

Study of sodium-chromium-iron-phosphate glass by XRD, IR, Chemical Durability and SEM

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ABSTRACT

Chromium iron phosphate glass was investigated for use as waste form because of its improved chemical durability. The introduction of chromium in sodium-iron-phosphate glasses is used to compare its effect with iron in inhibition of corrosion. The sodium-chromium-iron phosphate glass of composition $10\text{Na}_2\text{O}_3\text{-}30\text{Fe}_2\text{O}_3\text{-}5\text{Cr}_2\text{O}_3\text{-}55\text{P}_2\text{O}_5$ (mol %) was produced by melting batches of (99, 98% pure) Cr_2O_3 , Fe_2O_3 , Na_2CO_3 , and $(\text{NH}_4)_2\text{HPO}_4$ at 1080°C for one hour and pouring the liquid into steel mold. The Sample was annealed at 680°C for 48h. We have performed the measurement of X-Ray diffraction, SEM, IR Spectroscopy and the chemical durability. The IR of the glass studied, contains two dominant bands, which were characteristic of pyrophosphate groups, (P-O) stretching mode of P-O non bridging oxygen at 1055 cm^{-1} and sym stretching mode of bridging oxygen at 444 cm^{-1} respectively. There is also a band at 603 cm^{-1} attributed to isolated tetrahedral units $(\text{PO}_4)^{3-}$. The chemical durability of the glass was investigated by measuring the weight loss in distilled water at 90°C for 22 days.

Keywords: Chemical durability, IR spectroscopy, Scanning Electron Microscopy, glass formation, Sodium-chromium-iron-phosphate glasses, XRD

1 INTRODUCTION

The iron phosphate glasses have generally both excellent chemical durability and low melting temperature typical between 950 and 1100°C , [1]. Chromium phosphate glasses for the immobilisation and disposal of nuclear waste were reported 1984 [2]. The combination of chromium phosphate glasses with various types of simulated nuclear waste showed that it is possible to have a waste form with a corrosion rate more slowly than that of a comparable borosilicate glass. Therefore it has been suggested that the chemical durability of sodium-chromium-iron phosphate glasses is attributed to the replacement of P-O-P bonds by P-O-Cr and P-O-Fe bonds. The presence P-O-Fe bands in higher concentrations, makes the glass more hydration resistant [1, 3-6]. The P-O-Cr bands seem to play the same role than P-O-Fe bands [7].

2 EXPERIMENTAL

The glass of composition $10\text{Na}_2\text{O}\text{-}30\text{Fe}_2\text{O}_3\text{-}5\text{Cr}_2\text{O}_3\text{-}55\text{P}_2\text{O}_5$ (mol %) is obtained by the melting quench method in 1080°C . Appropriate mixture of mixing compounds Na_2CO_3 , ferric oxides, Cr_2O_3 and $(\text{NH}_4)_2\text{HPO}_4$ were initially tempered at various temperatures between $300\text{-}500^\circ\text{C}$ to achieve a preparation before the glass preparation.

The melt was achieved in alumina crucibles for about 30 mn at $1080\pm 10^\circ\text{C}$. The isolated glasses samples have an approximate of size 10mm diameter and 3 mm in thickness. The vitreous state was first evidenced from the shiny aspect and then confirmed from XRD patterns. Annealing of this glass was realized at 680°C for 48 hours. The first structural approach was made using X-rays diffraction which allowed to follow. The density of the glass was measured at room temperature using the helium pycnometry method. The chemical durability sample of the size $0.9\times 0.9\times 0.9\times 0.3\text{ cm}$ was used sample were first polished to a 400 grit finished with SiC paper, then they were immersed in a flask filled with 100ml of distilled water at 90°C for a time of 22 days. The dissolution rate (D_R) was then determined from the weight loss during the aqueous treatment at 90°C . The infrared (IR) spectra for each glass were measured between 400 and 1600 cm^{-1} using mX^{-1} and NIC-3600 FTIR spectrometers. The sample was prepared by pressing a mixture of about 2mg of glass powder and 100mg of anhydrous KBr powder. The chemical of composition of the analysed glass is given in Table 1.

Starting glass Composition (mol %)				[O/P] ratio	(D_R) (g/cm ² /mn)	ρ (g/cm ³)
Na ₂ O ₃	Fe ₂ O ₃	Cr ₂ O ₃	P ₂ O ₅		22 days	± 0.02
10	30	5	55	3,72	$(7,188\pm 0,001)\times 10^{-9}$	2,627

Table 1: bench composition, calculated (O/P) ratio, D_R and sensity of the glass studied

3 RESULTS

3.1 X-Ray diffraction, Thermal analysis, and density

No crystalline phase was detected by X-ray in the glass composition $10\text{Na}_2\text{O}_3\text{-}30\text{Fe}_2\text{O}_3\text{-}5\text{Cr}_2\text{O}_3\text{-}55\text{P}_2\text{O}_5$, whereas we notice that there is the existence of crystalline micro domain (Fig. 1,a,b).

