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Infrared spectra of WO_3 – PbO – P_2O_5 glasses

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The structure of $xWO_3\cdot(100-x)[2P_2O_5\cdot PbO]$ glass system with $0\leq x\leq 50$ mol% was investigated by FTIR spectroscopy. The characteristic bands of these glasses due to the stretching and bending vibrations were identified and analyzed by the increasing of WO_3 content. For this a deconvolution of each experimental spectrum was made using a Gaussian type function. Among standard deconvolution methods applied in vibrational spectroscopy of glasses, those assuming Gaussian band shapes for the IR and Raman spectra are mostly used because of the local disorder. This fact allowed us to identify the specific structural units which appear in these glasses and to carry out a quantitative analysis of the spectra. For higher concentration of tungsten oxide the W atoms prefer to bridge only with oxygen atoms which do not participate in phosphate structural groups and thus act as a network former.

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1. Introduction

Phosphate glasses make a special group of optical glasses of technological interest. Their specific properties include larger thermal expansion coefficient, smaller liquidus viscosity and softening temperatures than silicate glasses [1]. However, these glasses have a relatively poor chemical durability that often limits their usefulness [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].

Electrochromism is the phenomenon of inducing a reversible optical change in materials by the applications of a small electric field. Tungsten oxide (WO_3), due to this mixed oxidation states, is the most widely studied electrochromic materials. The optical reversible switch between the transparent and dark blue states is induced by an electrochromical process from a simultaneous injection and extractions of ions and electrons (double injection) [4, 5].

In order to obtain further information of the role of tungsten ions in phosphate glasses a new glass system $xWO_3\cdot(100-x)[2P_2O_5\cdot PbO]$ was prepared and investigated by FT-IR spectroscopy.

2. Experimental

The starting materials used in the present investigation were $(NH_4)_2HPO_4$, PbO and WO_3 of reagent grade purity. The samples were prepared by weighing suitable proportions of the components, powder mixing and mixture melting in sintered corundum crucibles at 1250^0 C for 5 min. The mixtures were put into the furnace directly at this temperature. The obtained glass-samples were quenched by pouring the molten glass on a steel plate.

The FTIR 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. The spectral resolution used for the recording of the IR spectra was 2 cm^{-1}. 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.

Because the majority of the bands are large and aymmetric, presenting also some shoulders, a deconvolution of the experimental spectra was necessary [6-10]. This was made with ORIGIN 7.0 program using a Gaussian type function and allowed us a better identification of all the bands which appear in these spectra and their assignments. Among standard deconvolution methods applied in vibrational spectroscopy of glasses, those assuming Gaussian band shapes for the IR and Raman spectra are used because the local disorder [11]. Thus, by determining the number of all independent components, it is possible to carry out a quantitative analysis of the spectra, and to find the concentration distribution of these components across the investigated mixtures. The proportion of particular structures corresponding to different vibration modes, was calculated from the areas of the fitted Gaussian bands divided to the total area of all bands. The four parameters of each band (peak frequency, half-width at half-height and relative areas) were allowed to float during the iterations.

3. Results and discussion

FT-IR spectra of studied glasses are shown in (fig. 1). It can be observed that their shapes are changed with the increase of WO_3 content. On the other hand the majority of the bands are large and asymmetric and they present some shoulders. Due to this reason a deconvolution of the experimental spectra with ORIGIN 7.0 program was made (fig. 2). The relative intensities (areas) of these bands were also determined and they are given in Table 1.

For x= 0 mol%, the presence of the PbO is observed in FTIR spectra by the existence of the Q^2, Q^1 and Q^0groups. In the Q^n terminology, n represents the number of bridging oxygens (BO) per PO_4 tetrahedron. The addition of PbO at the phosphate network results in the creation of non-bridging oxygens at the expense of the bridging oxygens [12].

The representative FTIR spectrum for $2P_2O_5PbO$ matrix meaning that 0≤ x ≤5 mol% range is given in fig. 2a (x= 1 mol%). The absorption band at 462 cm^{-1} is assigned to harmonics of bending vibrations of O=P-O linkages [13]. Others IR bands at 545, 713, 760 and 892 cm^{-1} are assigned to the bending mode of O-P-O in the Q^1 structure [114], symmetric stretching vibrations of P-O-P rings [15-17], symmetric and asymmetric modes of P-O-P bonds in Q^1 units respectively [5].

