

# Elaboration and Structural Investigation of Iron (III) Phosphate Glasses

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Received November 14, 2013; revised December 8, 2013; accepted December 21, 2013

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## ABSTRACT

The regular melting-quenching method allowed isolating very large vitreous domains within the ternary system  $\text{Li}_2\text{O}-\text{P}_2\text{O}_5-\text{Fe}_2\text{O}_3$  at  $1100^\circ\text{C}$ . The vitrification and crystallization effects are discussed in terms of phosphorus pentoxide concentration (mol%). In the course of the present study, we analyzed chemical durability along the glass domain and many sample glasses were isolated. We noticed that our compounds demonstrated very high chemical resistance to attack, even with very highly concentrated mineral acid solutions. This behavior can be assigned to the presence of poorly crystalline phases in these glasses, which tended to increase as the  $\text{Fe}_2\text{O}_3$  content increased. This property is a prerequisite for many interesting industrial applications. XRD, IR spectroscopy and SEM micrographs allowed an efficient investigation of the structural changes versus composition within ternary diagrams. The results were found to be consistent with the regular structural changes of phosphate glasses.

**Keywords:** Phosphate Glasses; Glass Formation; Chemical Resistance; IR Spectroscopy; XRD; SEM

## 1. Introduction

The practical application of phosphate glasses is often limited by their poor chemical resistance. Recently, several phosphate glasses with high aqueous corrosion resistance have been reported [1]. Compared with conventional oxide glasses such as  $\text{SiO}_2$ , phosphate glasses based on  $\text{P}_2\text{O}_5$  are technologically important materials, primarily due to their superior physical properties such as low glass transition temperatures, chemical durability, low optical dispersions and relatively high thermal expansion coefficients. These properties make these glasses as potential candidates for many technological applications such as sealing materials, bioglasses, and electronic and optical devices, as laser hosts, nuclear waste glasses, glass-to-metal seals and as solid state electrolytes, etc., [1-6]. With their unusually high chemical durability and low processing temperature, iron phosphate glasses have been considered better for the vitrifying of nuclear

wastes than borosilicate glasses [7,8]. The aim of the present work firstly is to define the glass area in a ternary diagram and especially in the  $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5$ . So we have explored that the introduction of iron oxide in the glass network can be up to 30 mol% according to the conditions in which we worked, either at atmospheric pressure or at  $1080^\circ\text{C} - 1100^\circ\text{C}$ . Secondly it is to investigate the chemical resistance and structural properties of lithium-iron phosphate glasses and to relate the improve of chemical resistance to the structural change using IR spectroscopies, XR diffraction and SEM. Hence with increasing  $\text{Fe}_2\text{O}_3$  content in the phosphate glass network, the P-O-P bands are replaced by more resistant Fe-O-P bands.

## 2. Experimental

The composition of the glasses was  $x\text{Li}_2\text{O}-y\text{Fe}_2\text{O}_3-\chi\text{P}_2\text{O}_5$ , with ( $\chi = (100 - (x + y))$ ; mol%), obtained by the melting-quenching method at  $1100^\circ\text{C}$ . An appropriate mixture of mixing compounds, *i.e.*  $\text{Li}_2\text{CO}_3$ , ferric oxides and

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$(\text{NH}_4)_2\text{HPO}_4$ , was initially tempered at various temperatures between  $100^\circ\text{C}$  -  $600^\circ\text{C}$  to achieve a preparation before glass preparation. The melts were achieved in alumina crucibles for about 15 min at  $1080^\circ\text{C} \pm 10^\circ\text{C}$ . The isolated glasses had regular shapes and an approximate size of 10 mm in diameter and 2 mm in thickness. The vitreous state was first evidenced from the shiny aspect and then confirmed from XRD patterns. Annealing of these glasses was performed at increasing temperatures in intervals of  $100^\circ\text{C}$ . The first structural approach was made using X-ray diffraction which allowed us to follow the crystallization of the vitreous domain of  $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5$ . The microstructure of sample glasses was characterized by scanning electron microscopy (SEM), equipped with a microanalyzer full system (EDX-EDAX). The chemical durability of the glasses with the composition  $x\text{Li}_2\text{O}-y\text{Fe}_2\text{O}_3-\chi\text{P}_2\text{O}_5$ ; ( $\chi = (100 - (x + y))$ ) were subjected to acid solutions using weak and strong concentrations of HCl and  $\text{H}_2\text{SO}_4$  (0.1 N, 1 N and 10 N). The duration of attack for some glasses and solution concentration continued for up to 30 days. The infrared (IR) spectra for each glass were measured between 400 and  $1400\text{ cm}^{-1}$  using mX-1 and NIC-3600 FTIR spectrometers. Samples were prepared by pressing a mixture of about 2 mg of glass powder with 100 mg of anhydrous KBr powder.

