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Spectroscopic investigation of some lead – phosphate glasses with tungsten and molybdenum ions

O. COZAR*, D. A. MAGDAS, I. ARDELEAN
Faculty of Physics, Babes-Bolyai University, 400084 Cluj-Napoca, Romania

The structure of $xWO_3\cdot(100-x)[2P_2O_5\cdot PbO]$ and $xMoO_3\cdot(100-x)[2P_2O_5\cdot PbO]$ glass systems with $0\leq x\leq 50$ mol% is investigated by IR, Raman and EPR spectroscopy. The characteristic absorption bands of these glasses due to the stretching and bending vibrations are identified and analyzed by the increasing of molybdenum and tungsten oxides content. These allowed us to identify the specific structural units which appear in these glasses and thus to point out the network modifier role for low concentrations and the former role at high concentrations of the tungsten and molybdenum oxides. EPR data show also that for $x \leq 10$ mol% the isolated Mo^{5+} and W^{5+} ions prevail in a square – pyramidal form (C_{4v}) and rhombic symmetry respectively. At high MoO_3 content ($x > 20$ mol%) the dipole – dipole and superexchange coupled Mo^{5+} ions appear. This fact does not occur in case of W^{5+} ions because of their small number.

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1. Introduction

The most common glasses are formed by mixing “glass forming substances” (typically, SiO_2, B_2O_3, P_2O_5) with “modifier” metal oxides. The oxygen from this metal oxide becomes part of the covalent glass network by creating more disorderly in the glasses. Many glass properties can be controlled by changing the structural units shape of the network former. The structural characterization of glasses with competitive network formation is a challenging task, because we have to determine whether the coordination of a glass former changes when mixed with another one, and how the modifiers oxygens are distributed among the units of the different species [1].

Phosphate glasses generally have low glass transition temperatures and thermal expansion coefficients larger than those found for silicate glasses, making them candidates for some glass-to-metal sealing applications. In addition, phosphate glasses have been proposed as laser hosts and solid state ionic conductors [2].

Lead oxide has been used as a constituent in several borate and phosphate glasses in order to achieve useful physical properties. The P-O-Pb bonds which appear in lead-phosphate glasses offer these a chemical durability; reduce the dissolution rate and melting temperature [3,4].

Tungsten-phosphate and molybdenum-phosphate glasses belongs to a group of glasses which incorporate distorted octahedral structural units $[MeO_6]$, (Me=Mo, W] within the glass network and whose structure is not well understood [5,6]. Beside they exhibit interesting electrochromic properties and high ionic conductivity that makes them potential materials for electro-optical applications [6,7].

In order to obtain further information on the local structure of these glasses the $xWO_3\cdot(100-x)[2P_2O_5\cdot PbO]$ and $xMoO_3\cdot(100-x)[2P_2O_5\cdot PbO]$ systems with $0\leq x\leq 50$ mol% where prepared and investigated by FT-IR, Raman and EPR spectroscopies.

2. Experimental Details

The starting materials used in the present investigation were $(NH_4)_2HPO_4$, PbO, WO_3 of reagent grade purity for the $xWO_3\cdot(100-x)[2P_2O_5\cdot PbO]$ system and $(NH_4)_2HPO_4$, PbO, MoO_3 of reagent grade purity for the $xMoO_3\cdot(100-x)[2P_2O_5\cdot PbO]$. The samples were prepared by weighing suitable proportions of the components, powder mixing and mixture melting in sintered corundum crucibles at 1250^0C for five minutes. The mixtures were put into the furnace directly at this temperature. For obtain the glass samples, the melts were poured onto stainless steel plates at room temperature.

The FT-IR absorption spectra of the glasses in the 400-1500 cm^{-1} spectral range were obtained with an Equinox 55 Bruker spectrometer. The IR absorption measurements were done using the KBr pellet technique. In order to obtain good quality spectra, the samples were crushed in an agate mortar to obtain particles of micrometer size. This procedure was applied every time to fragments of bulk glass to avoid structural modifications due to ambient moisture.

