Journal of Materials Science and Chemical Engineering **2013, 1, 1-6**
http://dx.doi.org/10.4236/msce.2013.13001 Published Online August 2013 (http://www.scirp.org/journal/msce)

Study of Sodium-Chromium-Iron-Phosphate Glass by XRD, IR, Chemical Durability and SEM

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Received May 13, 2013; revised June 19, 2013; accepted June 30, 2013

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 glass is used to compare its effect with iron in inhibition of corrosion. The sodium-chromium-iron phosphate glass of composition $10Na_2O$-$30Fe_2O_3$-$5Cr_2O_3$-$55P_2O_5$ (mol%) 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 steel mold. The sample was annealed at 680˚C for 48 h. We have performed the measurement of X-Ray Diffraction (XRD), Scanning Electronic Microscopy (SEM), Infra-Red spectroscopy (IR), 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 $(PO_4)^{3-}$. 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; Phosphate Glasses; XRD

1. Introduction

Phosphate glasses are of particular interest in both technological and scientifical fields because they generally have lower processing temperatures less than 1000°C, lower glass transition temperatures (Tg) [1-6], and higher thermal expansion coefficients (α) than silicate glasses in the range of 90 to 250 × 10^{-7}/°C [4-6]. These properties makes them a good candidates in many applications such as glass to metal seals, thick film paste, the molding of optical elements, low temperature enamels for metals [2-4]. However, their relatively poor chemical durability makes them unsuitable for practical applications [7-9]. It was reported [9-15] that the introduction of oxides such as SnO, PbO, ZnO, Cr_2O_3 and Fe_2O_3, results in the formation of Sn-O-P, Pb-O-P, Zn-O-P, P-O-Cr and P-O-Fe bonds, and leads to improvement in the chemical durability of the modified phosphate glasses.

The iron phosphate glasses have generally both excellent chemical durability and low melting temperature typical between 950 and 1100˚C, [16]. Chromium phosphate glasses for the immobilisation and disposal of nuclear waste were reported in 1984 [17]. The combination of chromium phosphate glass 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 concen- trations, makes the glass more hydration resistant [16,18-21]. The P-O-Cr bands seem to play the same role than P-O-Fe bands [22].

In this paper we present a study of sodium chromium iron phosphate glass $10Na_2O$-$30Fe_2O_3$-$5Cr_2O_3$-$55P_2O_5$ which is prepared by the melt quenching technique, and characterized by X-Ray Diffraction, Infra-Red spectroscopy, and Scanning Electronic Microscopy. The chemical durability was investigated in distilled water solution.

2. Experimental

The glass of composition $10Na_2O$-$30Fe_2O_3$-$5Cr_2O_3$-55 P_2O_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 $(NH_4)_2HPO_4$ were initially tempered at various temperatures between 300˚C -

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500˚C to achieve a preparation before the glass preparation.

The melt was achieved in alumina crucibles for about 30 mn at 1080˚C ± 10˚C. The isolated glasses samples have an approximate of size 10 mm 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 following. The density of the glass was measured at room temperature using the helium pycnometry method. The chemical durability sample of the size 0.9 × 0.9 × 0.9 × 0.3 cm was used sample were first polished to a 400 grit finished with SiC paper, then they were immersed in a flask filled with 100 ml 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 2 mg of glass powder and 100 mg of anhydrous KBr powder. The chemical of composition of the analysed glass is given in **Table 1**.

2.1. X-Ray Diffraction, and Density

No crystalline phase was detected by X-ray in the glass composition $10Na_2O$-$30Fe_2O_3$-$5Cr_2O_3$-$55P_2O_5$, whereas we notice that there is the existence of crystalline micro domain which means that the crystallization of the glass had just started, this observation comes from apearence of some peaks related to the crystalline phase $NaFeP_2O_7$ (**Figure 1(a)**). The XRD pattern of annealed glass (**Figure 1(b)**) shows more crystallization peaks of the same phase, this result might confirm that the glass structure could be composed by $NaFeP_2O_7$ pyrophosphates groups.

2.2. Infrared Spectroscopy Study

The infrared spectra shown in **Figure 2**, for the glass of composition $10Na_2O$-$30Fe_2O_3$-$5Cr_2O_3$-$55P_2O_5$ include two dominant bands. These bands are characteristics of pyrophosphate groups: the band at 1099 and 760 cm^{-1} are attributed to $(PO_3)^{1-}$ asymmetric stretching mode of non bridging oxygen (P-O-P) sym stretching mode of bridging oxygen, respectively [22-25]. The band at 992 cm^{-1} seems to be assigned to the isolated tetrahedral units $(PO_4)^{3-}$ [26-28].