### 3. Results

In the system  $\text{Li}_2\text{O}-\text{P}_2\text{O}_5$ , transparent glasses were prepared for  $0 \leq x \leq 62$  (Figure 1). These values are in agreement with published results [9,10], but they are superior to those given by other authors [11,12]. This was probably caused by the different experimental conditions (temperature of melting, speed of tempering, etc.)

[13]. In the binary system  $\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5$ , the substitution of  $\text{P}_2\text{O}_5$  with  $\text{Fe}_2\text{O}_3$  led to black glasses that were not hygroscopic for ironoxide contents between 0 and 30 mol% (Figure 1). Ternary glasses rich in  $\text{Fe}_2\text{O}_3$  content had a dark brown color which became more and more brown clear as the lithium oxide content increased and the  $\text{Fe}_2\text{O}_3$  content decreased. The demarcation of the glassy zone within the ternary diagram  $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5$  is given by the following limits:  $0 \leq x \leq 62$ ;  $0 \leq y \leq 30$ ;  $36 \leq \chi \leq 1$ ; (mol%) (Figure 1).

#### 3.1. Annealing Temperature

The annealing of the ternary glasses was performed by increasing the temperature in intervals of  $100^\circ\text{C}$ . An increase in the lithium oxide modifier led to a slight increase in the crystallization temperature. For the glasses with the composition  $x\text{Li}_2\text{O}-5\text{Fe}_2\text{O}_3-\chi\text{P}_2\text{O}_5$ , the crystallization temperature increased from  $390^\circ\text{C}$  to  $480^\circ\text{C}$  for  $x = 30$  to  $x = 50$ , respectively (Figure 2 [14]). On the other hand, Figure 3 shows that an increase in the  $\text{Fe}_2\text{O}_3$  content in the glasses  $x\text{Li}_2\text{O}-y\text{Fe}_2\text{O}_3-\chi\text{P}_2\text{O}_5$  (with  $x/\chi = 0.54$ ) caused a quick increase in the value of the crystallization temperature from  $120^\circ\text{C}$  for a binary glass  $\text{Li}_2\text{O}-\text{P}_2\text{O}_5$  ( $y = 0$ ) to  $540^\circ\text{C}$  for  $y = 18$  [6,15]. Figure 4 shows for the binary glasses  $\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5$  that the variation in the annealing temperature ( $T_c$ ) according to the  $\text{Fe}_2\text{O}_3$  content had a maximum at  $700^\circ\text{C}$  for the glass composition  $16\text{Fe}_2\text{O}_3-84\text{P}_2\text{O}_5$  and was constant when the  $\text{Fe}_2\text{O}_3$  content was more than  $y = 25$  [16,17].

#### 3.2. X-Ray Diffraction

The X-ray diffraction spectra show that the crystallized glasses seemed to be similar to the closest crystalline

