



Preparation and Characterization of Phosphate Material Doped with Chromium

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Abstract: The paper reports a study on phosphate glasses containing Chromium, Iron and Sodium oxides. The phosphate glasses have been obtained in air by direct melting of Cr_2O_3 , Fe_2O_3 , Na_2CO_3 , and $(\text{NH}_4)_2\text{HPO}_4$. The preparation temperature is 1020°C . After annealing at 650°C for 48h, the glasses were partially crystallized and contained $\beta\text{-CrPO}_4$ and $\text{Fe}_3(\text{P}_2\text{O}_7)_2$ crystalline phases. We have performed the measurement of X-Ray diffraction, and Infra-Infra-Red spectroscopy. The differential scanning calorimetry (DSC) was used in this work to determine the glass transition and the crystallization temperatures (T_g and T_c). We noticed that the T_g and T_c depends on the composition of the samples. The chemical durability was evaluated by weight losses of glass samples after immersion in hot distilled water at 90°C for 30 days. Weight loss measurements showed a good chemical durability against water and enhance the glass capacity to embed different chemical compounds. The density and molar volume were also measured.

Keywords: Chemical Durability, IR Spectroscopy, Differential Scanning Calorimetry, Glass Formation, Sodium-Chromium-Iron-Phosphate Glasses, XRD

1. Introduction

In the last years, phosphate glasses have been studied for their interesting properties [1, 2]. Recent studies of iron phosphate glasses have shown that the addition of iron to sodium phosphate glasses had a significant effect on the glass transition temperature, thermal expansion coefficient and chemical durability [3]. It has been suggested that the chemical durability of iron phosphate glasses is attributed to the replacement of P-O-P bonds by more water resistance P-O-Fe bonds [4]. The properties of phosphate glasses are largely determined by the cation additives used in their production, with di and multivalent ionic species having a more drastic effect [5-7]. Iron in particular has a strong effect on phosphate glasses, with these glasses demonstrating extremely good resistance to hydrolysis. Indeed the durability of some iron glass formulations has been shown to exceed that

of normal window glass [1-2], which has led to the consideration of these glasses for applications as extreme as long-term containment of high-level nuclear waste [5, 8-9].

With some types of nuclear waste the phosphate glasses have even been shown to be able to contain several times more waste material than the traditional borosilicate glasses used for containment [5]. Other properties of iron glasses, such as their infra-red absorption capabilities and of phosphate glasses in general (high expansion coefficients, colour center formation caused by radiation exposure, UV transparency) have led some consideration for myriad applications from optics [10-11] and lasers [6] through to high temperature seals [12], dosimeters [13], hyperthermal treatment [14] and heat shielding [15]. The objective of this paper is therefore to determine the effect of the oxide substitution on the physico-chemical properties of the glassy system of $(26-y)\text{Fe}_2\text{O}_3-y\text{Cr}_2\text{O}_3-19\text{Na}_2\text{O}-55\text{P}_2\text{O}_5$ (mol %), with $(0 \leq y \leq 4)$.

2. Materials and Methods

The glasses of compositions $(26-y)Fe_2O_3-yCr_2O_3-19Na_2O-55P_2O_5$ (mol %), with $(0 \leq y \leq 4)$ are obtained by the melting quench method at $1020^\circ C$. The corresponding mixture with compounds Na_2CO_3 , Fe_2O_3 ,

Cr_2O_3 and $(NH_4)_2HPO_4$ is introduced in porcelain crucible and then heated for 24 hours. Appropriate amounts of material were shown in Table 1.

The dissolution rates (D_R) of the analyzed glasses are also given in Table 1, measured from the weight loss experiments conducted in distilled water at $90^\circ C$.

Table 1. Compositions, chemical durability of $(26-y)Fe_2O_3-yCr_2O_3-19Na_2O-55P_2O_5$ (mol%), with $(0 \leq y \leq 4)$ glasses with the ratio $(o/p)=3,38$.

