CHEMICAL DURABILITY AND CHARACTERIZATION OF THE PHOSPHATE GLASSES CONTAINING IRON, SODIUM AND CHROMIUM

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Abstract

In order to prepare a high quality glass with high water resistance, we investigated chromium iron phosphate glass 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 $30Fe_2O_3$-xCr_2O_3-(15-x)Na_2O-$55P_2O_5$ (mol %),with ($0 \leq x \leq 4$) was produced by melting batches of (99,98% pure) Cr_2O_3, Fe_2O_3, Na_2CO_3, and $(NH_4)_2HPO_4$ at 1080°C for one hour and pouring the liquid into the bench. The sample was annealed at 650°C for 48h. We have performed the measurement of X-Ray diffraction, and Infra Red spectroscopy. The chemical durability was evaluated by weight losses of glass samples after immersion in hot distilled water (90°C) for 30 days. Weight loss measurements showed a good chemical durability unlike borosilicate glass.

Keywords: *Chemical durability, IR spectroscopy, Scanning electron microscopy, glass formation, Sodium-chromium-iron-phosphate glasses, XRD, iron oxide, chromium oxide, sodium oxide, phosphate oxide.*

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 in 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 one 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 of P–O–Fe bands in higher concentration 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. PREPARATION AND CHARACTERIZATION

The glasses of compositions $30Fe_2O_3$-xCr_2O_3-(15-x)Na_2O-$55P_2O_5$ (mol %) with ($0 \leq x \leq 4$) are obtained by the melting quench method in 1080°C. The corresponding mixture with compounds Na_2CO_3, Fe_2O_3, Cr_2O_3 and $(NH_4)_2HPO_4$ is introduced in porcelain crucible then heated for 24 hours. The temperature was then progressively raised to 1100°C and held in this temperature for few minutes. The molten glasses quenched in air and later annealed close to glass transition temperature.

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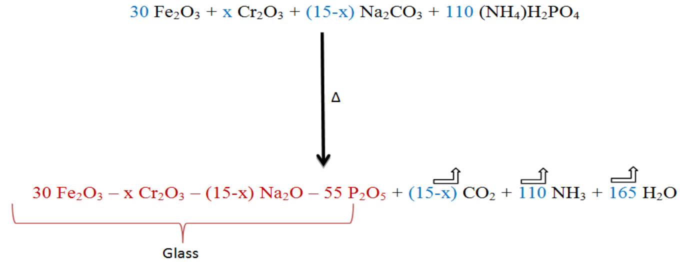
3. THE SYNTHESIS REACTION GLASSES



The synthesis reaction

The melt was achieved in porcelain crucibles for about 30 min at 1080±10°C. The isolated glasses samples have an approximate diameter of 10mm and 3 mm in thickness. The X-ray diffraction analysis was used to confirm the amorphous state of the samples. Annealing of this glass was realized at 650°C for 48 hours. The first structural approach was made using X-rays diffraction. The density of the glass was measured at room temperature using the Archimedes method [8]. The samples were immersed in a flask filled with 100ml of distilled water at 90°C for a time of 30 days. The dissolution rate (D_R) was then determined from the weight loss during the aqueous treatment at 90°C.
The chemical Durability of the analysed glass is given in Table 1.

Starting glass composition (mol %)				[O/P] ratio	(D_R) (g/cm^3/mn)	ρ (g/cm^3)
Fe_2O_3	Cr_2O_3	Na_2O	P_2O_5		30 days	±0,02
30	0	15	55	3,4545	(3,042±0,001)*10	2,66
30	1	14	55	3,4727	(3,0405±0,001)*10 9	2,66
30	2	13	55	3,4909	(3,0399±0,001)*10 9	2,63
30	3	12	55	3,5090	(3,0343±0,001)*10 9	2,61
30	4	11	55	3,5272	(3,0309±0,001)*10 9	2,66

Table 1: Compositions, density and chemical durability of $30Fe_2O_3xCr_2O_3$-(15-x)Na_2O_3-$55P_2O_5$(mol%)with (0≤x≤4) glasses

The glass density is given by the following equation:

$$\rho_{glass}=\left[\frac{m_{air}}{m_{air}+(m_{ortho}-m_{(ortho+glass)})}\right]*\rho_{ortho}$$

with:

