

The structural dual role of Fe₂O₃ in some lead-phosphate glasses

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ABSTRACT

The FT-IR study of iron concentration effect on the $x\text{Fe}_2\text{O}_3 \cdot (1-x)[2\text{P}_2\text{O}_5\text{PbO}]$ glass system with $0 \leq x \leq 50$ mol% has revealed the dual role of Fe₂O₃ both as network modifier and former. The addition of iron oxide leads to more P=O bond breakage and the formation of the P–O–Fe bonds. We concluded that at high content of Fe₂O₃ it acts in the structure of glasses as a network former. The presence of the Fe–O–P bonds for higher content of iron oxide in this glass system is consistent with the improving of their chemical durability. The appearance of these types of bonds and others structural units for Fe₂O₃–P₂O₅–PbO glasses are investigated by FT-IR spectroscopy.

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1. Introduction

The phosphate glasses have generally a poor chemical durability in contrast with the most silicate and borosilicate glasses, but iron phosphate glasses are an exception [1]. Due to their unusually high chemical durability and other properties, iron phosphate [2] and lead-iron-phosphate glasses are of interest for nuclear waste immobilization [3].

PO₄ tetrahedra are the basic structural units in phosphate glasses. The tetrahedral units are described by the Q^{*n*} notation, where “*n*” represents the number of bridging oxygens (BOs) that link neighboring P-tetrahedra. Vitreous P₂O₅ structure has Q³ P-tetrahedra with three BOs and one double bonded oxygen P=O, forming a three-dimensional cross-linked network. Ultraphosphate glasses have both Q³ and Q² P-tetrahedra structural units. Metaphosphate glasses have Q² P-tetrahedra with two terminal oxygens that are shared with the modifying cation polyhedra. The Q² tetrahedra link to form long chains (or rings). Phosphate glasses based on pyro (Q¹) and orthophosphate (Q⁰) are also possible [4].

In previous studies the IR spectra analysis of glasses, were mainly qualitative, based on the assignment and shift of infrared absorption bands. There are also studies focused on the chemical durability improvement of phosphate glasses by addition of oxides

like PbO, CuO or Fe₂O₃ were made. In this work, we paid attention to the quantitative analyses of these glasses IR spectra by using the deconvolution method to determine the relative concentration of structural units and thus, to analyze the modifier or former role of iron oxide versus its concentration. Deconvolution of IR spectra can be considered a useful tool to extract information about phosphate glass structure rather than the traditional analysis of IR spectra [5].

The structural role of PbO in many oxide glasses is unique since lead oxide is known to play a dual role both as a network modifier and former [6]. PbO is useful for shielding against high-energy radiations, including nuclear radiation [7] and its addition may result in the formation of P–O–Pb bonds. These bonds lead to an improvement of the chemical durability of phosphate glasses [8].

It has been suggested that the excellent chemical durability of iron phosphate is attributed to the replacement of P–O–P bonds by more moisture resistant P–O–Fe bonds [9]. By increasing iron content, the number of P–O–Fe bonds increases and the number of bridging oxygen P–O–P decreases [9,10], so that the phosphate network changes from the chain-like metaphosphate structure through the dimeric pyrophosphate to the isolated orthophosphate structure [11].

The $x\text{Fe}_2\text{O}_3 \cdot (1-x)[2\text{P}_2\text{O}_5\text{PbO}]$ glass system with $0 \leq x \leq 50$ mol% was prepared and characterized by IR spectroscopy in order to understand the role of Fe₂O₃ in the local structure. The objective of the present work is to study the compositional dependence of the different structural units which appear in these glasses with the increasing of the iron oxide content by maintaining the P₂O₅/PbO ratio constant.

