

Correlation between Chemical Durability Behaviour and Structural Approach of the Vitreous Part of the System $55\text{P}_2\text{O}_5-2\text{Cr}_2\text{O}_3-(43-x)\text{Na}_2\text{O}-x\text{PbO}$

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Abstract

Various characterisation techniques were used to study the composition of the glass series $55\text{P}_2\text{O}_5-2\text{Cr}_2\text{O}_3-(43-x)\text{Na}_2\text{O}-x\text{PbO}$ (with $8 \leq x \leq 38$; mole %) in terms of chemical durability, IR spectroscopy and scanning electron microscopy (SEM). The change in the dissolution rate as a function of time when the studied glasses were kept submerged in distilled water at 90°C for 20 days showed an improvement in the chemical durability when Na_2O content was substituted to PbO content. IR spectroscopy revealed a structural change from ultraphosphate groups to pyrophosphate, orthophosphate and probably ring metaphosphate groups. SEM revealed the existence of two phases: a vitreous phase and a crystalline phase. The presence of Cr_2O_3 , even in small amounts, seems to play an important role in the formation of crystallites in the glass network. The improved chemical durability is attributed to the replacement of the easily hydrated Na-O-P and P-O-P bonds by covalent and resistant Pb-O-P bands. Both the increase in PbO content and in the $\text{Pb} + \text{Cr}/\text{P}$ ratio causes an increase in the number of covalent Pb-O-P and Cr-O-P bonds, making the glass structure more rigid. The increase of the covalent Pb-O-P bands leads to a clear evolution of the structure and chemical resistance, caused by grain-boundary resistance as a result of glass crystallisation. The IR spectra indicate that the increase in PbO content favours the formation of isolated PO_4^{3-} orthophosphate groups at the expense of pyrophosphate groups. The radical change in the structure from ultraphosphate groups to pyrophosphate and orthophosphate groups seems to be the cause of the formation of crystallites. The existence of crystallites in these glasses results in a marked improvement in their chemical durability. However, when the crystallites exceed a certain

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limit, the equilibrium between the glass bath and these crystallites is no longer maintained; we notice, once, a decrease in the chemical durability.

Keywords

Phosphate Glasses, Chemical Durability, IR, SEM

1. Introduction

Phosphate glasses have been investigated principally because of their relatively low processing temperatures (1000°C - 1200°C) compared with borosilicate glasses (1200°C - 1500°C) and their relatively low softening temperature and liquid viscosity. Iron phosphate glasses, in particular, have shown the potential to vitrify many nuclear wastes that undergo completely unsuitable or poorly suitable vitrification in borosilicate glasses, such as heavy metals, phosphates, sulphates and chromium oxides that are insoluble in or chemically incompatible with borosilicate glass. The main problem in the use of phosphate glasses is their relatively low chemical resistance, which leads to relatively high leaching rates when they are exposed to humid environments [1] [2]. During the 1990s, an enhancement in chemical resistance was observed when iron and lead were used in the glass formulation [2]-[4]. This improvement resulted in reduced corrosion rates in aqueous environments and allowed the immobilisation of medium and high-activity radioactive wastes [4]-[9]. In this work, our aim is to contribute to the immobilisation of nuclear waste in a phosphate glass matrix, as a route to help in the prevention of environmental contamination. The study of the chemical durability and structural change along the series of phosphate glasses $55\text{P}_2\text{O}_5\text{-}2\text{Cr}_2\text{O}_3\text{-(}43\text{-}x\text{) Na}_2\text{O-xPbO}$ (with $8 \leq x \leq 38$ mol %) shows that an increase in PbO content in the glass network leads to an improvement in chemical durability which is explained by a radical change in the structure. This change is due to the increase of Pb-O-P covalent bonds in the glass. SEM micrographs show the presence of both a glass phase and a crystalline phase. The presence of both Pb-O-P and Cr-O-P covalent bands suggests that the formation of an increasing number of crystallites in the glass is the main cause of the increase in chemical durability. The IR spectra show a radical change in the structure from ultraphosphate groups to orthophosphate groups.