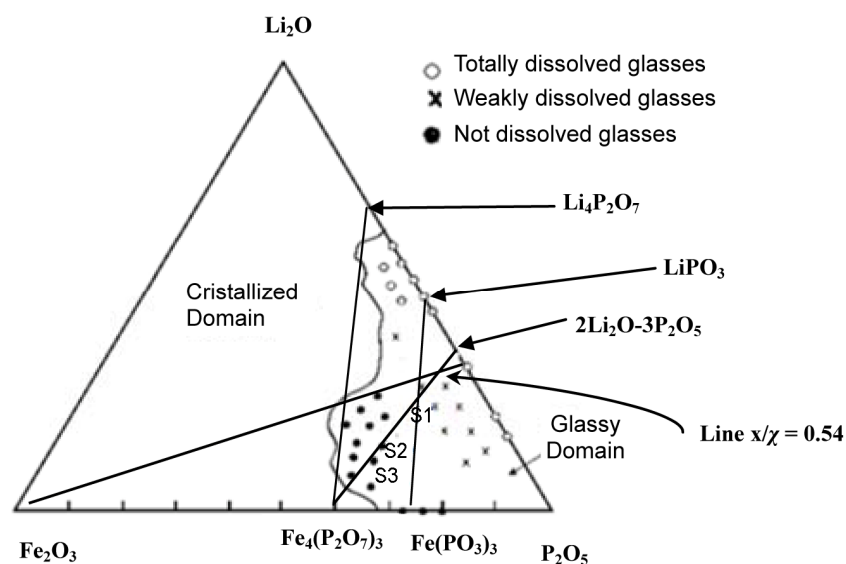
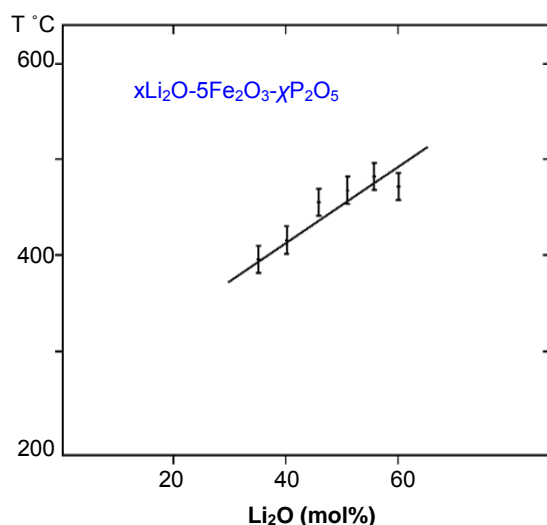
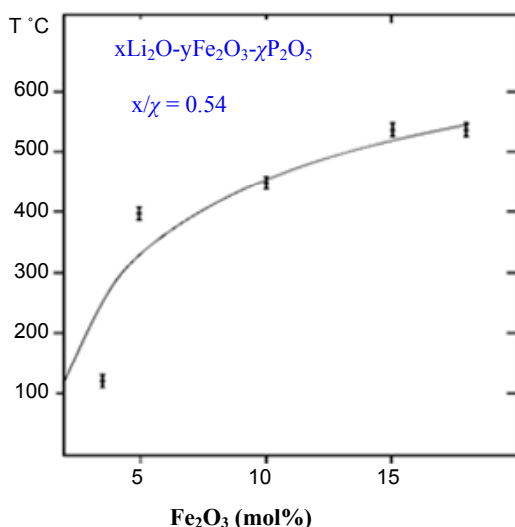


Figure 1. Extended from the vitreous field within the ternary diagram of  $\text{Li}_2\text{O}-\text{P}_2\text{O}_5-\text{Fe}_2\text{O}_3$  to  $1080^\circ\text{C}$  -  $1100^\circ\text{C}$ .



**Figure 2.** Crystallization temperature of iron phosphate glasses with the composition  $x\text{Li}_2\text{O}-5\text{Fe}_2\text{O}_3-\chi\text{P}_2\text{O}_5$ .



**Figure 3.** Crystallization temperature of iron phosphate glasses for the ratio  $\text{Li}_2\text{O}/\text{P}_2\text{O}_5 = 0.54$ .

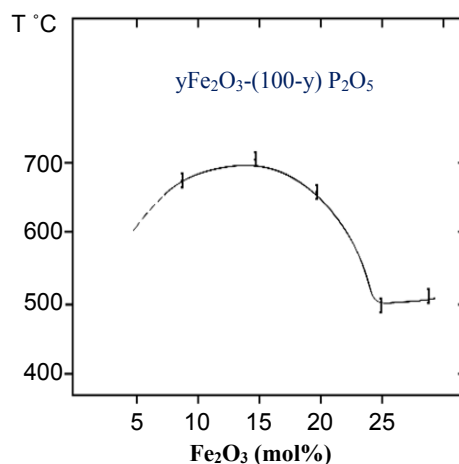
phases within the ternary diagram of  $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5$ . The X-ray diffraction spectra of crystallized glasses with the composition  $x\text{Li}_2\text{O}-5\text{Fe}_2\text{O}_3-\chi\text{P}_2\text{O}_5$  were similar to those of the  $\text{LiPO}_3$  glasses in the neighborhood of  $\chi = 50$  (**Figure 5(a)**) and those of  $\text{Li}_4\text{P}_2\text{O}_7$  for  $\chi \leq 45$  (**Figure 5(b)**). **Figure 6** shows the structural evolution for the ternary glasses  $x\text{Li}_2\text{O}-y\text{Fe}_2\text{O}_3-\chi\text{P}_2\text{O}_5$  localized along the line attributed to the ratio  $\text{Li}_2\text{O}/\text{P}_2\text{O}_5 = 0.54$ . We noted a mixture of metaphosphate phases for an  $\text{Fe}_2\text{O}_3$  content  $\leq 5$ , and pyrophosphate phases with an  $\text{Fe}_2\text{O}_3$  content  $\geq 15$  [1,18,19]. The x-ray diffraction spectra for crystallized glasses of the binary system  $y\text{Fe}_2\text{O}_3-(100-y)\text{P}_2\text{O}_5$  (**Figure 7**) seemed to favor the form of phases similar to  $\text{Fe}(\text{PO}_3)_3$  which become more obvious when the  $\text{Fe}_2\text{O}_3$  content increased to  $y = 25$ .

