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Structure of zinc-lead-iron phosphate glasses

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Abstract

A structural characterization of (100-x)(50P₂O₅-15ZnO-35PbO)-xFe₂O₃ phosphates glasses was accomplished using Raman, XPS, EPR and Mössbauer spectroscopies. The Raman study showed that the addition of Fe₂O₃ leads to the depolymerization of the glass network. The O1s spectrum was deconvoluted into three components, bridging oxygen atoms POP, non bridging oxygen atoms PO⁻ and more covalent bonds PO—M (Zn, Pb, and Fe). The Mössbauer spectroscopy reveals the presence of ferric and ferrous cations both located in octahedral sites while the ERP investigation indicates the coexistence of two kinds of trivalent iron sites.

Keywords : Phosphate glasses; Raman spectroscopy; XPS; Mössbauer spectroscopy; EPR.

1. Introduction

In our previous study [1], we proposed zinc-iron phosphate glasses as a good storage medium for toxic heavy metals because of their high stability under extreme leaching conditions. The composition dependence of density, glass transition temperature, Vickers microhardness and chemical durability were fully described. The addition of Fe₂O₃ to 50 P₂O₅ - 15 ZnO - 35 PbO glass have shown a significant variation in physical properties and in chemical durability. To understand these variations a structural approach seems to be interesting.

Raman scattering has been successfully utilised to give structural informations of glasses [2-3]. Their structure is dependent upon the covalente bonding between PO₄ tetrahedra forming a chains or rings via bridging oxygen. The chains are linked together by cross bonding between modifier cations and non bridging oxygens. The chemical bonding change was studied through X-ray photoelectron spectroscopy (XPS) by fitting O1s spectra and thus quantitatively measure percentage of bridging and non bridging oxygen [4, 5].

In order to get more information about iron valence and coordination in glass other investigations [6, 7] have been carried out using Mössbauer spectroscopy. Furthermore, the electronic paramagnetic resonance (EPR) has been used to give some structural informations. In fact, iron coordination has been provided using this technique [8].

2. Experimental procedures

Raman spectra of lead-zinc-iron phosphate glasses were measured in the Stokes spectral range from 200 to 1400 cm⁻¹ at room temperature. The samples were cut and polished to form parallel faces. The 514.5 nm wavelength of an argon-ion laser source was used as an excitation wavelength. The spectra were recorded using a double grating monochromator Jobin-Yvon U1000 driven by a microcomputer. The slit widths were set to obtain a resolution of 2.5 cm⁻¹.

XPS data were collected using a VG Scientific 220i-XL Escalab. Mg K α X-ray line from the non-monochromatized source (1253.6 eV) was used to acquire O1s small areas at a constant pass energy of 6 eV. The O1s spectra of the samples were carefully examined taking into account the contribution of C—O and C—C bonds resulting a surface pollution. The Binding energies were referenced to the C1s energy at 284.6 eV. All XPS peaks were simulated based on a Gaussian-Laurentzian hybrid peak fitting using a VG Scientific software. The half-width of the O1s fitting components was fixed at 1.6-1.8 range for the various compositions of glasses. To prevent a long term surface contamination, the XPS analyses were performed on pieces that were immediately placed under vacuum after being taken apart from freshly broken glasses.

Mössbauer spectra were measured at room temperature using a Halder spectrometer with a constant acceleration and ⁵⁷Co source (rhodium matrix). The Samples were prepared from glass powders mixed with a resin in order to get 10 mg/cm² of iron. The Mössbauer spectra were simulated with broadened paramagnetic Lorentzian doublets.

The EPR spectra were measured at room temperature with a Bruker EMX 8/12 spectrometer operating at an X band of 9.45 GHz and magnetic field ranging from 0 to 10000 G.