2. Experimental Procedures

The synthesis of chromium lead phosphate glasses of composition $55\text{P}_2\text{O}_5\text{-}2\text{Cr}_2\text{O}_3\text{ (}43\text{-}x\text{) Na}_2\text{O-xPbO}$ (with $8 \leq x \leq 38$ mol %) was carried out using direct fusion mixtures of $(\text{NH}_4)_2\text{HPO}_4$, Na_2CO_3 , Cr_2O_3 and PbO in suitable proportions. The reactants were finely ground and then introduced into a porcelain crucible. They were heated initially to 300°C for 1 hour then kept at 600°C for 1 hour to complete their decomposition. The reaction mixture was then heated to 1060°C - 1100°C for 20 minutes. The resulting homogeneous liquid was poured into an aluminium plate, preheated to 200°C to avoid thermal shock. In our experiments pellets about 1 cm in diameter and 2 to 3 mm thick were obtained. The chemical resistance of these glasses was evaluated from the sample weight loss. The samples were polished with carbon silica sandpaper (with CSI of sufficiently high level), cleaned with acetone and immersed in Pyrex beakers containing 100 ml of distilled water and carried to 90°C. The sample surface must be constantly submerged in distilled water for 20 consecutive days. The infrared spectra of the studied phosphate glasses were determined in the region between 1600 and 400 cm^{-1} with a resolution of 2 cm^{-1} . The samples were finely ground and mixed with KBr (potassium bromide), which is transparent in the infrared and serves as a template. The ratio of the matter/KBr in the pellets was 10% to 90% by weight. Infrared spectroscopic analysis of the materials was performed on a Fourier transform Vertex 70 spectrometer and recorded on a DTGS detector (deuterium triglycine sulphate). The microstructure of the glass samples was characterised using a scanning electron microscope (SEM) equipped with a complete system microanalyser (EDX-EDAX).

3. Results and Discussion

3.1. Chemical Durability

The chemical durability of the glass series $55\text{P}_2\text{O}_5\text{-}2\text{Cr}_2\text{O}_3\text{-(}43\text{-}x\text{) Na}_2\text{O-xPbO}$ (with $8 \leq x \leq 38$ mol %) was de-

terminated by measuring the dissolution rate (D_R) of glasses immersed for 20 consecutive days in 100 ml of distilled water heated to 90°C [6] [10]. The dissolution rate is defined as the loss of weight of the glass expressed in $\text{g}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$. The D_R and pH values are shown in **Table 1**. In **Figure 1** we see a gradual improvement in the chemical durability of glasses from 3.82×10^{-7} to 3.47×10^{-9} ($\text{g}/\text{cm}^2\cdot\text{min}$) when the PbO content varies at the expense of Na_2O from 8 to 28 mole % respectively. However, we noted a decrease in the chemical durability when the PbO content ranges from 28 to 38 mol %. **Figure 2** shows a slight increase in the pH when the PbO content increases. However, we note that the pH decreases slightly when PbO content ranges from 28 to 38 mol %. This appears to be explained by the presence of phosphoric polyacid or phosphoric acid in the solution caused by a small degradation of S4 glass, which also results in a slight decrease in the chemical durability.