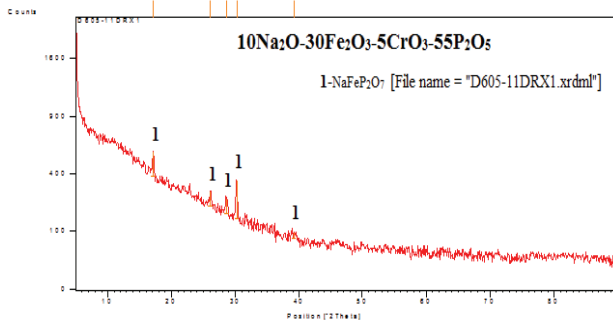


Fig. 1.a.- X-ray diffraction spectra for the sample $10\text{Na}_2\text{O}_3\text{-}30\text{Fe}_2\text{O}_3\text{-}5\text{Cr}_2\text{O}_3\text{-}55\text{P}_2\text{O}_5$

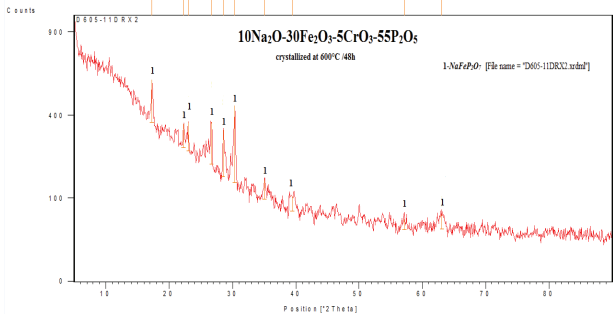


Fig. 1.b.- X-Ray diffraction pattern for $10\text{Na}_2\text{O}_3\text{-}30\text{Fe}_2\text{O}_3\text{-}5\text{Cr}_2\text{O}_3\text{-}55\text{P}_2\text{O}_5$ glass partially crystallized at 650°C for 48h

3.2 Infrared Spectroscopy Study

The infrared spectra shown in the Fig.2 , for the glass of composition $10\text{Na}_2\text{O}_3\text{-}30\text{Fe}_2\text{O}_3\text{-}5\text{Cr}_2\text{O}_3\text{-}55\text{P}_2\text{O}_5$ include two dominant bands. These bands are characteristics of pyrophosphate groups: the band at 1099 cm^{-1} and 760 cm^{-1} are attributed to $(\text{PO}_3)^{1-}$ asymmetric stretching mode of non bridging oxygen (P-O-P) sym stretching mode of bridging oxygen, respectively [7,9,10]. The band at 992 cm^{-1} seems to assigned to the isolated tetrahedral units $(\text{PO}_4)^{3-}$ [11,12] †.

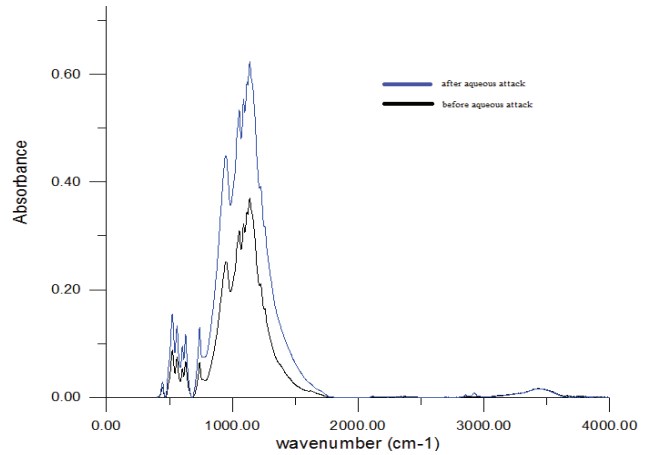


Fig. 2.-The IR spectra of sodium-chromium-iron-phosphate glass

3.3 Scanning Electron Microscopy

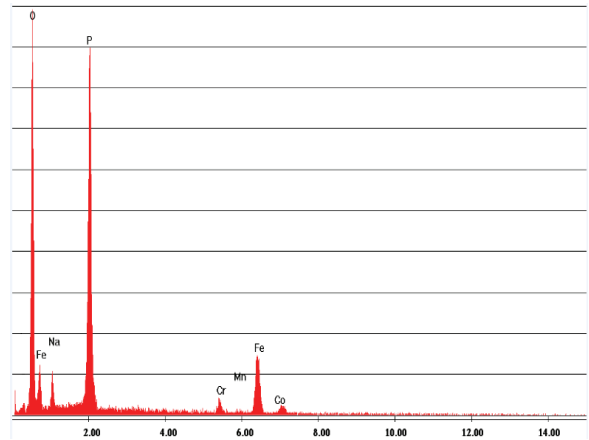


Fig. 3.a.- The SEM plot for the sample glass $10\text{Na}_2\text{O}_3\text{-}30\text{Fe}_2\text{O}_3\text{-}5\text{Cr}_2\text{O}_3\text{-}55\text{P}_2\text{O}_5$ (before aqueous attack)