2.3. SEM Microscopy Study

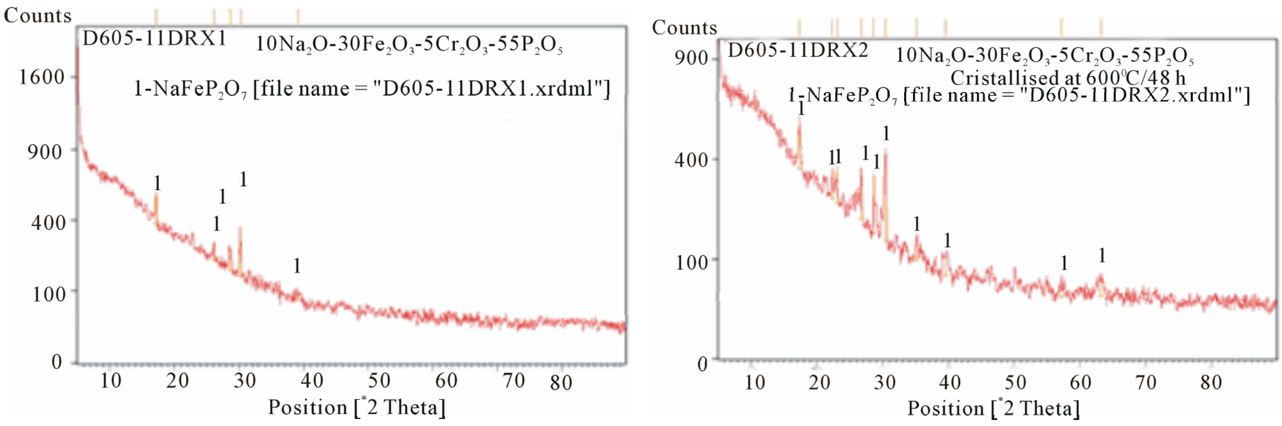
We noticed that the SEM plots (**Figures 3(a)** and **(b)**) for both glasses before and after aqueous dissolution confirms the presence of all the elements forming the glass. The proportions of the constituents seem as well to be in accordance with the theoretical composition.

The microscopic photograph was made at the nanometrical scale (as shown in **Figures 4(a)** and **(b)**).

The surface of the glass before the aqueous attack

Table 1. Bench composition, calculated (O/P) ratio, D_R and density of the glass studied.

Starting glass composition (mol%)				[O/P] ratio	(D_R) (g/cm²/mn)	ρ (g/cm³)
Na_2O	Fe_2O_3	Cr_2O_3	P_2O_5		22 days	±0.02
10	30	5	55	3.72	(7.188 ± 0.001) × 10^{-9}	2.627



(a) (b)

Figure 1. (a) X-Ray diffraction spectra for the sample $10Na_2O$-$30Fe_2O_3$-$5Cr_2O_3$-$55P_2O_5$; (b) X-Ray diffraction pattern for $10Na_2O$-$30Fe_2O_3$-$5Cr_2O_3$-$55P_2O_5$ glass partially crystallized at 650˚C for 48 h.

appears to be homogeneous in comparision with the attacked one which shows a deteriorated zone on its surface. Taking in consideration the dimension of the photographs, the etched surface remains very small.

3. Dissolution Rate

The dissolution rate (D_R) for sodium-lead-iron-phosphate glass is a function of time (see **Figure 5**). 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 *et al.* [29]. In the present work the dissolution rate for $10Na_2O$-$30Fe_2O_3$-$5Cr_2O_3$-$55P_2O_5$ 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.

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 [30]. The chemical durability of sodium-chromium-iron phosphate glass of composition $10Na_2O$-$30Fe_2O_3$-$5Cr_2O_3$-$55P_2O_5$ (regarding aqueous attack at 90˚C) is attributed to the increasing number of Fe-O-P bonds in the glass [30,31]. Such bonds are expected to be more water resistant than the P-O-P and Na-O-P bands [32]. 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 [32,33].

5. Conclusion

The structure and the chemical durability of sodium-chromium-iron phosphate glass of composition $10Na_2O$-$30Fe_2O_3$-$5Cr_2O_3$-$55P_2O_5$ (mol%) have been investigated using various techniques such IR, XRD, SEM....