3. Results and interpretations

- Raman Spectroscopy

It is known that the structure of phosphate glasses is based on PO_4 tetrahedra that are linked to each other by bridging oxygen atoms to form phosphate chains or rings [9]. The metal cations are cross linked to the non bridging oxygen atoms of each PO_4 tetrahedra. These bonds are essential the linkage between the phosphate chains. The Raman Spectra of $(100-x)(50\text{P}_2\text{O}_5-15\text{ZnO}-35\text{PbO})-x\text{Fe}_2\text{O}_3$ glassy samples recorded

between 200 and 1400 cm^{-1} are reported in the figure 1. We noticed that the spectrum of the lead-zinc metaphosphate is very common for metal metaphosphate glasses [10]. Two characteristic peaks were observed at about 700 cm^{-1} and 1160 cm^{-1} . These two peaks were attributed to the symmetric stretching mode of the $\text{P}-\text{O}-\text{P}$ bridging bonds and to the symmetric stretching $(\text{PO}_2)^-$ of the PO_4 tetrahedra, respectively, by analogy with other studies [2-11]. The band observed at 1240 cm^{-1} has been assigned to the asymmetric stretching of $(\text{PO}_2)^-$. The low frequency peak at about 340 cm^{-1} originates from the bend mode of the phosphate tetrahedra. The very weak shoulder observed at about 1070 cm^{-1} is due to the motion of the non bridging oxygen of PO_3 end groups [12].

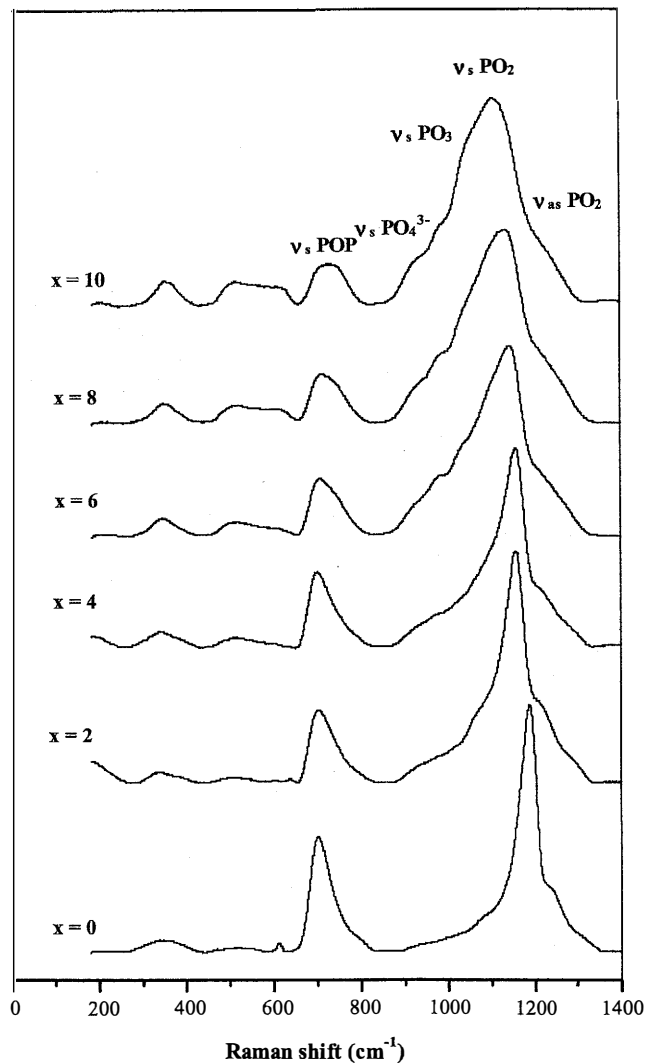


Figure 1 : Raman spectra at room temperature of $(100-x)[50\text{P}_2\text{O}_5-15\text{ZnO}-35\text{PbO}]-x\text{Fe}_2\text{O}_3$ glasses.