- m_{air} = mass of the sample (glass) measured in air
- m_{ortho} = mass diethyl orthophthalate only
- $m_{ortho\,+\,glass}$= mass of glass immersed in diethyl orthophthalate
  ρ_{ortho}=1,11422 g/cm³

4. THERMAL TREATMENT

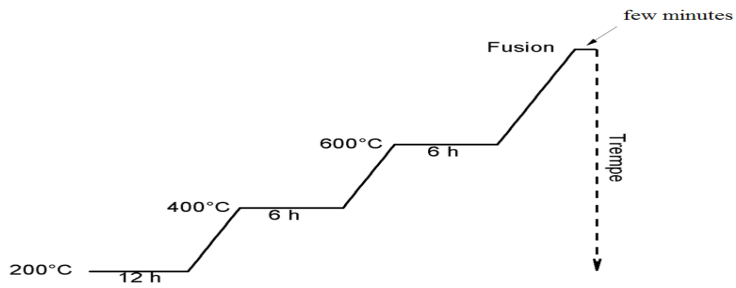


Fig.1 Thermal treatment carried out for the preparation of the glasses

5. RESULTS AND DISCUSSION

a. XRD STUDY

In this work we tried to develope new compositions of the quaternary oxides glasses system $30Fe_2O_3$-xCr_2O_3-$(15-x)Na_2O$-$55P_2O_5$ with (x=0,1,2,3,4), and to characterize them by the XRD, IR, and chemical
durability.

XRD studies were carried out in order to get an idea about the structure of $30Fe_2O_3$-xCr_2O_3-(15-x)Na_2O-$55P_2O_5$ (mol %), and to investigate the amorphous state of the prepared glasses before annealing.

We studied also the effect of substitution of Na_2O by Cr_2O_3 on the behavior of phosphate glasses.