The structure of the $10Na_2O$-$30Fe_2O_3$-$5Cr_2O_3$-$55P_2O_5$ (mol%) glass can be considered as pyrophosphate units

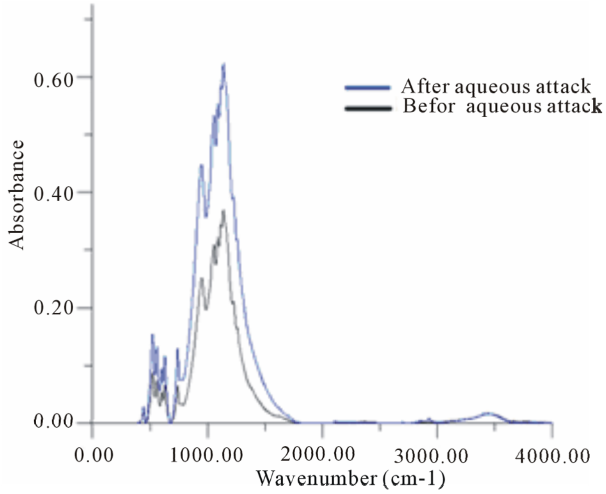
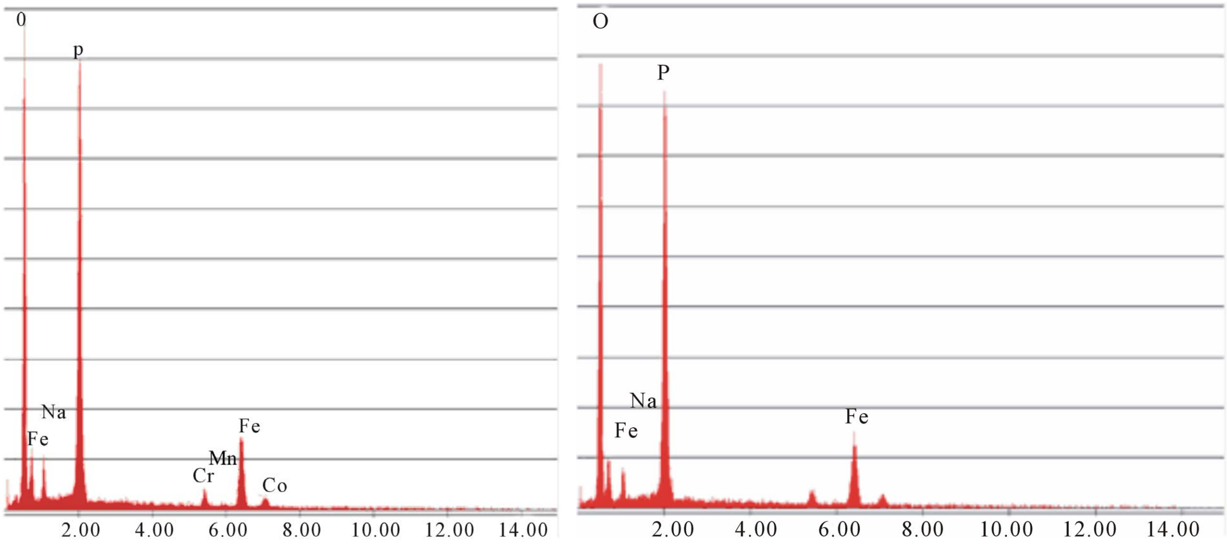
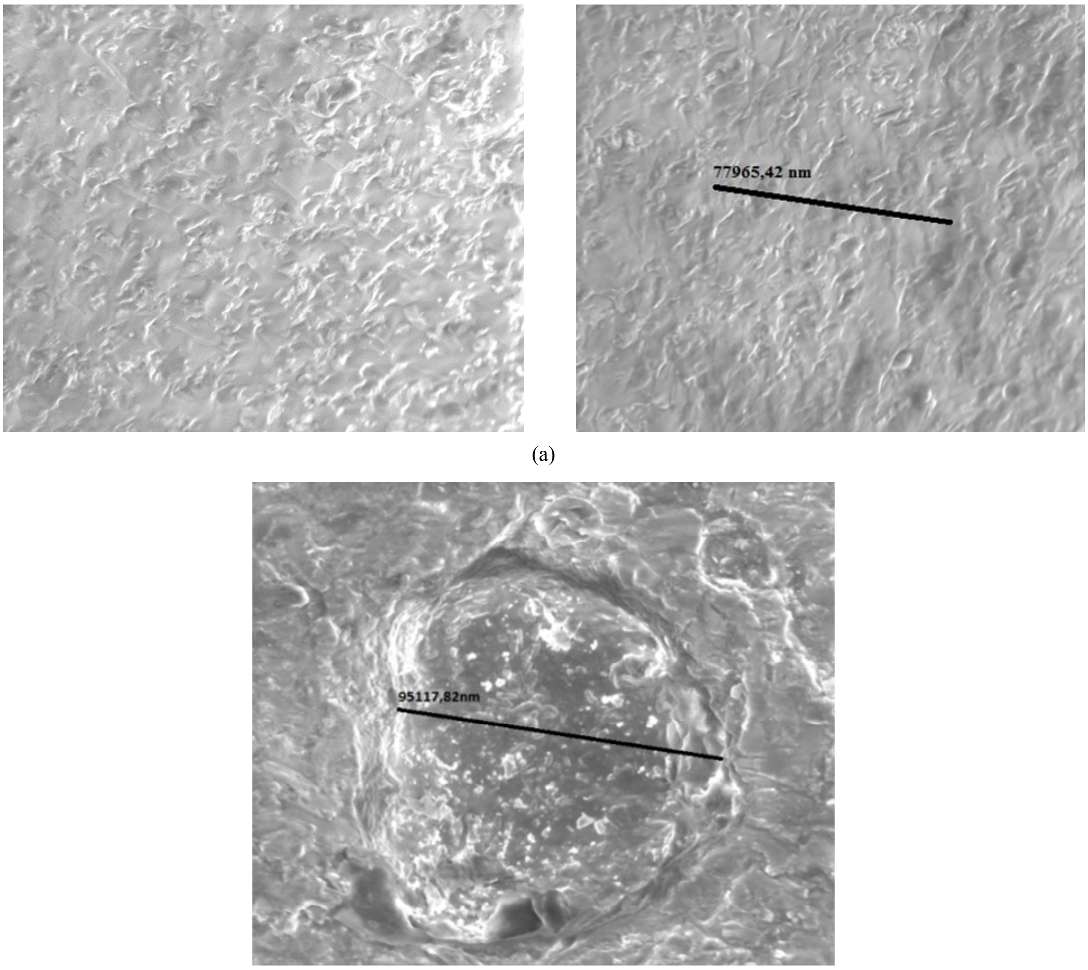