### 3.3. Chemical Stability

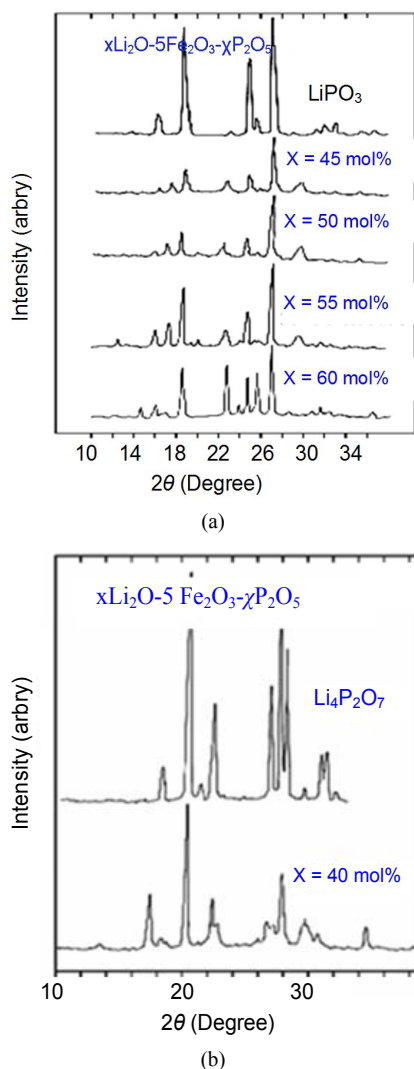
Binary glasses of the composition  $y\text{Fe}_2\text{O}_3-(100-y)\text{P}_2\text{O}_5$  had excellent chemical resistance toward chemical aggressors when the iron oxide content was increased in the glassy network. These glasses were immersed in weak and strong acid solutions of  $\text{HCl}$  (0.1 N, 1 N and 10 N) and  $\text{H}_2\text{SO}_4$  (0.1 N, 1 N and 10 N) for 30 days. Their weights before and after attack were practically the same. **Figure 1** shows that the iron ternary glasses had relatively weak chemical resistance to chemical aggressors when the  $\text{Li}_2\text{O}$  content was increased in the glass network. However, when this value decreased, the iron ternary glasses became resistant, even with a low  $\text{Fe}_2\text{O}_3$  content [1,5,20-22].

### 3.4. Infrared Spectra and SEM Analysis

The IR spectra of the binary  $y\text{Fe}_2\text{O}_3-(1-y)\text{P}_2\text{O}_5$  are shown in **Figure 8**. With an increase in the  $\text{Fe}_2\text{O}_3$  content, both the bands observed at  $1290$  and  $785\text{ cm}^{-1}$  and the band at  $940\text{ cm}^{-1}$  shifted to lower frequencies and the intensities decreased by changing the  $\text{Fe}_2\text{O}_3$  content from 10 to 28 mol%. The bands at  $1290\text{ cm}^{-1}$  assigned to  $\nu_{\text{as}}\text{PO}_2$  disappeared from the spectrum, while the band at  $725\text{ cm}^{-1}$  assigned to  $\nu_{\text{s}}\text{POP}$  became a simple shoulder. The intensity of the IR band at  $1070\text{ cm}^{-1}$  assigned to  $\nu_{\text{s}}\text{PO}_2$  increased broadly [1,23-25]. The IR spectra observed with the composition  $x\text{Li}_2\text{O}-5\text{Fe}_2\text{O}_3-\chi\text{P}_2\text{O}_5$  are shown in **Figure 9**. When lithium oxide was added to the glass network, this last one is depolymerized to the shorter group units, in agreement with results published by Ouchetto and al. [1,11,20-24]. The IR spectra show that the band at  $1280\text{ cm}^{-1}$  assigned to  $\nu_{\text{as}}\text{PO}_3$  decreased and shifted to lower frequencies when we shift away from the  $\text{P}_2\text{O}_5$  point. On the other hand, the intensity of the band at  $1100 - 1120\text{ cm}^{-1}$  was assigned to increased  $\nu_{\text{s}}\text{PO}_2$  when

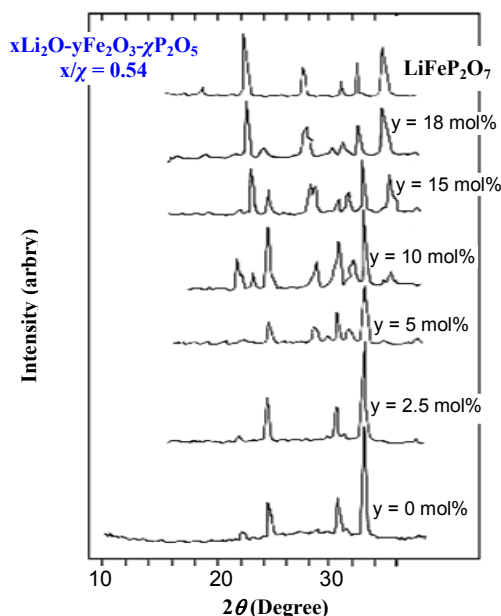


**Figure 4.** Crystallization temperatures of iron phosphate glasses with the composition  $y\text{Fe}_2\text{O}_3-(100-y)\text{P}_2\text{O}_5$ .