Raman spectra were obtained by means of a Horiba Jobin Yvon LabRam-HR system equipped with Olympus BX41 optical microscope, a grating with 1800 grooves per millimetre, and Peltier-cooled, Si-based CCD (charge-coupled device) detector. Spectra were excited using the 514.5 nm emission line of an argon ion laser. The laser power was about 1.5 mW (measured after the objective), which was low enough to avoid any sample alteration or decomposition due to local up heating as caused by heavy laser light absorption. Raman shifts were calibrated using the Raleigh line and Ne lamp emissions. The spectral resolution was about 1.3 cm^{-1}, and the wavenumber accuracy was 0.5 cm^{-1} [8]. Three multiple measurements per sample were done to check for potential micron-range heterogeneity and effects of sample orientation; both have not been found, as would be expected for a nearly homogeneous glass sample.

EPR measurements were performed at 9.35GHz (X-band) at room temperature using an EPR PS 8400 spectrometer equipment.

3. Results and Discussion

3.1 $xWO_3·(100-x)[2P_2O_5·PbO]$ glass system

Raman spectra of the $xWO_3·(100-x)[2P_2O_5·PbO]$ glass system are shown in Fig. 1. It can be observed that theirs shapes are changed with the increase of WO_3 content.

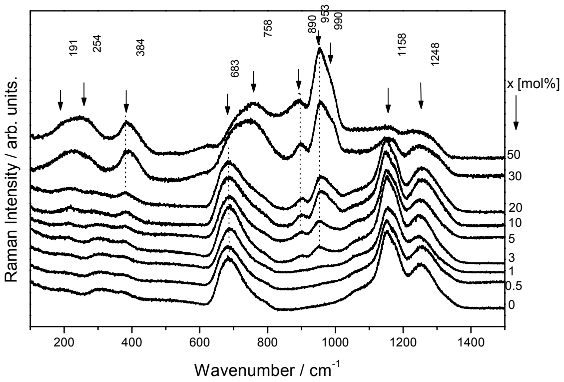

Fig. 1. Experimental Raman spectra of $xWO_3·(100-x)[2P_2O_5·PbO]$ glasses.

The Raman spectra of the glasses with x ≤ 1mol% show the characteristic bands of $2P_2O_5$ ·PbO matrix. So, the band at 683 cm^{-1} is attributed to the P-O-P symmetric stretching vibration [9, 10]. Another band due to P-O-P symmetric stretching vibration is observed in the metaphosphate spectrum at ca. 742 cm^{-1} [11]. The shoulder at about 1090 $cm^{-1}$is due to the (PO_3) of the Q_1 group [11]. In the Q^n terminology, n represents the number of bridging oxygens (BO) per PO_4 tetrahedron). The bands from 1158 cm^{-1} and 1248 cm^{-1} have been attributed to symmetric and asymmetric stretching motions of the two non bridging oxygen (NBO) atoms bonded to phosphorous atoms (PO_2) in the Q^2 phosphate tetrahedron [9-12].

New features appear around 890 cm^{-1} and 953 cm^{-1} with the increasing of the WO_3 content at x ≥ 3% mol. These bands become stronger with the addition of tungsten oxide content. In order to give better assignments for the new bands a comparison of our results with those reported for tungsten phosphate crystals [13] is done. A peak at 857 cm^{-1} in the spectrum of $W_2O_3(PO_4)_2$ crystal was assigned to W-O stretching vibration associated with linked WO_6 octahedra [13]. In the Raman spectra of the alkali tungstate crystals having $W-O^-$ bonds, the peaks observed in the wave number region of 900 to 965 cm^{-1} were assigned to stretching vibration of $W-O^-$ bonds [14-17].

In the Raman spectra of glasses with x≥10 mol% of WO_3 content, two new weak bands at 254 cm^{-1} and 384 cm^{-1} appear (Fig.1). Their intensity increase with the addition of modifier oxide (WO_3). These bands may be assigned to the deformation vibration of WO_6 octahedron and to the bending mode of the phosphate (PO_4) polyhedra taking into account the results reported on the WO_3 and $K_2W_4O_{13}$ crystals [14, 17-19]. The appearance of PO_4 polyhedra is due to the strong depolymerization of long phosphate chains [20].