3.2. Infrared Spectra

IR spectra of the glass series $55\text{P}_2\text{O}_5\text{-}2\text{Cr}_2\text{O}_3\text{-(}43\text{-x)Na}_2\text{O-xPbO}$ ($8 \leq x \leq 38$; mol %) are shown in **Figure 3**. All vibration bands of treated phosphate glasses are shown in the frequency range between 390 and 1590 cm^{-1} . The band at $500 - 510\text{ cm}^{-1}$ is assigned to the deformation of the skeleton δ_{ske} (P-O-P) [11]. The band at $730 - 750\text{ cm}^{-1}$ is assigned to the symmetric stretching ν_{sym} (P-O-P) phosphorus bridge tetrahedral [6], while the bands at $870 - 900$ and $975 - 980\text{ cm}^{-1}$ are assigned respectively to the vibration of asymmetric ν_{asym} (P-O-P) and $\nu_s\text{ PO}_4^{3-}$ due to non-bridging oxygen atoms [5] [12] [13]. The band at about 1069 to 1103 cm^{-1} is attributed to the stretching of $\nu_{\text{sym}}(\text{PO}_3)/\nu_{\text{asym}}(\text{PO}_3)$ while the band from 1222 to 1225 cm^{-1} is assigned to the stretching of $\nu_{\text{asym}}(\text{PO}_2)$ [5] [6]. With increasing values of x , the intensity of the bands characteristic of pyrophosphate groups tends to decrease while the bands typical of orthophosphate groups tend to increase and dominate as PbO content increases relative to Na_2O content. This phenomenon becomes apparent in the spectrum of the composition

Table 1. Glasses composition in mol % and selected properties of sodium lead chromium phosphate glasses.

Glass Sample	Starting mixtures oxide mol %				Ratio [O/P]	D_R ($\text{g}/\text{cm}^2/\text{min}$)	pH
	PbO	Na_2O	Cr_2O_3	P_2O_5			
S ₁	8	35	2	55	2.95	$(3.81 \pm 0.20) \times 10^{-7}$	6.47 ± 0.50
S ₂	18	25	2	55		$(3.50 \pm 0.20) \times 10^{-8}$	6.80 ± 0.50
S ₃	28	15	2	55		$(1.74 \pm 0.20) \times 10^{-9}$	6.70 ± 0.50
S ₄	38	5	2	55		$(3.50 \pm 0.20) \times 10^{-9}$	6.30 ± 0.50

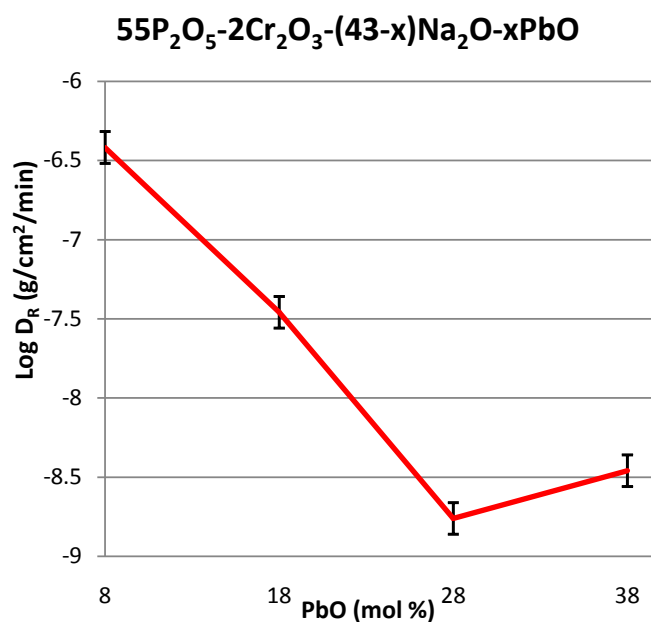


Figure 1. Dissolution rates (D_R) of the glass series $55\text{P}_2\text{O}_5\text{-}2\text{Cr}_2\text{O}_3\text{-(}43\text{-x)Na}_2\text{O-xPbO}$ versus PbO (mol%).