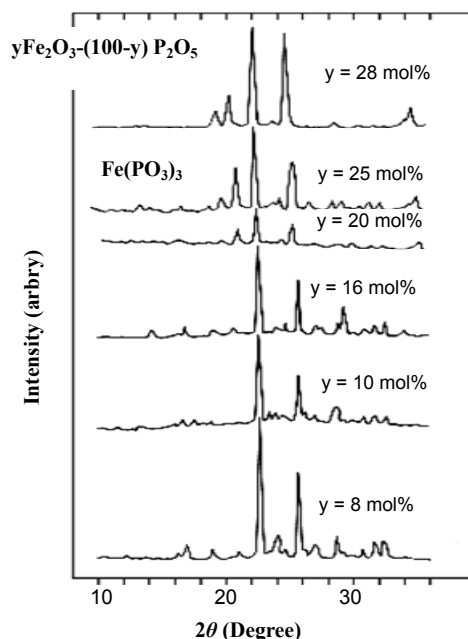


**Figure 5.** X-ray diffraction of crystallized lithium-iron phosphate glasses with the composition  $x\text{Li}_2\text{O}-5\text{Fe}_2\text{O}_3-\gamma\text{P}_2\text{O}_5$  compared with compounds  $\text{LiPO}_3$  (a) and  $\text{Li}_4\text{P}_2\text{O}_7$  (b).

the lithium oxide content increased. This increase in the  $\text{Li}_2\text{O}$  content breaks P-O-P bonds and increases the number of non-oxygen bridges. The IR spectra observed with these glasses were similar to the spectra of the  $x\text{Li}_2\text{O}-\gamma\text{P}_2\text{O}_5$  family, which can be explained by a similar structural evolution [1,10,12]. **Figures 10** and **11** show the IR spectra of glasses with the compositions  $x\text{Li}_2\text{O}-y\text{Fe}_2\text{O}_3-\gamma\text{P}_2\text{O}_5$  with  $x/\gamma = 0.54$  and  $x\text{Li}_2\text{O}-y\text{Fe}_2\text{O}_3-60\text{P}_2\text{O}_5$ , respectively. The analysis of these spectra showed that the band at  $1290\text{ cm}^{-1}$  assigned to  $\nu_{\text{as}}\text{PO}_2$  shifted toward lower frequencies and decreased when the iron oxides content increased. It disappeared completely when the  $\text{Fe}_2\text{O}_3$  content was  $>25$ . On the other hand, the band at  $1070 - 1100\text{ cm}^{-1}$  assigned to  $\nu_s\text{PO}_2$  with an iron oxide content of  $10 \leq y \leq 30$  seemed to form an envelope of the spectra of the compound  $\text{LiFeP}_2\text{O}_7$  (**Figure 10**), [1,19,23, 25-27]. These results suggest that these glasses were



**Figure 6.** X-ray diffraction after heat treatment at crystallization temperatures for lithium-iron phosphate glasses with the composition  $x\text{Li}_2\text{O}-y\text{Fe}_2\text{O}_3-\gamma\text{P}_2\text{O}_5$  with  $x/\gamma = 0.54$ .



**Figure 7.** X-ray diffraction of crystallized iron phosphate glasses of the binary system  $y\text{Fe}_2\text{O}_3-(100-y)\text{P}_2\text{O}_5$ .

formed, in general, by unit groups of pyrophosphate when the  $\text{Fe}_2\text{O}_3$  content increased. **Figure 12** shows SEM micrographs of sample S1 with the composition  $30\text{Li}_2\text{O}\cdot 10\text{Fe}_2\text{O}_3\cdot 60\text{P}_2\text{O}_5$  as well as micrographs of S2 and S3 with the composition  $20\text{Li}_2\text{O}\cdot 20\text{Fe}_2\text{O}_3\cdot 60\text{P}_2\text{O}_5$  and  $10\text{Li}_2\text{O}\cdot 30\text{Fe}_2\text{O}_3\cdot 60\text{P}_2\text{O}_5$ , respectively. The SEM micrograph of S1 (**Figure 12(a)**) shows an approximately homogenous glassy phase. However, SEM analysis