For x > 20mol% the bands at 254 cm^{-1}, 384 cm^{-1}, 890 cm^{-1} and 953 cm^{-1} increase in intensity and another shoulder at about 990 cm^{-1} due to W=O stretching vibrations appears too. The assignment of the 990 cm^{-1} band is made by comparing this result with the position of W=O stretching vibration which appears at 950 cm^{-1} in tungsten trioxide hydrate crystals [18] and at 1006 cm^{-1} in $W_2O_3(PO_4)_2$ crystal [13]. The bands characteristic to the O-P-O (1158 cm^{-1}) stretching vibration and to the O-P-O (1248 cm^{-1}) asymmetric stretching vibration decrease strongly in intensity at high WO_3 content (x ≥ 30 mol %).

The asymmetric 683 cm^{-1} band assigned to the P-O-P symmetric stretching vibration of the long-chain phosphate glasses is shifted to 690 cm^{-1} due to the decreasing of phosphate chains lengths [13]. The shift of this band may be also attributed to a change in the in-chain P-O-P bond angle as an effect of the WO_3 network modifier on glass structure [21, 22]. The larger wavenumber of the P-O-P symmetric band is a result of the smaller P-O-P bond angle, characteristic for shorter phosphate chain length [12, 23].

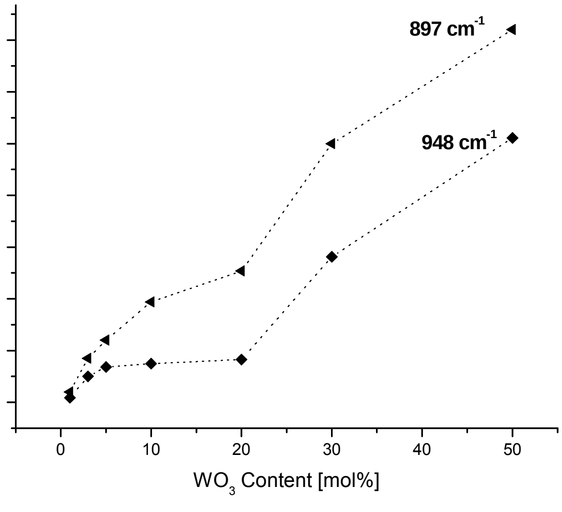

Fig. 2. The intensity of 897 cm^{-1} and 948 cm^{-1} bands versus WO_3 content. The lines are drawn as a guide for the eyes.

From these results we may conclude that by increasing of WO_3 content, the bands characteristic to phosphate network decrease strongly in intensity while the specific bands of the tungsten oxide become more intense. These bands grow in intensity and finally become the dominant features of the spectrum. In Fig.2 is shown the relative areas dependence of 897 cm^{-1} and 948 cm^{-1} corresponding to W – O stretching mode and W – O^{-} stretching mode versus WO_3 content.

Finally, we may conclude that the W atom prefers to bridge with oxygen that do not take part in a PO_4 unit and thus acts as a network former. Similar behavior in magnesium phosphate glasses was observed by Karakassides et al. [11] in the xMgO·(100-x)P_2O_5 system for 0.50≤x≤0.80 mol%. The FT-IR results for this system revealed the same trend in the tendency of the Raman bands. The specific bands of the Q^2 groups decrease in intensity while the specific bands of the tungsten oxide increase with the WO_3 content.

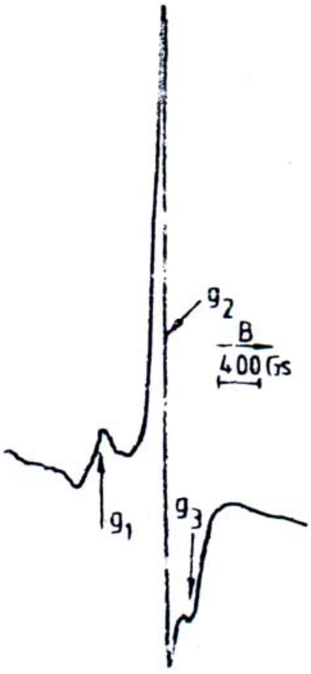

Fig.3. EPR spectrum of content. $20WO_3 \cdot 80[2P_2O_5 \cdot PbO]$ sample.

