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Raman and EPR investigation of some lead-phosphate glasses with vanadium and copper ions

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$x(CuO\bullet 2V_2O_5)(1-x)[2P_2O_5\bullet PbO]$ glass system with $0 \leq x \leq 40$ mol% was investigated by EPR and Raman spectroscopy in order to see the structural changes induced by both copper and vanadium ions in different ratios and their modifier or former role. EPR spectra and parameters ($g_\parallel = 2.44$, $g_\perp = 2.08$ and $A_\parallel = 117.6\bullet 10^{-4}$ cm^{-1}) obtained for the studied glasses with x≤10 mol% suggest a tetrahedral (Td) coordination of Cu^{2+} ions and not a tetragonally elongated octahedron as has been assumed in previous works. The resonance parameters for V^{4+} suggest a pentacoordinated C_{4v} local symmetry for them. The hyperfine structures characteristic for Cu^{2+} and V^{4+} ions disappear for 10≤x≤40 mol% due to the mixed exchange Cu^{2+}-V^{4+} pair formation in these glasses. Raman spectra of the studied glass system show for low concentration of ions the specific bands belonging to the phosphate groups, but at high concentration of V^{4+} (x ≥20 mol%) the bands belonging to the vibration of V_2O_5 groups dominates the spectra. In the same time the bands belonging to the phosphate groups are strongly reduced except the specific bands of the short chain phosphate units. This suggest that in the studied glasses vanadium acts as a network former at high concentration of V_2O_5.

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1. Introduction

Phosphate glasses doped with transitional metal (TM) ions are technologically important because of their semiconducting properties, optical absorption, memorizing and photoconducting properties which makes them suitable for a lot of applications [1-3].Vanadium and copper ions are very suitable to be used in glasses because they are characterized by partially filled d shell which can exist in at least two valency states [3].

Majumdar et al. [4] found that chromium, manganese or vanadium are almost completely reduced while copper, molybdenum, titanium remain mostly in the higher valency states. A lot of papers [3,5-7] showed that in vanadium doped phosphate glasses the main redox state is V^{4+} but spectroscopic data show the appearance of vanadyl VO^{2+} ions. Copper ions introduced in sodium phosphate glasses [3,8] exist in Cu^{2+} valence state and similar results were obtained for copper in calcium phosphate glasses [6].

A new problem related to phosphate glasses containing TM oxides is related with their mixed dual role, as modifiers but also as network formers. It was demonstrated by means of Raman spectroscopy that tungsten, iron or vanadium ions act as network modifiers but also as network formers depending by their concentration in the glass matrix. [6,8,9].

In order to put in evidence the structural changes induced by CuO and V_2O_5 in lead phosphate glasses and their modifier or former role $x(CuO\bullet 2V_2O_5)(1-x)[2P_2O_5\bullet PbO]$ glass system with $0 \leq x \leq 40$ mol% was prepared and investigated by means of Raman and EPR spectroscopy.

2. Experimental

In order to prepare $x(CuO\bullet 2V_2O_5)(1-x)[2P_2O_5\bullet PbO]$ glass system with $0 \leq x \leq 40$ mol% we used $(NH_4)H_2PO_4$, CuO, V_2O_5 and PbO 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.

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. Raman spectroscopy

The network structure of phosphate glasses is based as it is known from literature [1,10] upon tetrahedral PO_4 structural units. An additional π- bond is created with an P atom and one of the neighbouring oxygen. The excess of terminal oxygen atoms makes phosphate glasses suitable for various modifier cations as vanadium or copper ions.

Structural units that can be built from individual phosphorous centers were described by Van Wazer [11]. As the oxides are added to P_2O_5, structural groups pass from Q_3 to Q_2, Q_1 and Q_0 where Q_n with n = 0, 1, 2, 3 represents the number of bridging oxygen per tetrahedron [12].

This structural reduction from a long – chain phosphate network to very short chain phosphate units or ring structures [9,13] indicating the depolymerization of the phosphate network and the formation of P-O-V and P-O-Cu bonds can be clearly observed in the Raman spectra of the studied glasses (Fig. 1)

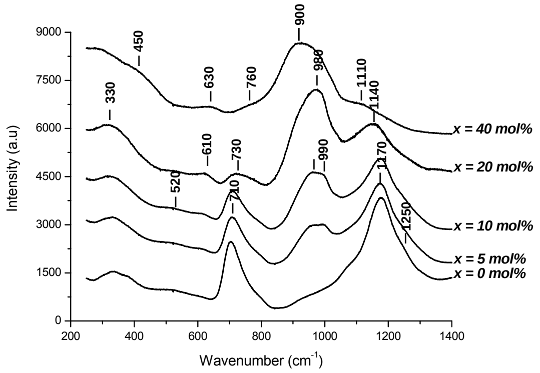

Fig. 1.Raman spectra of x(CuO•2V_2O_5)(1-x)[2P_2O_5•PbO] glass system.