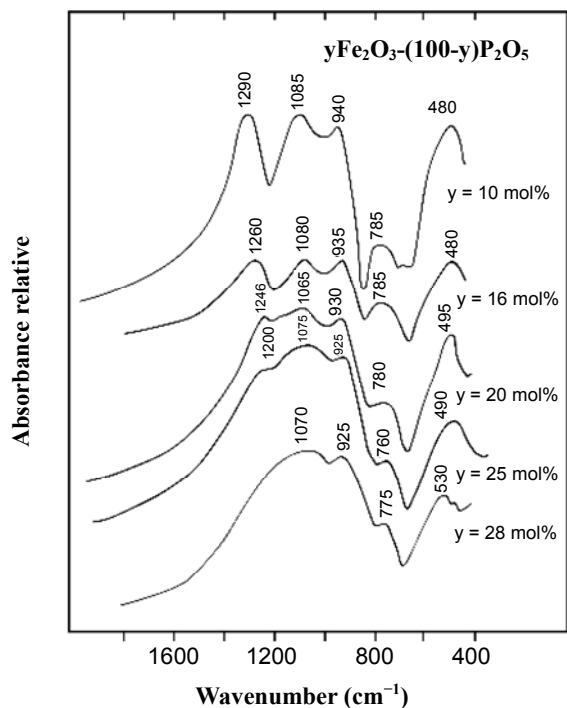


Figure 8. IR spectra of iron phosphate glasses with the composition  $y\text{Fe}_2\text{O}_3-(100-y)\text{P}_2\text{O}_5$ .

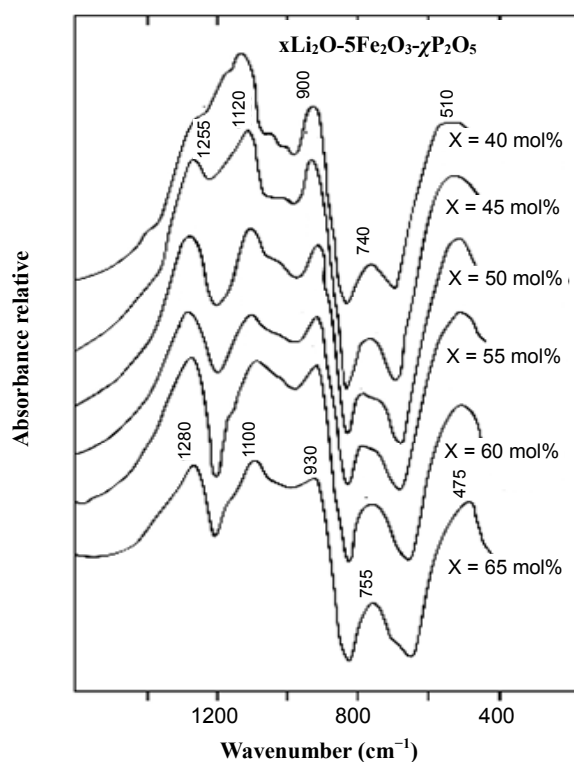


Figure 9. IR spectra of iron phosphate glasses with the composition  $x\text{Li}_2\text{O}-5\text{Fe}_2\text{O}_3-\gamma\text{P}_2\text{O}_5$ .

indicated the presence of crystalline phases in samples S2 and S3 which had an  $\text{Fe}_2\text{O}_3$  content  $\geq 20$  (mol%),

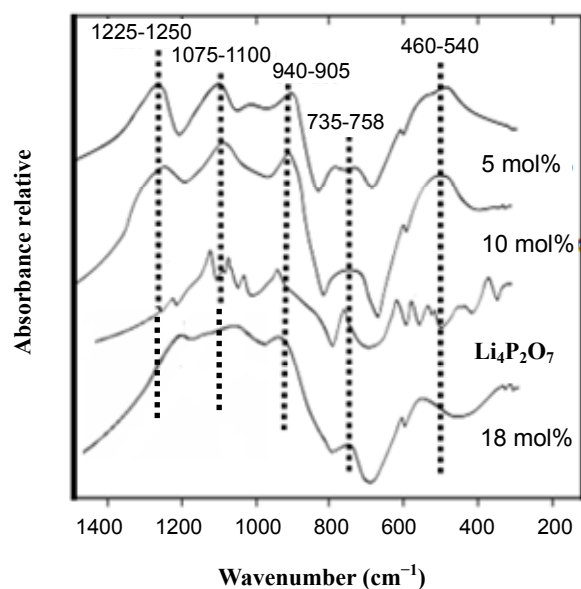


Figure 10. IR spectra of lithium-iron phosphate glasses with the composition  $x\text{Li}_2\text{O}-y\text{Fe}_2\text{O}_3-\gamma\text{P}_2\text{O}_5$  with  $x/\gamma = 0.54$ .