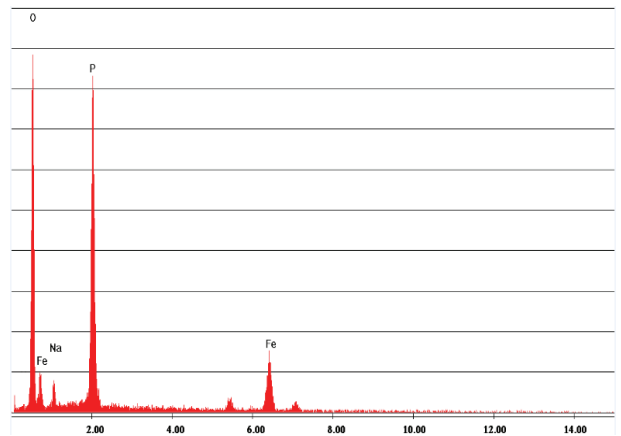


Fig. 3.b.- The SEM plot for the sample glass $10\text{Na}_2\text{O}_3\text{-}30\text{Fe}_2\text{O}_3\text{-}5\text{Cr}_2\text{O}_3\text{-}55\text{P}_2\text{O}_5$ (after aqueous attack)

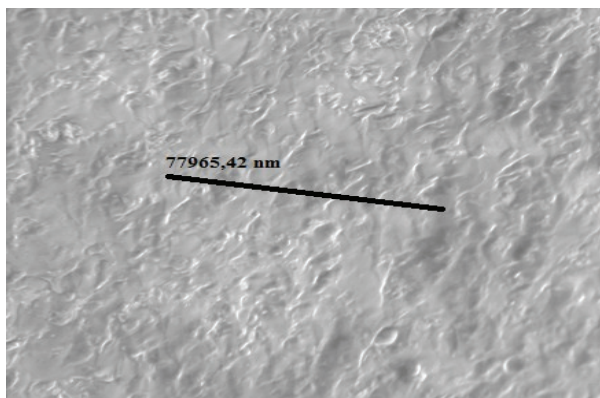
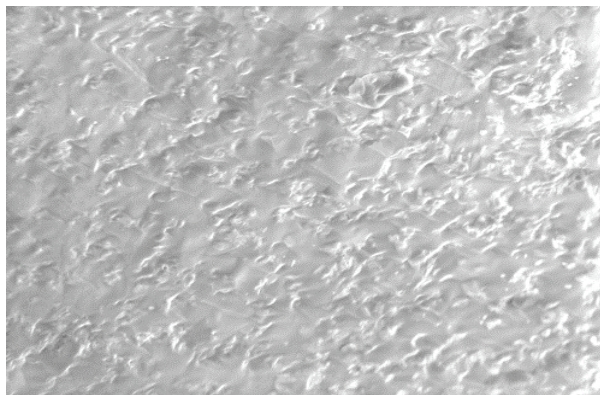
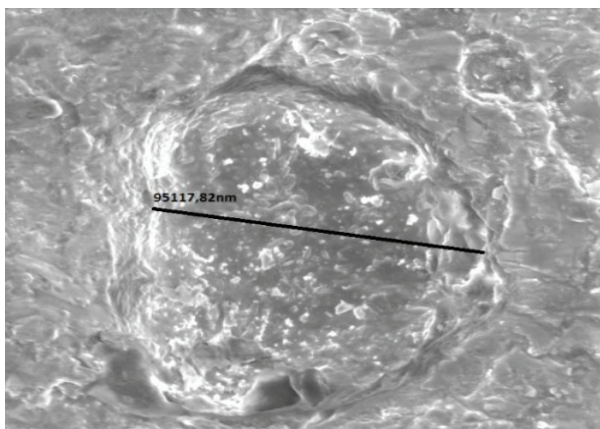


Fig. 4.a. Microscopic photograph of the surface of the glass $10\text{Na}_2\text{O}_3\text{-}30\text{Fe}_2\text{O}_3\text{-}5\text{Cr}_2\text{O}_3\text{-}55\text{P}_2\text{O}_5$,



before aqueous attack (Resolution of $50\mu\text{m}$).