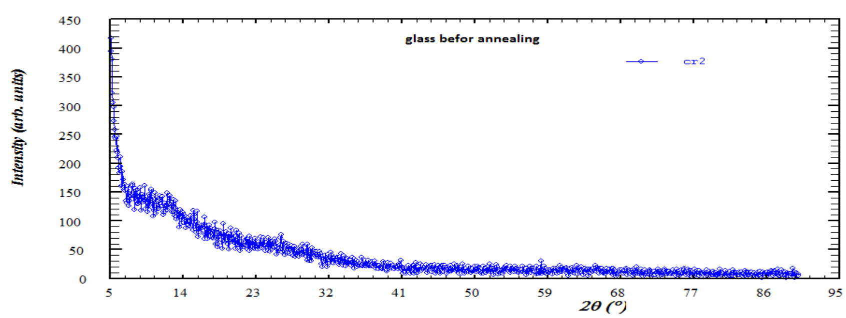


Fig.2 XRD of glasses before annealing

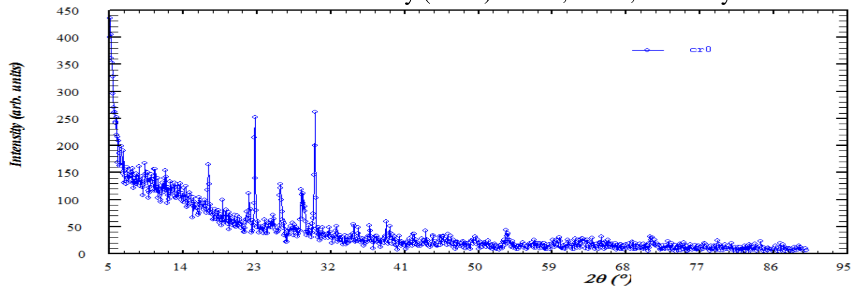


Fig.3 XRD of glasses(Cr0) after annealing at 650 ° C

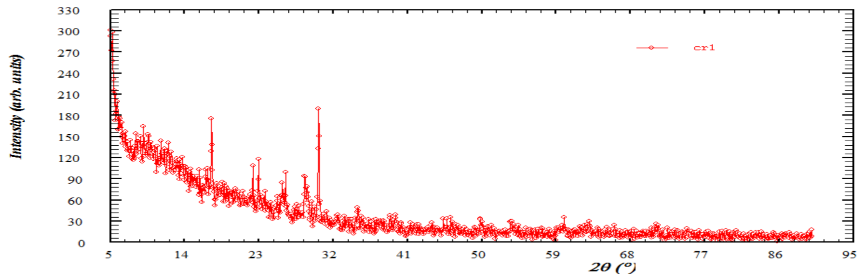


Fig.4 XRD of glasses(Cr1) after annealing at 650 ° C

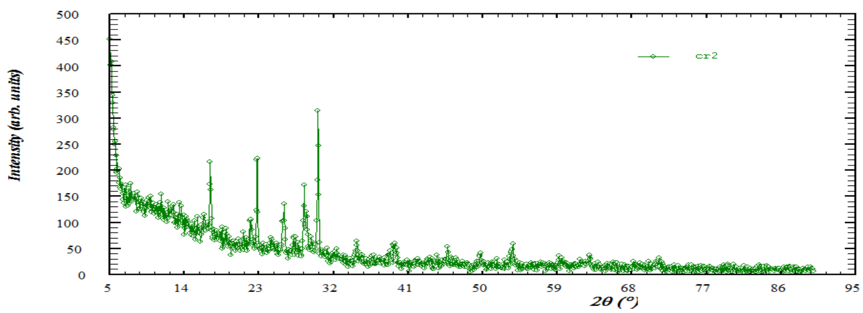


Fig.5 XRD of glasses(Cr2) after annealing at 650 ° C

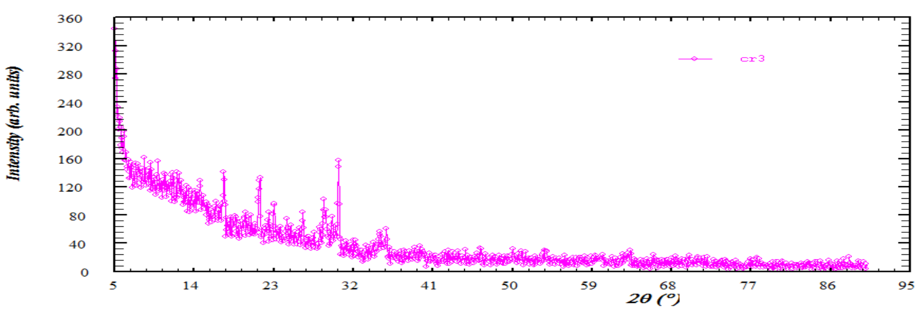


Fig.6 XRD of glasses(Cr3) after annealing at 650 ° C

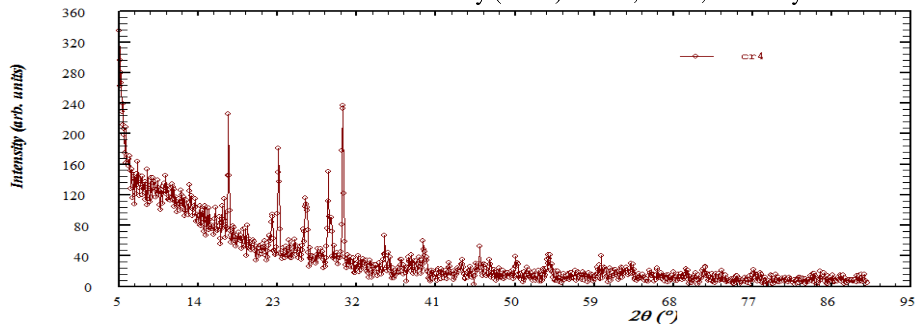


Fig.7 XRD of glasses(Cr4) after annealing at 650 ° C

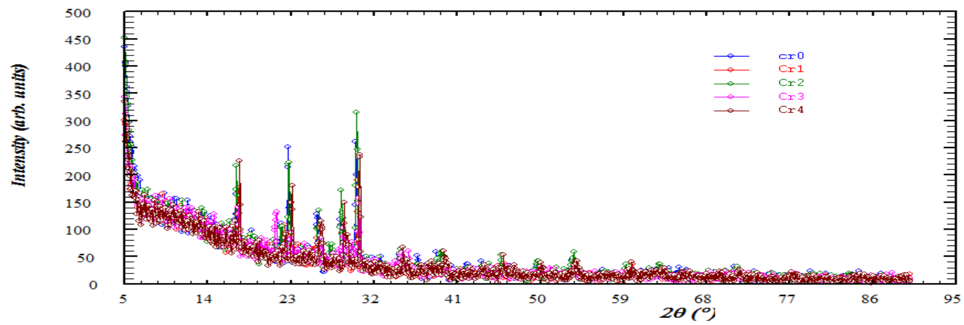


Fig.8 The overlay graphs of the five samples

No crystalline phase was detected by X-ray in the glass composition $30Fe_2O_3$-xCr_2O_3-(15-x)Na_2O-$55P_2O_5$ before annealing Fig.2. Whereas after annealing at 650°C, we notice the existence of crystalline micro domain in the samples (Fig.3,4,5,6,7),which means that the crystallization of the glass was just starting [9]. This observation comes from the appearance of some peaks related to the $Na_2FeP_2O_7$ phase, and non-identified peaks.