Figure 2. The IR spectra of sodium-chromium-iron-phosphate glass.



(a) (b)

Figure 3. (a) The SEM plot for the sample glass $10Na_2O$-$30Fe_2O_3$-$5Cr_2O_3$-$55P_2O_5$ (before aqueous attack); (b) The SEM plot for the sample glass $10Na_2O$-$30Fe_2O_3$-$5Cr_2O_3$-$55P_2O_5$ (after aqueous attack).



(a)

(b)

Figure 4. (a) Microscopic photograph of the surface of the glass $10Na_2O$-$30Fe_2O_3$-$5Cr_2O_3$-$55P_2O_5$, before aqueous attack (Resolution of 50 µm); (b) Microscopic photograph of the surface of the glass $10Na_2O$-$30Fe_2O_3$-$5Cr_2O_3$-$55P_2O_5$, after 22 days of aqueous attack.

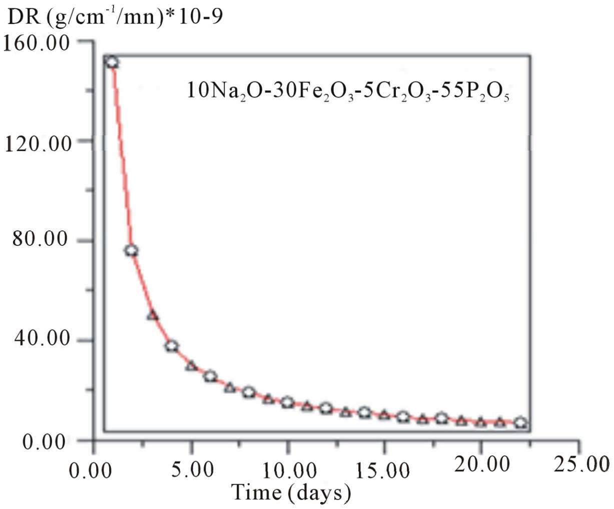


Figure 5. Dissolution rate for sodium chromium iron phosphate glassas a function of immersion time in aqueous solution at 90˚C.

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 recorded IR spectra indicate that these glasses are dominated by $(P_2O_7)^{4-}$ dimmer units, and contain a large number of Fe-O-P bonds.

The studied glass possesses a strong chemical durability. This can be used in many domains, especially in the vitrification of nuclear wastes which represents a clean alternative to the traditional way of burying hazardous wastes in isolated lands.

6. Acknowledgements

The authors wish to thank National Center for Scientific and Technical Research [Division of Technical Support Unit for Scientific Research (TSUSR) Rabat, Morocco] for helpful discussions. The present work is supported by the Laboratory of Physics of High Energy and Condensed Matter, and Laboratory of Inorganic Chemistry (University Hassan II, Faculty of Sciences Ain Chock).

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