The addition of Fe_2O_3 dramatically affects the trend of the Raman spectra. We clearly noticed that the intensity of the band observed at about 700 cm^{-1} decrease when x increases, and its frequency shifts from 700 cm^{-1} to 730 cm^{-1} as shown in figure 2. These evolutions could result from the new interaction of divalent (Zn^{2+} , Pb^{2+}) and trivalent (Fe^{3+}) cations with bridging oxygen atoms, which is likely going to affect the orientation and strength of the P—O—P bonds. The dominant band frequency shifts from 1160 cm^{-1} to 1106 cm^{-1} (figure 2). This decrease is attributed to the shortening of the length of the

phosphate chains. Moreover, the appearance of a shoulder at 930 cm^{-1} for the higher Fe_2O_3 content can be attributed to the $(\text{PO}_4)^{3-}$ isolated monomers, whereas the shoulders at 980 and 1070 cm^{-1} can be attributed to $(\text{PO}_3)^{2-}$ end units in the polyphosphate entities such as $[(\text{P}_2\text{O}_7)^{4-}]$ diphosphate, $[(\text{P}_3\text{O}_{10})^{5-}]$ triphosphate or $[(\text{P}_4\text{O}_{13})^{6-}]$ tetrphosphate groups in agreement with the literature [12-13]. The frequency of the band located at 1070 cm^{-1} decrease as x increases and its intensity increases especially for $x \geq 6$. In low frequency range, the new bands can be assigned to the cation motion and chain conformations [14].

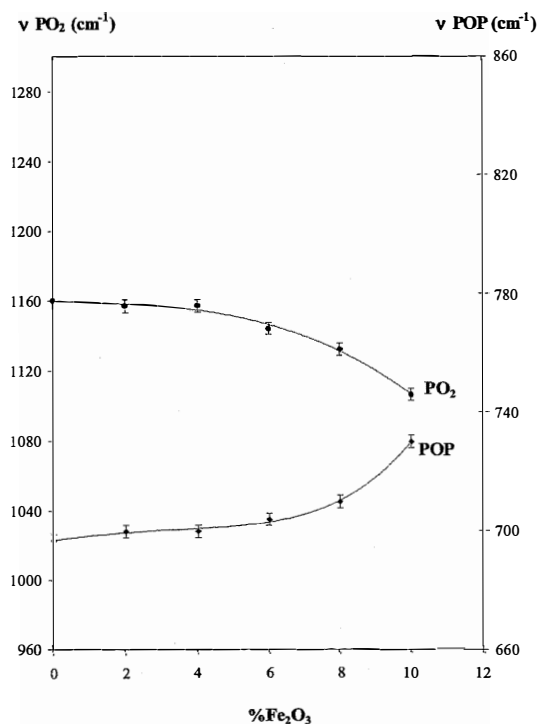


Figure 2 : Frequencies variations of $\text{vs}(\text{POP})$ and $\text{vs}(\text{PO}_2)$ modes vs Fe_2O_3 content in the $(100-x)[50\text{P}_2\text{O}_5-15\text{ZnO}-35\text{PbO}]-x\text{Fe}_2\text{O}_3$ glasses.

- X-ray photoelectron spectroscopy (XPS)

It is known that bridging and non-bridging oxygen atoms in phosphate glasses can be distinguished by fitting the O1s peak from XPS data. Figure 3 presents the XPS O1s spectra of the glasses as a function of x . As reported elsewhere [13, 15], the two components at smaller and higher energies are assigned to the non-bridging oxygen atoms (NBO) and bridging oxygen atoms (BO), respectively. The

intermediate component (ABO) can be attributed to the oxygen atoms that are linked to phosphorus and to divalent or trivalent cations forming a more covalent bond than that formed with ordinary modifier cations. These assignments are in good agreement with the results reported by Liu et al. [16].

The evolution of the three components area fractions are shown in figure 4. We mainly noticed that the fractions of BO and NBO decrease while that of ABO increases with x increase.