Fig. 4.b. Microscopic photograph of the surface of the glass $10\text{Na}_2\text{O}_3\text{-}30\text{Fe}_2\text{O}_3\text{-}5\text{Cr}_2\text{O}_3\text{-}55\text{P}_2\text{O}_5$, after 22 days of aqueous attack

3.4 Dissolution rate

The dissolution rate (D_R) for sodium-lead-iron-phosphate glass is a function of time (see fig. 3.b.). The dotted line indicates the dissolution rate of the glass which is included for comparison. Experimental dissolution rate for lead-iron-phosphate glass were reported by Day and Al [19]. In the present work the dissolution rate for $10\text{Na}_2\text{O}\cdot 30\text{Fe}_2\text{O}_3\cdot 5\text{Cr}_2\text{O}_3\cdot 55\text{P}_2\text{O}_5$ glass decreases as the time of immersion in water increases. This decrease is observed in this type of glass because in the early stage the solution is still dilute and the increase of glass leaching product has a relatively minor effect upon the rate of reaction.

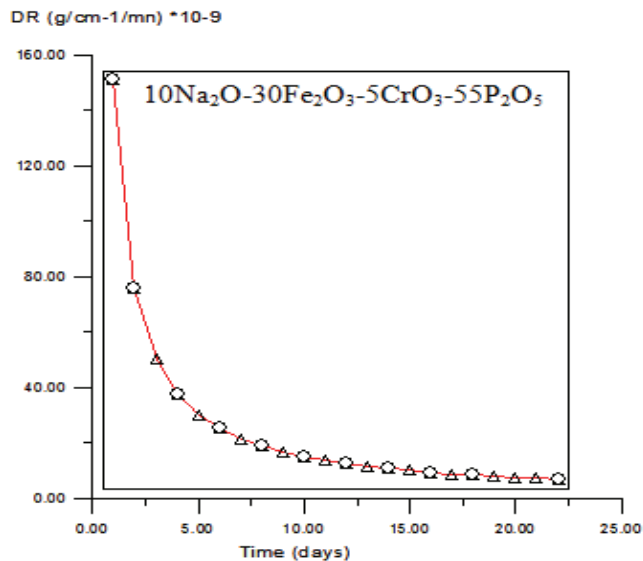


Fig. 5.-Dissolution rate for sodium chromium iron phosphate glass as a function of immersion time in Aqueous solution at 90°C .

4 DISCUSSION- CORRELATION BETWEEN THE STRUCTURE AND THE HIGH DURABILITY OF IRON PHOSPHATE GLASSES

Both XRD and IR techniques have confirmed the structural evolution of the glass network towards the pyrophosphate. So the structure of sodium-chromium-iron phosphate glass can be considered as pyrophosphate units connected with ferric and ferrous ions in octahedral or distorted octahedral coordination. The chemical durability of sodium-chromium-iron phosphate glass of composition $10\text{Na}_2\text{O}_3\text{-}30\text{Fe}_2\text{O}_3\text{-}5\text{Cr}_2\text{O}_3\text{-}55\text{P}_2\text{O}_5$ (regarding aqueous attack at 90°C) is attributed to the increasing number of Fe-O-P bonds in the glass [6, 20, 21]. Such bonds are expected to be more water resistant than the P-O-P and Na-O-P bands. This glass have a (D_R) 50 times less than the DR of window glass and ~ 150 times less than the D_R for BABAL glass which have been considered as alternative

materials for the immobilization of nuclear waste substance[11, 13].

4 CONCLUSION

The structure and the chemical durability of Sodium-chromium-iron phosphate glass of composition $10\text{Na}_2\text{O}_3\text{-}30\text{Fe}_2\text{O}_3\text{-}5\text{Cr}_2\text{O}_3\text{-}55\text{P}_2\text{O}_5$ (mol %) have been investigated using various techniques such IR, XRD, SEM....

The structure of the $10\text{Na}_2\text{O}_3\text{-}30\text{Fe}_2\text{O}_3\text{-}5\text{Cr}_2\text{O}_3\text{-}55\text{P}_2\text{O}_5$ (mol %) glass can be considered as pyrophosphate units connected with chromium. This glass have a (D_R) ~ 200 times less than the D_R for BABAL glass which have been considered as alternative materials for the immobilization of nuclear waste substance. This result is very important for applications in the nuclear waste management. The improved chemical durability is attributed to the replacement of the easily hydrated Na-O-P and P-O-P bonds by corrosion resistant Fe-O-P and Pb-O-P bands. The recorder IR spectra indicate that these glasses are dominated by $(\text{P}_2\text{O}_7)^+$ dimer units, and contain a large number of Fe-O-P bonds.

5 ACKNOWLEDGMENT

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