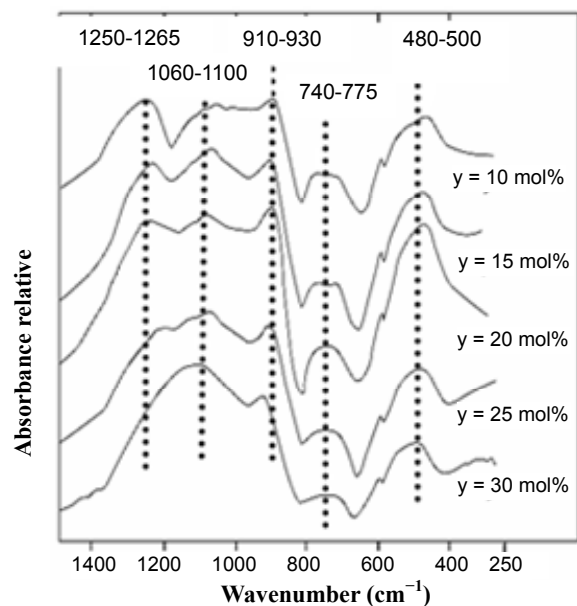


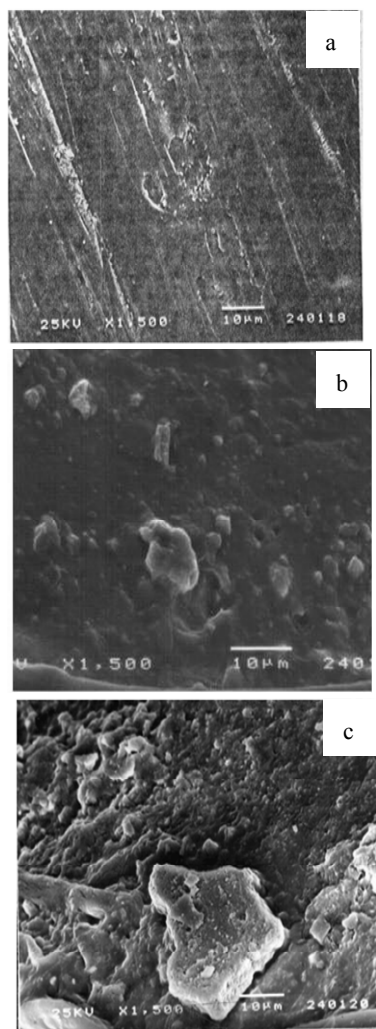
Figure 11. IR spectra of lithium-iron phosphate glasses with the composition  $(40-y)\text{Li}_2\text{O}-y\text{Fe}_2\text{O}_3-60\text{P}_2\text{O}_5$ .

shown in Figures 12(b) and (c), respectively. Hence, it seems that with an increasing  $\text{Fe}_2\text{O}_3$  content, the crystallization tendency is enhanced; the  $\text{LiFeP}_2\text{O}_7$  and  $\text{Fe}(\text{PO}_3)_3$  phases almost certainly crystallized in these glasses.

#### 4. Discussion

The regular melting-quenching method allowed for isolating a very large vitreous domain within the ternary system  $\text{Li}_2\text{O}-\text{P}_2\text{O}_5-\text{Fe}_2\text{O}_3$ . An increase in the lithium oxide content in phosphate glasses caused a small increase





**Figure 12.** SEM micrographs of samples with the composition  $(40-y)\text{Li}_2\text{O}-y\text{Fe}_2\text{O}_3-60\text{P}_2\text{O}_5$ .

in the crystallization temperature. However, an increase in the  $\text{Fe}_2\text{O}_3$  content in phosphate glasses initiated an important increase in the crystallization temperature. This was more significant for the binary glasses  $\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5$  where the crystallization temperature reached  $700^\circ\text{C}$  for the sample with the composition  $16\text{Fe}_2\text{O}_3\cdot 84\text{P}_2\text{O}_5$ . The X-ray diffraction spectra indicate the structural evolution of crystallized glasses in the ternary diagram of  $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5$ . The results show that when the composition of the vitreous zone was moved away from the  $\text{P}_2\text{O}_5$  point, the structure evolved toward one with a known crystallized composition neighborhood,  $\text{LiPO}_3$ ,  $\text{Fe}(\text{PO}_3)_3$ ,  $\text{Li}_4\text{P}_2\text{O}_7$ ,  $\text{LiFeP}_2\text{O}_7$ . When the iron oxide content increased in the glass network, both binary and ternary glasses showed excellent chemical resistance toward chemical aggressors. However, an increase in the  $\text{Li}_2\text{O}$  content led to poor chemical resistance. The IR spectra for glasses with the composition  $x\text{Li}_2\text{O}-5\text{Fe}_2\text{O}_3-\chi\text{P}_2\text{O}_5$  show that an increase in the lithium oxide content