Recent papers [6,8] reported the dual role of V_2O_5 introduced in the phosphate glasses. This means that V_2O_5 acts partly as a network modifier and partly as a network former oxide. In this second case, it is possible that the network evolve from a phosphate to a pure vanadate network in which PO_4 tetrahedra are isolated.

The Raman spectra of the studied glasses (Fig. 1) suggest this dual role of vanadium oxide as for low concentration of V_2O_5 the spectra are dominated by the bands belonging to phosphate groups and for high concentration of V_2O_5 the spectra are dominated by the bands belonging to vanadate groups.

Table 1 indicates the values and the bands attribution in x(CuO•2V_2O_5)[2P_2O_5•PbO] glass system.

Table 1. Band assignement for different vibration bands in the Raman spectra of x(CuO•2V_2O_5)[2P_2O_5•PbO] glass system.

ν (cm^{-1})	Band assignment
330 - 450	bending modes of the chain network and O-P-O in Q_0 units
~ 520	bending modes of the chain network and vibrations of V-O-V modes
610 – 630	P-O-P symmetric stretching in Q_2 units
630 - 760	V-O-V, P-O-P and V-O-P combination of various vibrations
710 – 730	P-O-P symmetric stretching in Q_1 units
940 – 980	vibrations of PO_4^{3-} in Q_0 units
~ 920	V=O vibration in the VO_5 tetragonal pyramid
1110 -1170	vibrations of PO_2^- in Q_2 units
1250	symmetric stretching of P=O bond

The bands obtained in the region of 330-520 cm^{-1} are attributed to the bending vibrations of O-P-O of the phosphate chains [2,7]. The bands around ~ 520 cm^{-1} can be also assigned to low energy vibrations of V-O-V chains. For high concentration of V_2O_5 and CuO ($x \geq 20$ mol%) a small shoulder at ~ 450 cm^{-1} appears, characteristic to O-P-O bending vibrations in Q_0 units specific to isolated PO_4 groups.

The band observed at 610-630 cm^{-1} belong to symmetric stretching vibration in Q_2 units; this band decrease increase in intensity and this fact is related with the formation of isolated phosphate chains with the addition of modifier transitional ions. The shift of the band at 610 cm^{-1} is due to the formation of new V-O-P or V-O-V bonds in the region 630 – 730 cm^{-1} with the depolymerization of the phosphate network [2,5,14]. The bands observed in the region 710-760 cm^{-1} are characteristic to P-O-P symmetric stretching in Q_1 [2] units and also decrease in intensity ($x \geq 20$ mol%) probably for the same reason already mentioned.

The band at 900-940 cm^{-1} is assigned to the PO_4^{3-} ionic groups in Q_0 units [2, 5]. As it was expected, this band increase in intensity with the formation of isolated structural units or ring units at high concentration of TM ions. A new band at ~ 980 cm^{-1} strongly increase in the spectra; this band is attributed to V=O [5] vibration with the formation of individual vanadate groups when the content of V_2O_5 increase. This is an important information because it suggest that at high concentration of V_2O_5, vanadium atom prefers to bridge to a free oxygen and not to one belonging to the PO_4 units and in consequence it acts as a network former.

The band at ~1170 cm^{-1} attributed to vibrations of PO_2^- in Q_2 units [2,9] shifts to lower wavenumber and decrease in intensity with the formation of isolated Q_0 groups.

The band at ~1250 cm^{-1} is assigned to the vibration of P=O double bond [5,6] and appears in the spectra only at low concentration of TM ions only as a small shoulder. For medium and high concentration of modifier ions this shoulder disappears because new M-O-P bonds are created which make weaker the initial P=O bond.

4. EPR spectroscopy

EPR spectra of x(CuO•2V_2O_5)[2P_2O_5•PbO] glasses for x <10 mol% show a well-resolved hyperfine structure typical for isolated Cu^{2+} and V^{4+} ions (Fig.2) while for $x \geq 10$ mol% the hyperfine structures disappear and a broad line characteristic for the clustered ions appear. With the increasing of TM ions content the number of clustered ions increases and the super-exchange interactions prevail, leading to the formation of mixed Cu^{2+} -V^{4+} pairs.