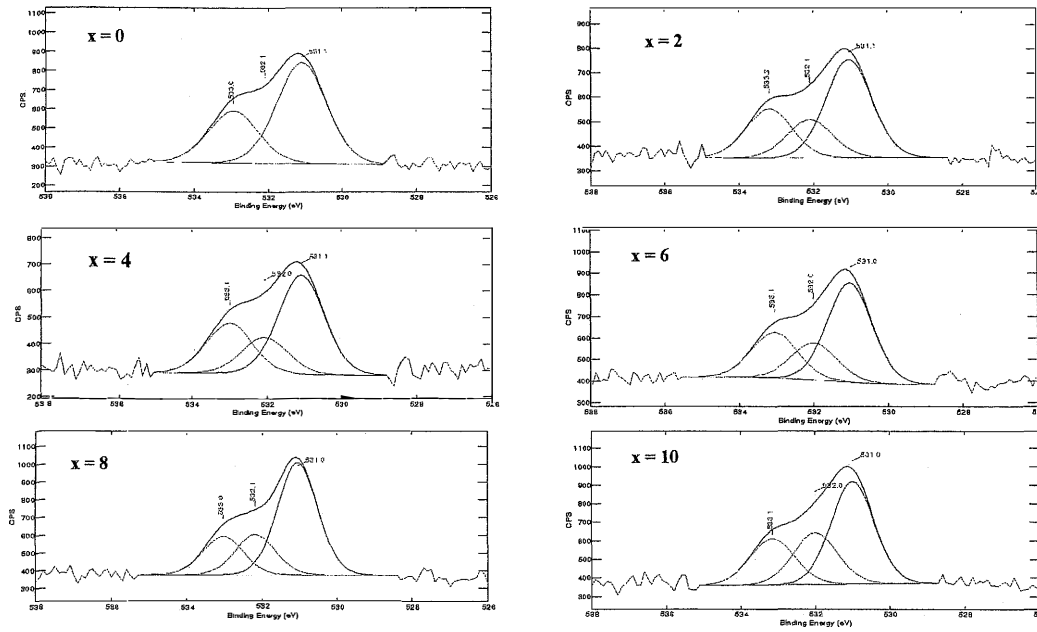


Figure 3 : XPS O1s spectra of $(100-x)[50P_2O_5-15ZnO-35PbO]-xFe_2O_3$ glasses.

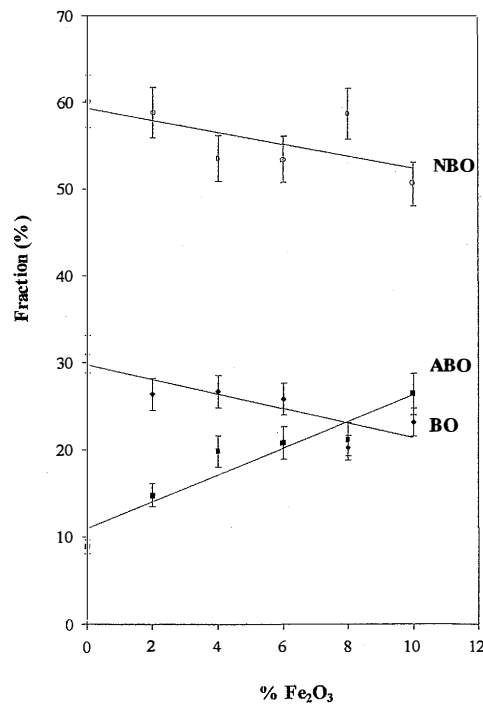


Figure 4 : Experimental area percentages of various components of the O1s core level electrons vs Fe_2O_3 content.

