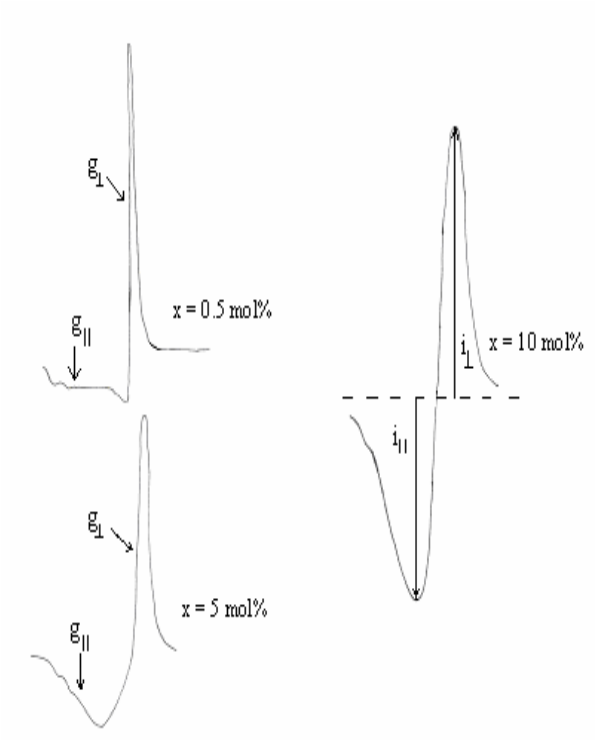

Fig. 2. EPR spectra of xCuO(1-x)[P_2O_5·CaO] glasses.

The spin Hamiltonian parameters evaluated from the observed spectra are given in Table 1. It can be seen that $A_\parallel$ and $g_\parallel$ values are very sensitive to glass composition suggesting the modification of the local environment of Cu^{2+} ions [11]. The values obtained at x = 0.5 mol% ($g_\parallel$ = 2.38; $A_\parallel$ = 172.15 10^{-4} cm^{-1}) indicate a hexacoordinated tetragonal symmetry. With the increase of CuO content $g_\parallel$ and $A_\parallel$ become 2.44 and 114.77 10^{-4} cm^{-1} respectively for x= 5 mol%. These values are characteristic for tetracoordinated Cu^{2+} ions in tetrahedral local symmetry [12,9]. In this case the paramagnetic "hole" is not in a pure 3d orbital, but in a state containing an admixture of 3d and 4p orbitals [12].

Table 1. EPR parameters for xCuO(1-x)[P_2O_5.CaO] glass system.

x mol%	$g_\parallel$	$g_\perp$	$A_\parallel$ 10^{-4} cm^{-1}	α^2	$(\alpha'')^2$
0.5	2.38	2.04	172.15	0.73	0.04
1	2.40	2.04	155.75	0.77	0.04
3	2.42	2.03	127.68	0.81	0.05
5	2.44	2.02	114.77	0.84	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 ($(\alpha'')^2$ = 0.04-0.05, Table 1) in the $3d_{xy}$ ground state leads to a considerable diminishing of the hyperfine splitting [12], α'' being the mixture coefficient of the two mentioned orbitals.

The variation of α parameter for the in-plane σ-bonding (α^2 = 0.73-0.84) indicates a decrease of the covalency degree.

By defining the asymmetry parameter η as the ratio of the heights of $g_\perp$ and $g_\parallel$ absorptions, a decrease of η values can be observed (Fig. 3). This fact is explained by the increasing of the number of Cu^{2+} clustered ions with CuO content. These ions are manifesting in the spectra by a single symmetric line at g ~ 2.

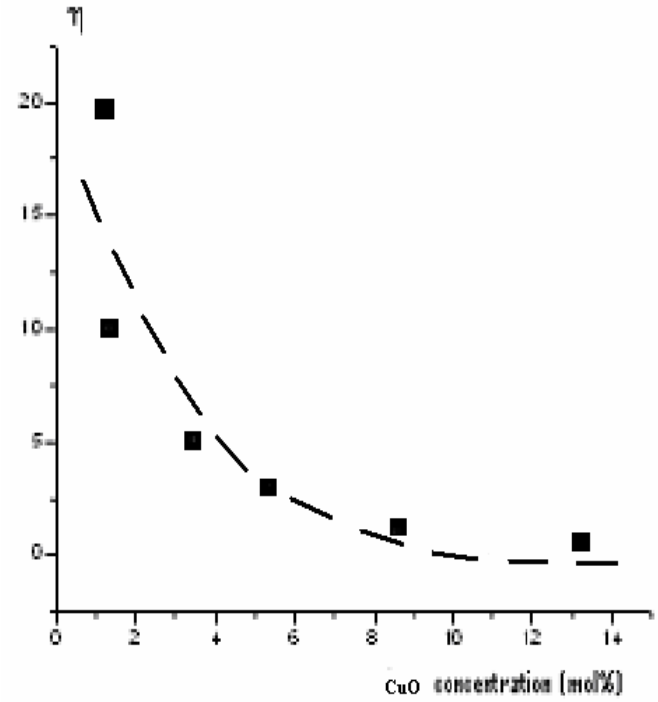

Fig. 3. The composition dependence of the asymmetry parameter.