in the glass network induced the birth of small units, more than in the binary system  $\text{Li}_2\text{O}-\text{P}_2\text{O}_5$  [1,9,11]. Hence, the introduction of a low  $\text{Fe}_2\text{O}_3$  content ( $y < 10$ ) in the glass had no effect on the structural evolution. The IR spectra in the region between  $1060$  and  $1100\text{ cm}^{-1}$  for the glasses with the composition  $x\text{Li}_2\text{O}-y\text{Fe}_2\text{O}_3-\chi\text{P}_2\text{O}_5$  with  $x/\chi = 0.54$  and  $(40-y)\text{Li}_2\text{O}-y\text{Fe}_2\text{O}_3-60\text{P}_2\text{O}_5$  confirmed the formation hypothesis of more small groups of  $\text{P}_2\text{O}_7^{4-}$  [28,29] when the  $\text{Fe}_2\text{O}_3$  content increased in the glass-network. IR spectra of the binary glasses  $\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5$  show that the band at  $1290\text{ cm}^{-1}$  assigned to  $\nu_a(\text{PO}_3)$  [1,2,7,9] disappeared when the  $\text{Fe}_2\text{O}_3$  content increased from  $y = 10$  to  $y = 28$ , which assigns the band at  $1070\text{ cm}^{-1}$  to  $\nu_s(\text{PO}_2)$  [1,9]. These results agree with those obtained by X-ray diffraction. Hence, these results indicate that iron phosphate glasses which have a high  $\text{Fe}_2\text{O}_3$  content are dominated by  $\text{P}_2\text{O}_7^{4-}$  and  $(\text{PO}_3)_3^{3-}$  dimer units and contain a large number of Fe-O-P bonds which are responsible for their excellent chemical durability [16, 30-31]. The X-ray diffraction and IR spectra for the iron phosphate glasses depend considerably on the composition and glass structure. The changes in the characteristic features of these spectra follow the changes in the glass network and glass stability in addition to crystallization.

In the model of the samples glasses S1, S2 and S3 we noted a clear evolution in chemical resistance, probably caused by grain boundary resistance as a result of partial glass crystallization [26,32]. It was found that the introduction of a small amount of  $\text{Fe}_2\text{O}_3$  ( $y < 10$ ) in the glass doesn't change the glass structure (Figure 9) and no significant effect on the chemical resistance. Looks like, it dissolves in the glass to give a homogeneous glass phase. When the iron oxide content reaches  $10\text{ mol}\%$ , there is the beginning of crystallites having a glassy phase dominant. Beyond  $10\%$  mole  $\text{Fe}_2\text{O}_3$  content in the glass, the number of crystallites becomes increasingly important, and size becomes larger when approaching the boundary between the glass and the crystal (border).

## 5. Conclusion

The regular melting-quenching method allowed isolating a very large vitreous domain within the ternary system  $\text{Li}_2\text{O}-\text{P}_2\text{O}_5-\text{Fe}_2\text{O}_3$ . The structure and properties of lithium iron phosphate glasses were investigated using various techniques. Both X-ray diffraction and IR spectra indicate a structural evolution of glasses with composition in the ternary diagram of  $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5$ . The results show that when the composition of the vitreous zone was moved away from the  $\text{P}_2\text{O}_5$  point, the structure evolved toward one with a known crystallized composition neighborhood,  $\text{LiPO}_3$ ,  $\text{Fe}(\text{PO}_3)_3$ ,  $\text{Li}_4\text{P}_2\text{O}_7$ ,  $\text{LiFeP}_2\text{O}_7$ . These glasses showed good chemical resistance for compositions with a high  $\text{Fe}_2\text{O}_3$  content. The iron phosphorus-oxygen network became stronger with an increase in

the Fe<sub>2</sub>O<sub>3</sub> content. The improved chemical resistance of iron phosphate glasses was attributed to the replacement of the easily hydrated P-O-P and Li-O-P bonds by corrosion-resistant Fe-O-P bonds. As the Fe<sub>2</sub>O<sub>3</sub> content in the glass increased, the number of Fe-O-P bands also increased. The IR spectra indicates that iron phosphate glasses are dominated by P<sub>2</sub>O<sub>7</sub><sup>4-</sup>, (PO<sub>3</sub>)<sub>3</sub><sup>3-</sup> dimer units and contain a large number of Fe-O-P bonds. The structural change caused an important tendency for crystallization which is the origin of the high chemical durability.

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