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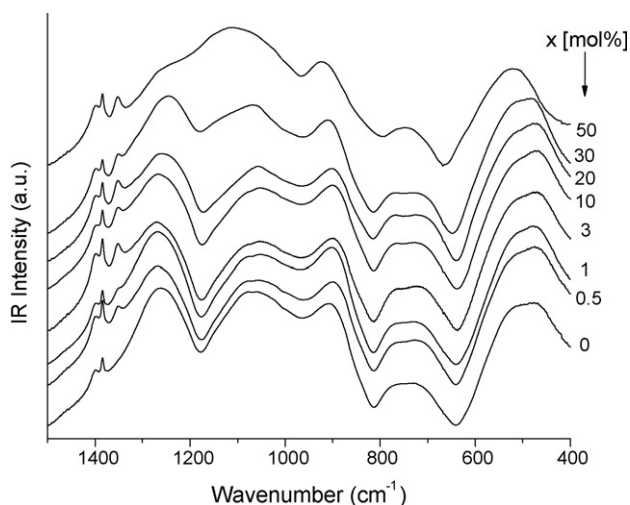


Fig. 1. Experimental FT-IR spectra of $x\text{Fe}_2\text{O}_3 \cdot (100 - x)[2\text{P}_2\text{O}_5 \cdot \text{PbO}]$ glasses.

2. Experimental

The starting materials used in the present investigation were $(\text{NH}_4)_2\text{HPO}_4$, PbO and Fe_2O_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°C for 5 min. The mixtures were put into the furnace directly at the considered temperature. The obtained glass-samples were quenched by pouring the molten glass on a steel plate.

The FT-IR absorption spectra of the glasses in the $400\text{--}1500\text{ cm}^{-1}$ 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.

3. Results and discussion

Fig. 1 shows the experimental FT-IR spectra of the $x\text{Fe}_2\text{O}_3 \cdot (1 - x)[2\text{P}_2\text{O}_5 \cdot \text{PbO}]$ glass system with $0 \leq x \leq 50$ mol%. Because the vibrational line widths of ion bonds in glasses are of considerable interest for the structural properties of the vitreous state [12] and because most of the bands are large and asymmetric (see Fig. 1) a deconvolution of each spectrum was made [13–17]. In

these glasses the line broadening is related to the existence of many different sites for the Fe ions and also to the site-to-site variations of the local field symmetries. This broadening is commonly assumed to give rise to Gaussian line shapes [18]. For this reason, we used Gaussian lines for the deconvolution procedure. Depending on the iron oxide content, a number of 10–12 peaks have been obtained by deconvolution in the $400\text{--}1500\text{ cm}^{-1}$ wavenumber region. The wavenumber of the deconvoluted peaks, their assignments and the relative intensities of the suitable bands are given in Table 1.

The specific deconvoluted spectrum for $x = 0$ mol% is given in Fig. 2a. The absorption band at 462 cm^{-1} is assigned to harmonics of bending vibrations of $\text{O}=\text{P}-\text{O}$ linkages [6]. Others IR bands at 547 , 711 , 768 and 900 cm^{-1} are assigned to the bending mode of $\text{O}-\text{P}-\text{O}$ in the Q^1 structure [19], symmetric stretching vibrations of $\text{P}-\text{O}-\text{P}$ rings [20–22], symmetric and asymmetric modes of $\text{P}-\text{O}-\text{P}$ bonds in Q^1 units, respectively [23]. Another band due to the asymmetric stretching vibrations of PO_4^{3-} structural group is located at 989 cm^{-1} [19,24,25]. The band at 1080 cm^{-1} is attributed to symmetric stretching vibrations of PO_4^{3-} tetrahedra (PO^- ionic group) [5,26]. The 1145 cm^{-1} band is associated with the $(\text{PO}_3)^-$ groups in Q^2 [19]. The other two bands observed at about 1260 and 1393 cm^{-1} have been attributed to the asymmetric stretching of the double bonded oxygen vibrations [27] and to the $(\text{P}=\text{O})$ symmetric stretching vibrations [28,29].