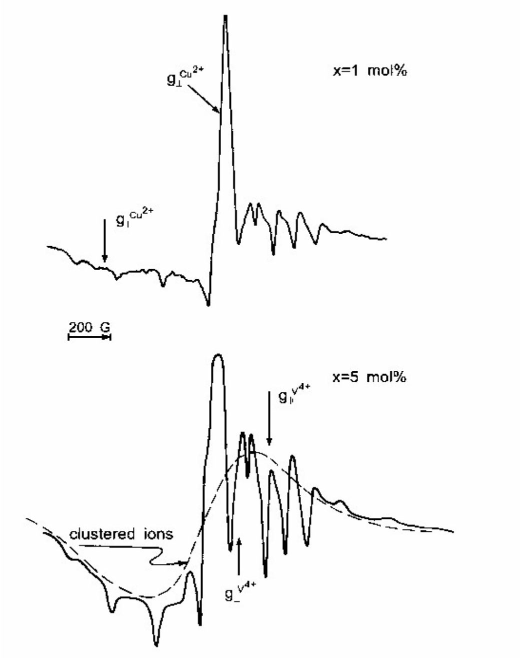

Fig. 2. EPR spectra of $x(CuO{\bullet}2V_2O_5)(1-x)[2P_2O_5{\bullet}PbO]$ glass system.

The values of g and A parameters obtained for Cu^{2+} ions (Tab.2) are suggesting a tetrahedral T_d coordination for these ions [6] and not a tetragonally elongated octahedron D_{4h} as has been assumed in other papers [3, 15-18]. This configuration may be attributed to the polymeric structure of the phosphate glasses which involve a weak Cu-O bond along Oz-axis and a notable distortion of the other four Cu-O bonds from the planar structure D_{4h} to the tetrahedral configuration T_d. In this hypothesis the paramagnetic "hole" is not a pure 3d orbital, but a state containing an mixture of 3d wave function with 4p wave function.

Table 2. EPR parameters for Cu^{2+} ions in $x(CuO{\bullet}2V_2O_5)(1-x)[2P_2O_5{\bullet}PbO]$ glass system.

x (mol%)	$g_\parallel$	$g_\perp$	$A_\parallel$ ($10^{-4}cm^{-1}$)	α^2	$(\alpha'')^2$
1	2.465	2.080	102.01	0.89	0.07
3	2.440	2.084	109.14	0.84	0.06
5	2.445	2.082	109.37	0.85	0.06

The large values of g and the small values of A aris from the contribution of p - type wave function which has a canceling effect of the d – type wave function, for it always appear with an opposite sign. In consequence, a small admixture of $4p_z$ orbital in the $3d_{xy}$ ground state [6,19,20] leads to an important diminishing of the hyperfine splitting [20,21]. $(\alpha'')^2$ coefficient calculated according [21-23] suggests for the studied glasses an admixture of about 6% of the $4p_z$ character in the $3d_{xy}$ ground state.

EPR parameters for V^{4+} ions (Tab.3) were evaluated by using relations known in papers [3,24-29] and they are consistent with a square –pyramidal C_{4v} coordination specific for vanadyl ions.

Table 3. EPR parameters for V^{4+} ions in $x(CuO{\bullet}2V_2O_5)(1-x)[2P_2O_5{\bullet}PbO]$ glass system.

x (mol %)	$g_\parallel$	$g_\perp$	$A_\parallel$ ($10^{-4}cm^{-1}$)	$A_\perp$ ($10^{-4}cm^{-1}$)	β^2	K	P ($10^{-4}cm^{-1}$)
1	1.929	1.988	172	72	0.90	0.90	117
3	1.931	1.992	185	74	0.91	0.85	131
5	1.929	1.990	184	72	0.89	0.83	132

Fermi contact term K, β^2 coefficient and dipolar hyperfine coupling parameter P evaluated with Kivelson and Lee [30] show a weak covalence degree for the in – plane π – bond and a great tetragonal character of the coordination polyhedra with a strong V=O bond along the z-axis[3,5,31].

By increasing the TM ions content in the studied glass systems ($x \geq 10$ mol%) a broad line with $\Delta B > 300G$ appears in the spectra suggesting the appearance of mixed exchange Cu^{2+} -V^{4+} pairs [31, 32].

5. Conclusions

Raman spectra of the studied glasses put in evidence the specific bands for the phosphate groups and for vanadium and copper oxides for different content of TM ions.

The addition of TM oxides (V_2O_5 and CuO) in the studied glass system leads to the depolymerization of the phosphate network acting as network modifiers.

For high concentration of V_2O_5 ($x \geq 20$ mol%) it seems to act also as a network former because its specific bands dominate the spectra.

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

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

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