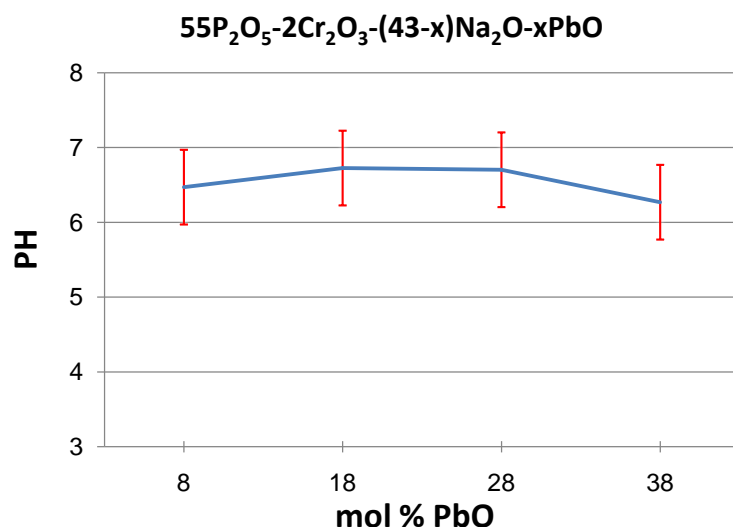


Figure 2. The pH values of the solution of sodium-lead chromium phosphate glasses were, immersed at 90°C for 20 days versus PbO (mol %).

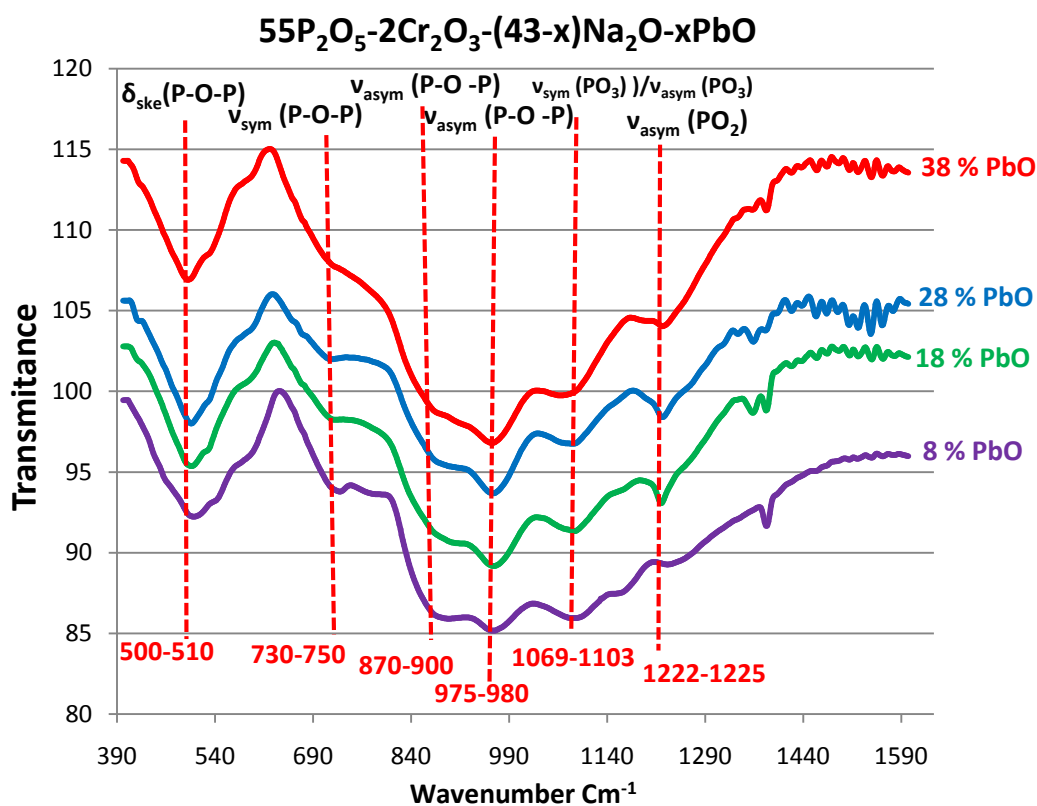


Figure 3. IR spectra of the series $55P_2O_5-2Cr_2O_3-(43-x)Na_2O-xPbO$; $x = 8, 18, 28$ and 38 .