The deconvoluted spectrum for $x = 30$ mol% which is shown in Fig. 2b and is representative for the entire $1 \leq x \leq 50$ mol% range. New bands appear in the following spectral ranges: (a) $500\text{--}600\text{ cm}^{-1}$, (b) $1100\text{--}1200\text{ cm}^{-1}$ and (c) a sharp band around 1380 cm^{-1} for $x \geq 1$ mol%. The 584 cm^{-1} band can be assigned to the $\text{Fe}-\text{O}-\text{P}$ bonds [30,31]. The intensity of this band increases with the Fe_2O_3 content (Table 1 and Fig. 3); suggesting that the number of these types of bonds increases, too. We assume that the stretching band corresponding to $\text{P}-\text{O}-\text{Fe}$ linkage might be located around 1200 cm^{-1} similar to $\text{P}-\text{O}-\text{Sn}$ linkage in $\text{Sn}-\text{P}-\text{O}-\text{F}$ [32,33] whose positions are near 1100 cm^{-1} . The higher wavenumber of the $\text{P}-\text{O}-\text{Fe}$ linkage is due to the mass difference between the two cations; taking into account that Sn and Fe electro-negativities are very close. The intensity of this band also increases with the iron oxide content (Table 1 and Fig. 3). With the addition of Fe_2O_3 another weak band due to the $(\text{P}=\text{O})$ symmetric stretching vibration at about 1380 cm^{-1} appears. Similar bands were observed in the IR study of binary Li-, Fe- or Cu-ultraphosphate glasses and attributed to the π -bond delocalization of Q^3 species as a result of formation of non-bridging oxygens. π -Bond delocalization on Q^3 species in ultraphosphate structures results in longer $\text{P}=\text{O}$ bond length [34]. Therefore, the frequency shift of $(\text{P}=\text{O})$

Table 1

The assignments and relative areas of different vibrational bands from FT-IR spectra of $x\text{Fe}_2\text{O}_3 \cdot (100 - x)[2\text{P}_2\text{O}_5 \cdot \text{PbO}]$ glasses

ν (cm^{-1})	Assignments	Relative areas dependence of vibrational bands vs. Fe_2O_3 concentrations (x mol%)*							
		0*	0.5*	1*	3*	10*	20*	30*	50*
460–469	$\text{O}=\text{P}-\text{O}$ bending	20.2	25.6	25	26.6	24.6	25.8	18.8	10.3
532–550	$(\text{O}-\text{P}-\text{O})$ bending (Q^1)	5.93	6.3	4.4	6.3	5.4	5.5	6.4	8.8
584–599	$\text{Fe}-\text{O}-\text{P}$	–	–	0.23	1.4	1.4	1.5	2.12	2.63
707–720	$(\text{P}-\text{O}-\text{P})_{\text{sym}}$ stretch in rings	2.72	3.15	3	4.2	4.14	4	2.5	1.87
766–774	$(\text{P}-\text{O}-\text{P})_{\text{sym}}$ stretch (Q_1)	2.7	3	2.6	2.4	2.7	3.4	2.9	2.6
890–900	$(\text{P}-\text{O}-\text{P})_{\text{asym}}$ stretch (Q^1)	13	9.8	9.9	8	9.25	8.5	9.4	11.8
984–997	$(\text{PO}_4)^{3-}$ asym. stretch in Q^0	9.07	13.9	14.7	12.2	14	12.2	13.3	13.1
1075–1088	$\text{P}-\text{O}^{2-}$ sym. stretch in Q^0	17.7	9.5	11.4	10	10.5	9.8	12	15.8
1136–1152	$(\text{PO}_3)^-$ asym. stretch (Q^2)	1.3	1.6	1.5	1.8	1.5	2.9	5.2	8.9
1208–1215	$\text{Fe}-\text{O}-\text{P}$	–	–	1.2	1.3	1.9	1.6	2.8	2.1
1260–1272	$(\text{P}=\text{O})_{\text{asym}}$ stretch	22.6	20.4	19.3	17	17.5	16.5	16.2	15.4
1380–1393	$(\text{P}=\text{O})_{\text{sym}}$ stretch	4.7	6.6	6.7	8.6	6.9	8.1	6.3	6.2

* mol%.

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