- Mössbauer spectroscopy

Figure 5 shows the Mössbauer spectra of glass samples recorded at room temperature. These spectra are characteristic of paramagnetic

compounds. To get a best fit, two quadrupole distributions were considered. It is known that the isomer shift (δ) is sensitive to the coordination since the quadrupole splitting at each site is due to the

interaction between the ^{57}Fe quadrupole moment and the electric field generated by the surrounding oxygen anions. The values $0.37 <$

$\delta < 0.47$ and $1 < \delta < 1.3$ correspond respectively to the presence of Fe^{3+} and Fe^{2+} cations in octahedral sites [6].

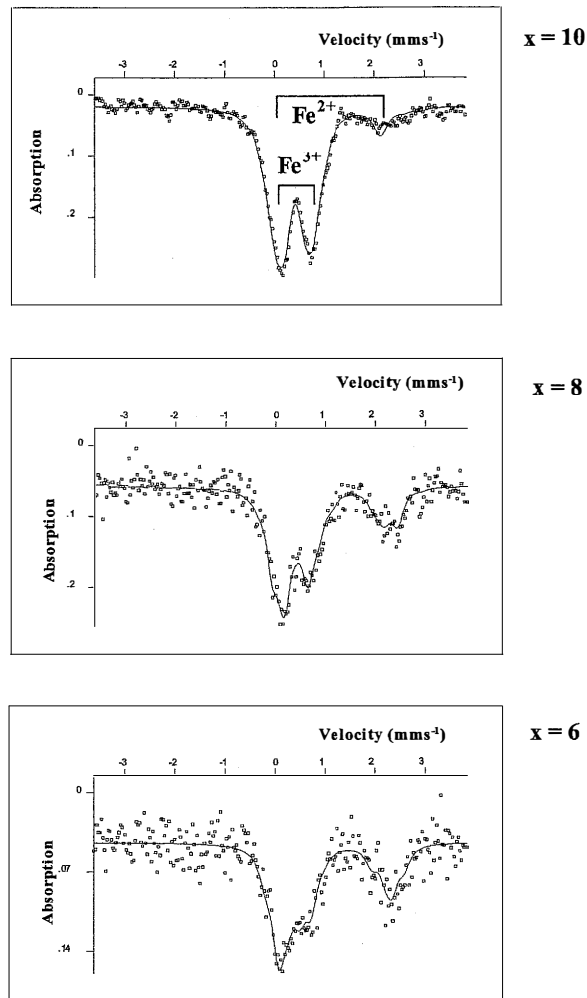


Figure 5 : Mössbauer spectra at room temperature of $(100-x)[50\text{P}_2\text{O}_5-15\text{ZnO}-35\text{PbO}]-x\text{Fe}_2\text{O}_3$ glasses.

The hyperfine parameters and the fractions of each ion are listed in table 1. Even though the iron is entirely in form of Fe_2O_3 in the starting compositions, the glasses clearly contain Fe^{2+} cations for which the content decreases with x . The ferrous ions origin is the reduction of Fe^{3+} ions by NH_3 coming from $(\text{NH}_4)_2\text{HPO}_4$ decomposition in the batch. In the similar preparation procedure the content of reduced Fe^{3+} cations depend in the iron concentration,

consequently the NH_3 concentration, in the melt and may explain a high Fe^{2+} content for the higher $(\text{NH}_4)_2\text{HPO}_4$ percentage. This behaviour is in agreement with previous works [7]. The origin of ferrous ions can be also, attributed to the O^{2-} activity in the melt which may affect the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple equilibrium. Indeed, the increase of Fe_2O_3 content in the glass results in an increase of the oxygen activity, which may explain the large concentration of Fe^{3+} cations [17].