S4 where vibration bands at $730 - 750\text{ cm}^{-1}$ and $840 - 900\text{ cm}^{-1}$ become a simple shoulder while the band at $975 - 980\text{ cm}^{-1}$ becomes wider and more intense [3] [5] [14] [15]. On the other hand, **Figure 4** and **Table 2** show that the studied glasses are located in the field of ultra-phosphate chains. As we expected that the structural change would be schematically the same as that found in the ternary diagram (**Figure 4**), we Remarque that it doesn't the case. This is seems to due to the physical and chemical properties of the intermediate oxide that participates in the glass formation (melting temperature, rate of Pb + Cr/P...) [2].

3.3. SEM Analysis

The SEM micrograph (Figure 5) shows the existence of two phases, a vitreous phase and a crystalline phase [5] [15]. It also indicates the formation of crystalline phase agglomerates of various sizes, ranging from some microns to several tens of microns as seen from Figure 5(a) to Figure 5(c) attributed respectively to the samples S1, S3 and S4. This probably explains the structural change towards more short chains as the rate of PbO increases in the glass network. On the other hand the micrographs of the samples after attack by distilled water at 90°C for 20 consecutive days (Figure 5(d) to Figure 5(f)), attributed respectively to the samples S1, S3 and S4, indicate these glasses are intact, and deposits in the bottom of the containers bottom are not visible to the naked eye.

3.4. Discussion

In our study, we prepared a glass series with different percentages of phosphate oxides: PbO, Na₂O, Cr₂O₃ and P₂O₅ were used as the basic constituents. In this series we substituted the Na₂O oxide with PbO oxide while keeping the percentage of P₂O₅ and Cr₂O₃ oxides constants. Both the presence of Cr₂O₃ and the substitution of Na₂O by PbO in the glass network lead to a considerable improvement in the chemical durability [3] [5] [15]. The improved chemical durability is attributed to the replacement of the easily hydrated Na-O-P and P-O-P bonds by covalent and resistant Pb-O-P bands. Both the increase in PbO content and in the Pb + Cr/P ratio cause an increase in the number of covalent Pb-O-P and Cr-O-P bands and make the glass structure more rigid. This represents a clear evolution in the structure and chemical resistance, caused by grain-boundary resistance as result of glass crystallisation [16]-[20]. On the other hand, IR spectra indicated that both the presence of Cr₂O₃ and increasing PbO content from 8 to 38 mol % at the expense of Na₂O promote depolymerisation of the glass network by creating short chain pyrophosphates, orthophosphates and probably ring metaphosphate chains. Furthermore a large band attributed to the stretching of vs PO₄³⁻ [15] appears at 975 - 980 cm⁻¹, to the detriment of the band at 870 - 900 cm⁻¹, which becomes a simple shoulder when the PbO content reach 38 mol %. This

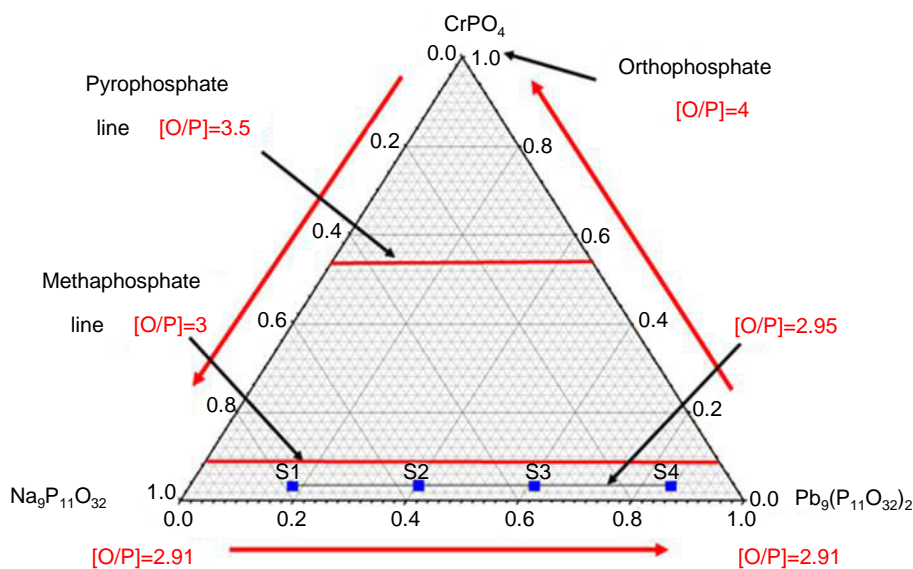


Figure 4. Localization of the investigated glass compositions in the ternary diagram.