3.2 Raman spectra

Raman spectra of $xCuO(1-x)[P_2O_5 \cdot CaF_2]$ glass system with $0 \leq x \leq 40$ mol% are given in Fig. 4. The main bands and their attributions for the studied glasses are given in Table 2.

Table 2. Raman bands assignment for $xCuO(1-x)[P_2O_5 \cdot CaF_2]$ glasses.

Wavenumber (cm^{-1})	Band assignment
~ 350	the network bending vibrations and Cu-O-P vibrations
~ 720	P-O-P in-chains stretching vibrations in the long chain phosphate species
~980	symmetric stretching vibrations in PO_4 groups
~1030	symmetric stretching vibrations in PO_3 groups
1150 - 1180	symmetric stretching vibrations in PO_2 groups or "strained" structures
~ 1280	symmetric stretching vibrations in P= O bonds

The evolution of these bands is influenced by the CuO content.

The band at ~350 cm^{-1} is approximately constant with the rate of the modifier oxide and this shows that PO_4 chains exist in the structure of the glass for both small and high CuO content [13,14].

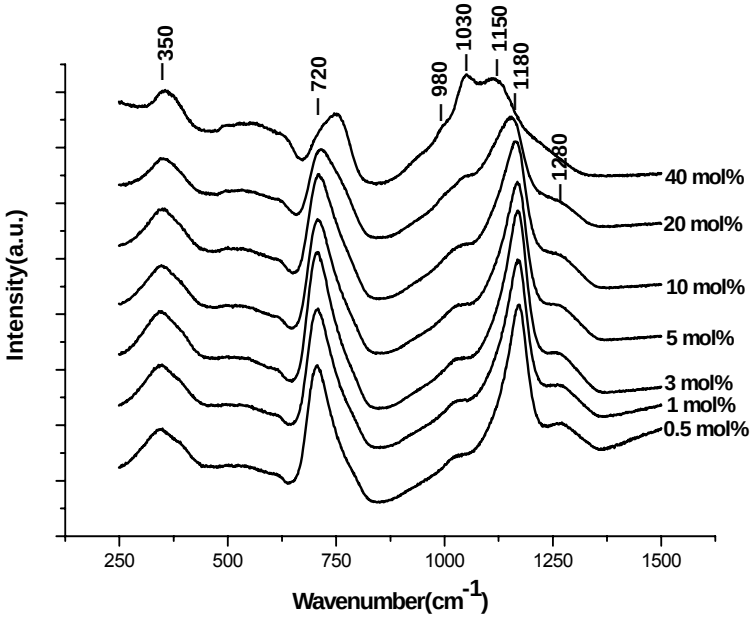

Fig. 4. Raman spectra of xCuO(1-x)[P2O5•CaF2] glass system.

The asymmetric band at ~720 cm^{-1} has a shift of ~ 40 cm^{-1} for $x \geq 20$ mol%, due to the change of the in-chain P-O-P bond angle because of CuO effect. A higher wavenumber of this band is a result of a smaller P-O-P bond angle which results from a shorter phosphate chain length due to the depolymerization of the phosphate structure with the addition of Cu^{2+} ions [7]. Thus the position of this band shifts to a larger wavenumber with increasing CuO content.

The band at ~ 980 cm^{-1} and ~1030 cm^{-1} belongs to the symmetric stretching vibrations in PO_4 out of chain groups and PO_3 groups respectively [11]. The bands slowly increase in intensity as the phosphate chains breaks and the number of PO_3 and PO_4 groups increase ($x \geq 20$ mol%).

The band at ~1180 cm^{-1} belongs to PO_2 symmetric stretching vibrations [7,14]. The decrease in intensity of this band and the shift to 1150 cm^{-1} with the increase of CuO content is consistent with the depolymerization of the three dimensional network [7]. Rouse at al. [7,17] have shown that as the metal oxygen bond force increase the average PO_2 angle decrease and in consequence PO_2

symmetric stretching vibrations increase in frequency. This band is often attributed in literature [14] to some "strained" structures; their presence as distinct bands rather than a broadening of the main band suggests a specific structure. Similar features were found in some borate glasses [15] or in some silicates including those prepared by sol-gel method [16].

The band at ~1280 cm^{-1} is due to the symmetric stretching vibrations of P=O double bond. The decrease in intensity of this band is explained by breaking the P=O initial bond and the formation of some new Cu-O-P bonds [4] with the depolymerization of the phosphate network.

4. Conclusions

EPR analysis indicates a change of the coordination polyhedra of Cu^{2+} ions from a tetragonal to a tetrahedral local symmetry in the studied glasses. For high CuO content ($x \geq 10$ mol %) the presence of clustered ions results from the spectra. Raman scattering of copper phosphate glasses is affected by CuO content. The intensities of the bands due to P=O and P-O-P groups gradually decrease whereas those belonging to PO_3 and PO_4 vibrations increase as CuO is added to the phosphate glass. This is due to the convertion of P-O-P bridging oxygen to P-O-Cu bridging oxygen and in consequence to the depolymerization of the phosphate network that occurs at high rate of Cu^{2+} ions.

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