Fe ₂ O ₃	DIS	δ (mm.s ⁻¹)	Γ (mm.s ⁻¹)	Δ (mm.s ⁻¹)	% population	Site
10 %	$\Delta 1$	1.20	0.28	2.13	14.7	Fe ²⁺ O _h
	$\Delta 2$	0.40	0.28	0.68	85.3	Fe ³⁺ O _h
8 %	$\Delta 1$	1.20	0.28	2.16	39.8	Fe ²⁺ O _h
	$\Delta 2$	0.40	0.28	0.66	60.2	Fe ³⁺ O _h
6 %	$\Delta 1$	1.20	0.28	2.20	50.0	Fe ²⁺ O _h
	$\Delta 2$	0.40	0.28	0.54	50.0	Fe ³⁺ O _h

DIS : distribution, δ : isomer shift, Δ : quadrupole splitting, Γ : linewidth, Oh : octahedral site

Table 1 : Hyperfine parameters at 22 °C and the valence and site iron in (100-x)[50P₂O₅-15ZnO-35PbO]-xFe₂O₃ glasses

- Electronic paramagnetic resonance (EPR)

Figure 6 shows the evolution of the EPR spectra with the concentration of iron. The spectra are mainly characterised by two lines centred around effective values of $g = 4.3$ and $g = 2$. Since the Fe²⁺ cation is known to be sensitive to EPR spectra only at low temperatures, the features of these spectra, obtained at room temperature, are related only to the trivalent iron. So the resonance at $g = 4.3$ and $g = 2$ are respectively assigned to Fe³⁺ cations in low and higher symmetry as suggested by Kukjian and Sigety [8]. The existence of some distorted FeO₄ tetrahedra could explain

the resonance at $g = 4.3$. This hypothesis seems realistic and would correspond to the introduction of small quantities of isolated Fe³⁺ cations into the phosphate chains. The ferric tetrahedra would share corners with phosphorus tetrahedra. These FeO₄ polyhedra would disappear when iron content increases in agreement with the vanishing of $g = 4.3$ line. For $x > 6$, the width of $g = 2$ line increases. This phenomenon is due to the appearance of magnetically exchange coupled pairs of Fe³⁺ cations. For higher iron content ($x = 10$) the widening could be related to the short range magnetic interactions as reported by Menil et al [7].

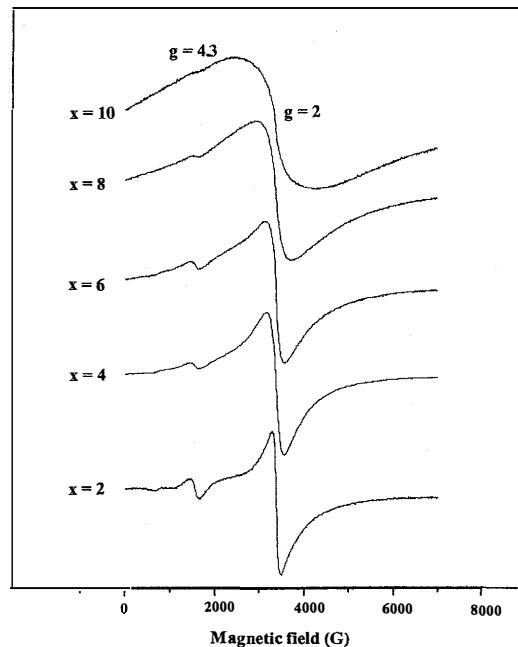


Figure 6 : EPR spectra at room temperature of (100-x)[50P₂O₅-15ZnO-35PbO]-xFe₂O₃ glasses.

4. Structure-properties correlation

Due to the fact that the Raman spectrum for the iron-free glass ($x = 0$) shows the presence of PO₃ end groups, we logically conclude that there is a

shortening of the zinc-lead metaphosphate chains. This tendency is in good agreement with other studies [12,18], in which the ³¹P NMR analysis

indicates the presence of Q^1 sites when ZnO is substituted for PbO in metaphosphate glasses [18]. For $x = 0$ glass, the ^{31}P NMR study reveals the presence of small quantities of Q^3 in addition to Q^2 and Q^1 that can be generated from the disproportionation reaction $Q^2 \rightarrow Q^1 + Q^3$. This tendency was confirmed by our XPS study in which the percentage of BO is slightly smaller than the theoretical value (33.33%) in metaphosphate glasses.