Table 2. Glass composition expressed as in terms of ternary and quaternary systems.

Glass samples	Chemical composition	Composition of glasses in the ternary diagram
S ₁	35 Na ₂ O·8 PbO·2Cr ₂ O ₃ ·55 P ₂ O ₅	0.044 (Cr ₂ O ₃ -P ₂ O ₅)·0.778 (Na ₂ O-P ₂ O ₅)·0.178 (PbO-P ₂ O ₅)
S ₂	25 Na ₂ O·18 PbO·2Cr ₂ O ₃ ·55 P ₂ O ₅	0.044 (Cr ₂ O ₃ -P ₂ O ₅)·0.556 (Na ₂ O-P ₂ O ₅)·0.4 (PbO-P ₂ O ₅)
S ₃	15 Na ₂ O·28 PbO·2Cr ₂ O ₃ ·55 P ₂ O ₅	0.044 (Cr ₂ O ₃ -P ₂ O ₅)·0.333 (Na ₂ O-P ₂ O ₅)·0.622 (PbO-P ₂ O ₅)
S ₄	5 Na ₂ O·38 PbO·2Cr ₂ O ₃ ·55 P ₂ O ₅	0.044 (Cr ₂ O ₃ -P ₂ O ₅)·0.111 (Na ₂ O-P ₂ O ₅)·0.845 (PbO-P ₂ O ₅)