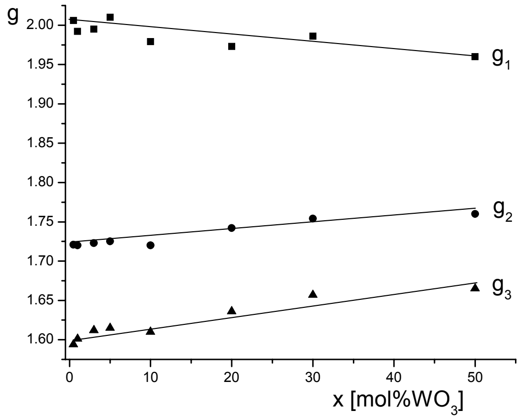

Fig. 4. The g values dependence versus WO_3

EPR spectra show a rhombic local symmetry for W^{5+} ions (Fig. 3) and the characteristic g values are: $g_1 \cong 1.98$, $g_2 \cong 1.73$ and $g_3 \cong 1.62$.

The possible hyperfine structure due to the ^{183}W isotope (I = ½) [24] not appears in the spectra. The shape of the EPR spectra and magnetic susceptibility data suggest that only a small quantity of W^{6+} ions change into the W^{5+} ions. Even for x = 50% mol the samples show a small paramagnetism and the broad symmetric line typical for clustered paramagnetic ions not appears in the spectra. However the dependence of the g values versus WO_3 content (Fig. 4) suggests a gathering of their values and a weak clustering association tendency of the W^{5+} ions.

The presence of W^{5+} ions in a rhombic symmetry was also confirmed by optical spectra and it is explained by the big dimensions of tungsten atoms [25].

3.2 $xMoO_3 \cdot (100-x)[2P_2O_5 \cdot PbO]$ glass system

FT-IR spectra of the $xMoO_3 \cdot (100-x)[2P_2O_5 \cdot PbO]$ glasses exhibit the characteristic bands for the $2P_2O_5 \cdot PbO$ matrix and of MoO_3 oxide (Fig.5). At low concentration of MoO_3 dominate the bands characteristic for phosphate oxide. Thus for x=0mol% the 500 cm^{-1} is described as a fundamental frequency of Q^0 species or as harmonics of P-O bending vibration [26]. The absorption band near 780 cm^{-1} is assigned to the symmetric stretching mode of the P-O-P linkages of the Q^1 species [26-28]. The strong band around 900-950 cm^{-1} were assigned to the asymmetric stretching vibration of P-O-P bond, whereas the 1047 cm^{-1} band is due to the asymmetric stretching vibration of the $(PO_3)^{2-}$ terminal groups in Q^1 units [29]. The weak band around 1150 cm^{-1} is assigned to the P-O$^{(-)}$ [3] ionic stretching vibration whereas the strong band around 1239 cm^{-1} is attributed to the P=O stretching vibration. Taking into account the IR results reported about some phosphate glasses [30] we may assigned the 1400 cm^{-1} band to P=O stretching vibration, too.