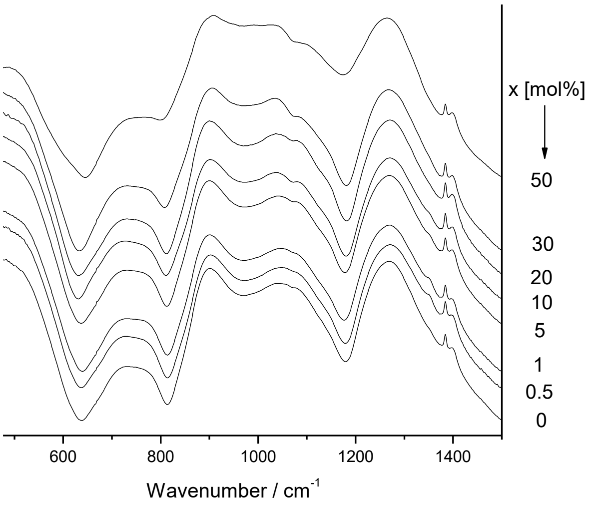

Fig. 1. Experimental FT-IR spectra of xWO_3·(100-x)[$2P_2O_5$·PbO] glasses.

Another band due to the asymmetric stretching vibrations of PO_4^{3-} structural group is located at 990 cm^{-1} [14, 18-19]. The band from 1065 cm^{-1} is attributed to symmetric stretching vibration of PO_4^{3-} tetrahedral (PO^- ionic group) [20,21]. The 1152 cm^{-1} band is associated with the asymmetric stretching vibrations in Q^2 groups $(PO_3)^-$ [14]. The other two bands observed at about 1262 cm^{-1} and 1380 cm^{-1} have been attributed to the asymmetric stretching of the double bonded oxygen vibrations [22] and to the (P=O) symmetric stretching vibrations [23,24].

For higher content of tungsten oxide (10≤ x≤ 50 mol%) when it clearly affects the phosphate network, a representative deconvoluted spectrum is given in Fig. 2b (x=50mol%). A new band in the FTIR spectra of these glasses due to the (W=O) vibration in (WO_6) polyhedra [19, 25] appears at about 972 cm^{-1} for x ≥10 mol%.

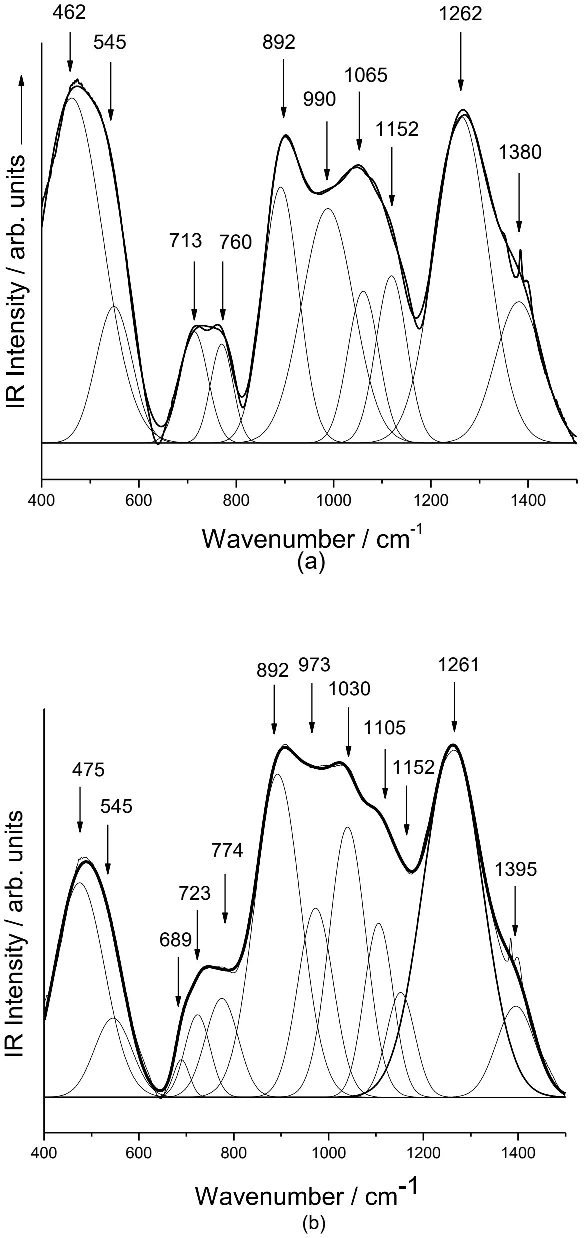

Fig. 2. Deconvoluted FTIR spectra of xWO_3·(100-x)[$2P_2O_5$·PbO] glasses using a Gaussian-type function for x=1% mol (a) and x=50% mol (b).

Table 1. The assignments and relative areas of different vibrational bands from FT-IR spectra of $xWO_3 \cdot (100-x)[2P_2O_5 \cdot PbO]$ glasses.