The five samples has joined the same region of the crystalline phases (Fig.8)

b. INFRARED STUDY

Infrared absorption spectra of $30Fe_2O_3$-xCr_2O_3-(15-x)Na_2O-$55P_2O_5$ (mol %),with (0≤x≤4) glasses, have been studied in the region of 400–1500 cm^{-1}. Spectra were analyzed to determine the relative intensity of the IR bands responsible for the different phosphate units. [10]

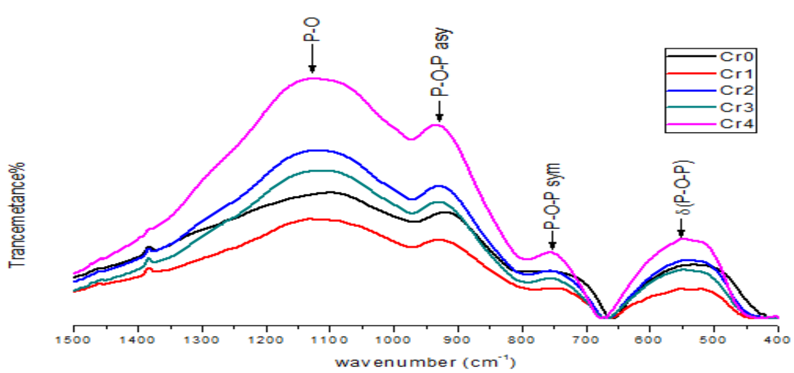


Fig.9

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 1102 cm^{-1} and sym stretching mode of bridging oxygen at 750 cm^{-1} respectively. There is also an angular bending vibration δ(O-P-O) at 530 cm^{-1} attributed to isolated tetrahedral units $(PO4)^{3-}$.[11]

attribution	glass Cr_0	Glass Cr_1	Glass Cr_2	Glass Cr_3	Glass Cr_4
	1360	1361	1361	1361	1358
P-O	1091M	1100-1140f	1108f	1102f	1130F
P-O-P Asymmetric stretching	910M	918M	930F	931F	940
P-O-P Symmetric stretching		740-460Tf	750M	750M	753F
angular bending vibration δ(O-P-O)	530TF	520-550Tf	540F	540-550Tf	551-519Tf

Table.2 Dominant bands

c. CHEMICAL DURABILITY

The chemical durability of the glass strongly depends on its composition. In the case of our glass doped with chromium we found that it has a slower rate of corrosion.The amount of dissolved species of glass in solution for a time of 30 days and in a temperature of 90°C is very low ($10^{-9}g/cm^2/min$) (table1), so these glasses have a better resistance towards the water at a temperature of around 90°C [12].

It was noted that the addition of Cr_2O_3 in the glass $30Fe_2O_3$-xCr_2O_3-(15-x)Na_2O-$55P_2O_5$ may decrease the melting temperature and the glass transition temperature Tg [13].

It was noted also for the compositions prepared in a platinum crucible, that it was difficult to clean, although several washes with nitric acid with heating at 200°C, resulting in a probable chemical resistance against nitric acid and water.

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

The XRD technique has 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 [14]. The chemical durability of sodium-chromium-iron phosphate glass of composition $30Fe_2O_3$-xCr_2O_3-(15-x)Na_2O-$55P_2O_5$ (regarding aqueous attack at 90°C) is attributed to the increasing number of Fe-O-P bonds in the glass[14,15]. Such bonds are expected to be more water resistant than the P-O-P and Na-O-P bonds [16]. This glass have a (D_R) 50 times less than the D_R 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[16,17].

7. CONCLUSION

In this work, we presented the preliminary results obtained for $30Fe_2O_3$-xCr_2O_3-(15-x)Na_2O-$55P_2O_5$ ($0 \leqslant x \leqslant 4$) glasses investigated by XRD, IR, and chemical durability.

At the glass compositions studied, the main crystalline phase formed after annealing at 650°C was $Na_2FeP_2O_7$.

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