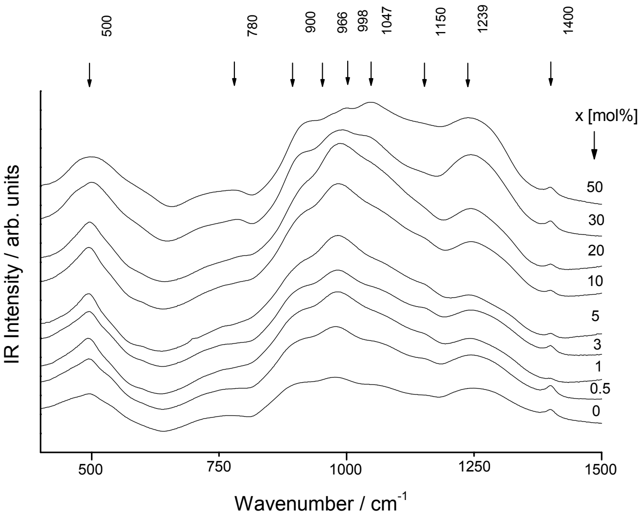

Fig. 5. FT-IR spectra of $xMoO_3 \cdot (100-x)[2P_2O_5 \cdot PbO]$ glasses

With the increase of the molybdenum oxide content, $x \geq 0.5$mol%, the shape of the bands is changing. The strong bands of the matrix around 900-950 and 1047 cm^{-1} become narrower and more intense because of the superposition with the bands belonging of the MoO_3 oxide. The 500 and 900 cm^{-1} bands increases in intensity because of their overlapping with the Mo-O-Mo and Mo=O stretching vibration [31], while the band from 980 cm^{-1} become narrower and more intense due to the increasing of the Q^0 groups [4]. Also the band around 780 cm^{-1} due to the symmetric stretching vibration of the P-O-P linkages of the Q^1 groups appears more intense for high concentration of the MoO_3 oxide. The band in the 500 cm^{-1} region becomes narrower with the increase of MoO_3 content and for concentration x>20mol% becomes larger due to its superposition with the band belonging to MoO_3 [31].

Moguš-Milanković et al. attributed the Raman spectra of MoO_3-Fe_2O_3-P_2O_5 glass system [20] to the monomeric orthophosphate, $(PO_4)^3$, and also to Mo-O stretching mode in highly deformed (MoO_6) units the band from 970 cm^{-1} [32-36]. They suggest that besides phosphate units, more complex structural units containing tetrahedral (MoO_4) and octahedral (MoO_6) species are present in the glasses [37]. In our Raman spectra this band appears for concentrations of molybdenum oxide more than 5 mol% [38].

The results obtained by N. Machida and H. Eckert [31] in AgI-Ag_2O-MoO_3 glass system have shown that for the Ag_2O/MoO_3 ratio of unity the molybdenum species are present only as tetrahedral monomeric orthomolybdate anions, MoO_4^{2-}, while in the glasses with Ag_2O/MoO_3 molar ratios less the unity, molybdenum species are present as tetrahedral orthomolybdate anions, MoO_4^-, and a second more complex, presumably polymeric species, the quantity of which increases with increasing MoO_3 content of the glasses.

A very strong depolymerisation appears in our system with the increasing of MoO_3 content. The FT-IR and Raman studies have shown that for higher concentration of molybdenum content prevail the specific bands of MoO_3 and the bands of Q^0 and Q^1 groups as well, with no evidence of the formation of Mo-O-P bonds as in other reported works. This fact suggests that the Mo atoms prefers to bridge with oxygen that do not take part in a PO_4 unit and thus act as a network former.

EPR spectra of glasses with $x \leq 10$ mol% show a weak hyperfine structure with six lines in both parallel ($g_{\|}$) and perpendicular ($g_{\perp}$) bands (Fig. 6). 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 central absorption line belongs to the ^{96}Mo isotope which has the nuclear spin I=0.The characteristic EPR parameters are: $g_{\|} = 1.867$, $g_{\perp} = 1.928$, $A_{\|} = 94.1 \times 10^{-4}$ cm^{-1} and $A_{\perp} = 48.6 \times 10^{-4}$ cm^{-1} for sample with x = 3 mol%.

These data suggest that Mo^{5+} ions are essentially coordinated in these glasses by five oxygen ligands in a square-pyramidal form C_{4v} symmetry with a Mo=O double bond [39, 40].

This local vicinity is also confirmed by optical spectra which show two absorption bands at 14000 cm^{-1} and 24500 cm^{-1}. These may be attributed to the $| B_2 \rangle$ — $| E \rangle$ and $| B_2 \rangle$ — $| B_1 \rangle$ transitions characteristic of the d^1 configuration in C_{4v} symmetry [41].