ν[cm^{-1}]	**Assignments**	**Relative areas dependence of vibrational bands versus WO_3 concentrations [x mol%]***							
		0*	0.5*	1*	5*	10*	20*	30*	50*
458-475	O = P- O bending	23.4	25.2	24.7	25.0	24.4	21.9	20.8	12.8
545	(O-P-O) bending (Q^1)	4.7	5.7	5.7	6	6.15	5.7	4.7	3.5
689	(P-O-W) $_{sym.}$ stretch.	-	-	-	-	-	1.6	1.16	0.7
700-723	$(P\text{-}O\text{-}P)_{sym.}$ stretch. in rings	3.7	3.9	3.4	3.7	3.2	1.85	2.6	2.5
760-774	$(P\text{-}O\text{-}P)_{sym.}$ stretch. (Q_1)	2	1.9	2.4	2.6	3.7	2.5	3.44	3.8
892	(P-O-P) $_{asym}$ stretch (Q^1)	2.8	3.2	3.5	5.7	8.9	6.1	11.1	14.7
956-973	(W=O) in WO_6 polyhedra	-	-	-	-	3	5.2	5.9	8
990-1030	$(PO_4)^{3-}_{asym.}$ stretch. in Q^0	13.9	13.6	13.9	15	11.8	10.6	11.5	11.9
1065-1105	$P\text{-}O^{(-)}_{sym.}$ stretch. in Q^0	3.7	4.6	5.4	4.2	7.7	7.7	6.5	6.4
1146-1152	$(PO_3)^{-}_{asym}$ stretch (Q^2).	9	7.6	5.9	4.9	1.3	1.6	1.7	3.6
1262	$(P{=}O)_{asym.}$ stretch.	21.5	19.5	20	21	18.9	21.3	21.8	25
1380-1395	$(P{=}O)_{sym.}$ stretch.	5.9	7.8	7.5	6.5	6.5	5.9	5	4.2

Another weak band due to the symmetric stretching vibrations of P-O-W bonds appear for x ≥20 mol%, around 689 cm^{-1} [1, 26].

The intensities and the shifts of the FT-IR bands versus WO_3 content and the correlation of these data with the structural groups which appear in studied glasses is also done (Table 1). These results allowed us to understand the modifier and former role of the tungsten oxide.

With the addition of WO_3 content, the bands from 475, 723, 1395 cm^{-1} characteristic to phosphate glasses decrease strongly in intensity (Table 1) except the specific bands of the small groups Q^1 and Q^0 (774, 892, 1105 cm^{-1}) which become more intense.

The band shift of the ionic groups, PO_4^{3-} (1065-1105 cm^{-1}) and the increase of its relative area is an indication for the formations of more non-bridging oxygen ions [3]. On the other hand, by increasing the modifier oxides content, the Q^2 groups (band at 1152 cm^{-1}) characteristics for the long phosphate chains decrease strongly in intensity (table1). From these considerations we can conclude that with the addition of WO_3 in the glass systems a very strong depolymerization appears.

For x ≥ 10% mol the band due to the W=O vibration in WO_6 polyhedra (972 cm^{-1}) increases in intensity, while the band characteristic to symmetric stretching vibration of P-O-W bonds decreases with the addition of modifier oxide (689 cm^{-1}). So, the number of the W atoms which form W-O-P type bonds is smaller than the number of tungsten atoms which prefers to bridge with oxygen and decrease by the addition of WO_3. This fact confirms our previous results [6], obtained by Raman spectroscopy, that for higher concentration of tungsten oxide 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.

4. Conclusions

The shape of the FTIR spectra is influenced by the presence of tungsten oxide in the studied glasses.

The characteristic bands of phosphate glasses strongly decrease in intensity except the specific bands of the very short chain phosphate units Q^1 and Q^0 (774, 892, 1105 cm^{-1}) which become more intense with the increasing of tungsten oxide. The band due to the symmetric stretching vibrations in Q^0 groups is shifted from 1065 cm^{-1} up to 1105 cm^{-1}, and also its area increase due to the formations of more non-bridging oxygen ions [3].

These results indicate that with increases of modifier oxide content a very strong depolymerization appears in these glasses.

The W=O stretching vibration band from (972 cm^{-1}), increases in intensity while the weak band from 689 cm^{-1},due to P-O-W symmetric stretching vibration, decreases in intensity with the addition of modifier oxide. This fact suggests that for higher concentration of tungsten oxide the W atoms prefer to bridge only with oxygen atoms which not participate in phosphate structural groups and thus act as a network former.

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