The addition of Fe_2O_3 in the zinc-lead metaphosphate glass results in a shortening of the average phosphate chain length. The later can approximately reach 4 phosphorus for $x = 10$ (experimental O/P ratio equal to 3.27). The general effect of the Fe_2O_3 addition can be summarized as follows:

1) A shift of the symmetric PO_2 band towards lower frequencies, and the decrease in the intensity of the P—O—P band along with the appearance of new bands corresponding to the change of the chain ends and existence of monomer units detected the Raman technique.

2) A decrease of the BO fraction and an increase of ABO fraction of O1s spectra.

The role iron atoms can be interpreted in different ways according to its oxidation state. The Fe^{2+} cations could be considered as a network modifier in octahedral environment. Its relatively high percentage for a low Fe_2O_3 content does not clearly affect the physical properties expect for the glass transition T_g which reaches a minimum for x close to 2 [1].

According to the Mössbauer results, the Fe^{3+} cations are mainly in octahedral coordination while the EPR spectra can be interpreted in term of the coexistence of two kinds of trivalent iron sites. The ferric cations are probably used as branching agents to reticulate the short polyphosphate groups (average $\text{P}_4\text{O}_{13}^{6-}$ for $x = 10$) assuming the compensation of the depolymerisation effect. The increase in the PO—M bond strength (intermediate component in XPS O1s spectra) contributes in the reticulation increase and leads to a higher vitreous stability (T_g increase) and a greater hardness (Hv)[1].

In general, the phosphate glass dissolution can be governed by a hydration process. It leads to a disruption of the modifying cations ionic bonds cross-linking the phosphate chains that are afterward released into solutions. For the more durable phosphate glasses, the hydrolysis process results in a cleavage of P—O—P bonds which namely controls the corrosion.

The improvement in the chemical durability, as reported in our previous study [1], can be related to strengthening not only of the P—O—Fe bonds as reported in other work [19] but also of the P—O—P bridging bond with the shortening of the phosphate chains when x increases. In this case, the hydration of the phosphate network becomes difficult. The ion exchange process due to the hydration becomes thermodynamically less probable and the degradation of the glass surface is mainly realised by hydrolysis in good agreement with pH fall [1] and high reticulation of the glass network. At the beginning of the glass corrosion, a preferential attack could happen at the end of the short polyphosphate chains by hydrolysis of P—O—Zn bonds keeping out the more covalent bonds such as P—O—Fe and P—O—Pb in agreement with the weak presence of these cations in the leachant [1]. Latter on, the acidic medium could involve a corrosion enhancement with partial hydrolysis of P—O—Pb and P—O—Fe bonds.

5. Conclusion

Zinc-iron phosphate glasses have been investigated using different techniques. Physical properties show a high reticulation of glass network [1]. These results are in good agreement with the improvement of the chemical durability especially for glass with the ratio $\text{O/P} = 3.27$ ($x = 10$). This improvement is related to the formation of P—O—M ($M = \text{Pb}$ and Fe) and more resistant P—O—P bonds. The XPS study shows the decondensation of the phosphate network and the formation of P—O—M (Pb and Fe) bonds. Raman spectra indicate the presence of terminal groups PO_3 related to the formation of short chains resulting from Fe_2O_3 addition. Mössbauer's data indicate the mixed valence of iron in phosphate glasses and octahedrally coordination for Fe^{2+} and Fe^{3+} . Complementary informations are taken by EPR study and indicate that Fe^{3+} is in two different sites. For the higher Fe_2O_3 glasses, the ferric cations play the role of branching agent to reticulate the short phosphate groups ($\text{P}_4\text{O}_{13}^{6-}$) assuming the compensation of the phosphate network decondensation effect.

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