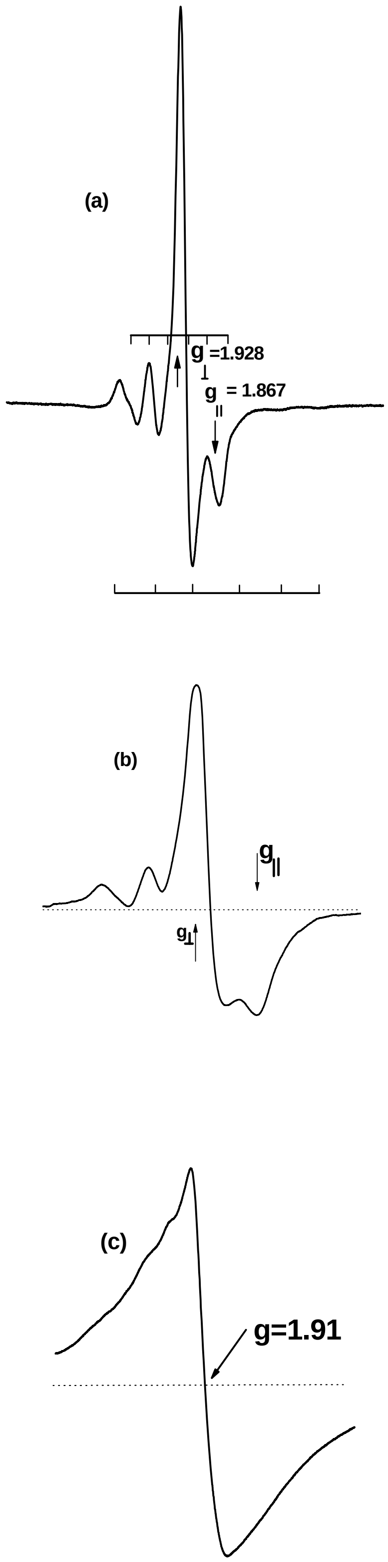

Fig. 6. EPR spectra of Mo^{5+} ions in lead – phosphate glasses with x = 3 mol% (a), x = 10 mol % (b) and x = 50 mol % (c).

The shape of EPR spectra is modified by the increase of the MoO_3 content (Fig. 1). This consists of the partial disappearance of the hyperfine structure and the appearance of a broad line at $g \approx 1.91$ value characteristic for dipole-dipole and superexchange coupled Mo^{5+} ions [39]. Thus, the spectra obtained for x>10 mol% may be considered as the result of the superposition of two EPR signals, one with resolved hyperfine structure typical for isolated Mo^{5+} ions and one consisting of a single broad line, typical for clustered ions. Their number increases with the increase of MoO_3 content. This fact influences the shape of EPR spectra by widening the signal from the $g_\perp$ absorption and by symmetrizing the spectrum.

4. Conclusions

FT-IR and Raman data studies indicate that at low concentrations (x < 20 mol%) of WO_3 and MoO_3 oxides, they play a strong modifier role which consists in the appearance of short chain phosphate units or ring structure, and finally a very strong depolymerization of the glass network.

At high content of tungsten and molybdenum oxides (x ≥ 30 mol %) the W and Mo atoms prefer to bridge with oxygen that to not take part in PO_4 units and thus playing a former role.

The specific bands of the tungsten oxide and molybdenum oxide as well, grow in intensity and finally become the dominant features of the spectra while the most of the specific bands of the phosphate network almost disappear.

EPR data show that for x ≤ 10 mol% the isolated Mo^{5+} and W^{5+} ions prevail in a square – pyramidal form (C_{4v}) and rhombic symmetry respectively. When the MoO_3 content increases over 20 mol%, the dipole – dipole and superexchange coupled Mo^{5+} ions appear. Because of the small number of W^{6+} ions changed in the W^{5+} ions they remain in isolated form even at x = 50% mol.

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[*] Corresponding author: cozar@phys.ubbcluj.ro