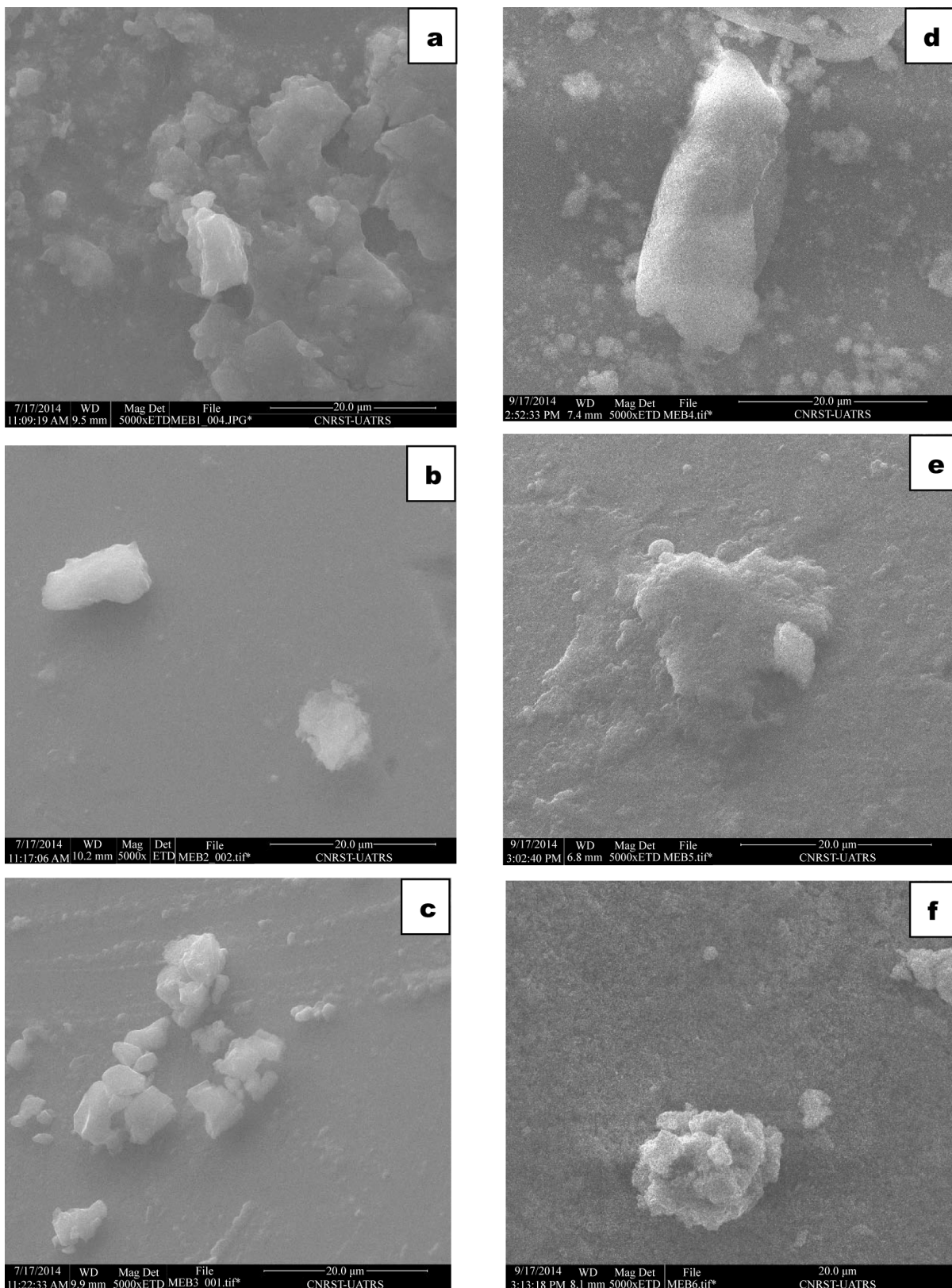


Figure 5. SEM micrograph showing the visual structure of the samples S1 (a), S3 (b), S4 (c) before the aqueous attack and of the samples S1 (d), S3 (e), S4 (f) after the aqueous attack.

indicates the predominance of isolated orthophosphate groups (Q^0). The decrease in chemical durability beyond 28 mol % PbO seems to be explained by the increase of crystallites in the glass, which contain the majority of the isolated orthophosphate phases (Q^0). According to the IR spectra, the (Q^0) groups increase at the expense of both pyrophosphate groups (Q^1) and metaphosphates (Q^2) [12]. Generally an increase in crystallites in glasses causes an increase in chemical durability. This paradox can be explained by the fact that when the crystallites that dominate the glass belong to orthophosphate crystal phases ($O/P = 4$), this indicates that we are near the border between the glass and the crystal [2]. In this case, the chemical durability becomes relatively low due to the break of the glass structure, probably caused by a lack of equilibrium between the glass phase and the crystallites formed. The SEM micrographs of samples S1, S3 and S4 are consistent with this theory, with this theory that probably explains the decrease in crystallites size when the PbO content increases from S1 to S4. Therefore we can predict a depolymerisation of the largest phosphate network to isolated short chains of the orthophosphate (Q^0) type.

4. Conclusion

The influence of PbO on the glass forming characteristics and properties of $55P_2O_5-2Cr_2O_3-(43-x) Na_2O-xPbO$ ($8 \leq x \leq 38$; mol %) was investigated. The change in the dissolution rate over time of such glasses shows an improvement in chemical durability with increasing PbO content to the detriment of Na₂O content. Both the increase in PbO content and in the Pb + Cr/P ratio causes an increase in the number of covalent Pb-O-P and Cr-O-P bands, making the glass structure more rigid. IR spectra indicate the formation of short chain pyrophosphates, orthophosphates and probably ring metaphosphates. This radical change in the glass structure led to the formation of crystallites of different sizes. These crystallites seem to play a primary role in the increase in chemical durability of the studied glasses. However, when the crystallites exceed a certain limit, the equilibrium between the glass bath and these crystallites is not longer maintained; we notice, once, a few decrease in the chemical durability. The dissolution rate (D_R) obtained is 50 times less than those of borosilicate glasses, which is used as an alternative method for the vitrification of nuclear waste substances.

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