Starting glass composition (mol %)				(D_R) (g/cm ³ /mn)
Fe_2O_3	Cr_2O_3	Na_2O	P_2O_5	30 days
26	0	19	55	$(3,042 \pm 0,001) * 10^{-9}$
25	1	19	55	$(3,041 \pm 0,001) * 10^{-9}$
24	2	19	55	$(3,040 \pm 0,001) * 10^{-9}$
23	3	19	55	$(3,034 \pm 0,001) * 10^{-9}$
22	4	19	55	$(3,031 \pm 0,001) * 10^{-9}$

3. The Synthesis Reaction of Glasses

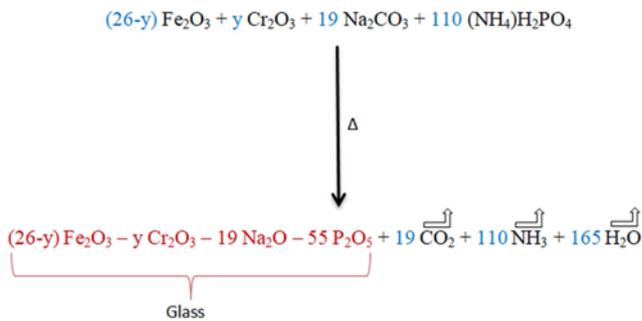


Figure 1. The synthesis reaction of the glasses.

The melting was achieved in porcelain crucibles for about 30 min at $1020 \pm 10^\circ C$. The isolated glasses samples have an approximate diameter of 10 mm and 3 mm in thickness. The densities were determined on bulk of glasses by the

Archimedes’ method at room temperature using diethyl phthalate as fluid [8]. The samples were immersed in a flask filled with 100 ml of distilled water at $90^\circ C$ for 30 days. The dissolution rate (D_R) was then determined from the weight loss during the aqueous treatment at $90^\circ C$.

$$D_R = \frac{\Delta_m (g)}{[S (cm^2) * t (min)]} \tag{1}$$

Where Δ_m = The difference in mass weighed
 S = the surface of the aqueous attack
 t = time

4. Heat Treatment

Figure 2 shows the heat treatment of the glassy system.

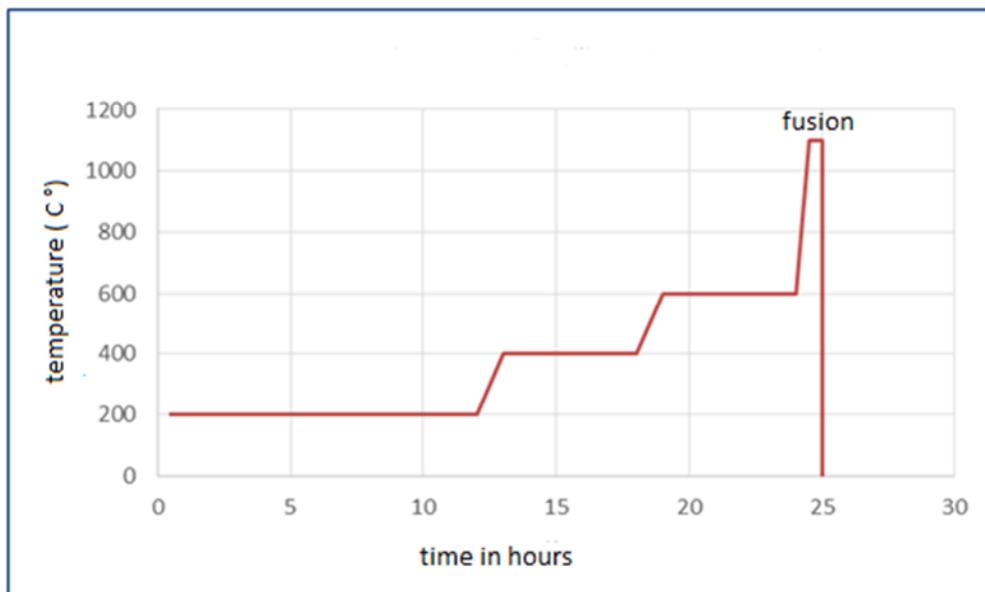


Figure 2. Thermal treatment carried out for the preparation of the glasses.

After 24 hours the samples were removed from the furnace, swirled to homogenise the melt and then cast onto a polished

plate at room temperature. The glass was then allowed to cool in air.

5. Density Measurements

The density was obtained by employing the relation:

$$\rho_{\text{glass}} = \left[\frac{m_{\text{air}}}{m_{\text{air}} + (m_{\text{ortho}} - m_{\text{(ortho+glass)}})} \right] \times \rho_{\text{ortho}} \quad (2)$$

Where m_{air} is the weight of glass sample in air, m_{ortho} is the weight of diethyl orthophthalate only, $m_{\text{(ortho + glass)}}$ is the weight of glass immersed in diethyl orthophthalate and ρ_{ortho} is density of the buoyant $\approx (1,11422 \text{ g/cm}^3)$. All the measurements were made using a digital balance (contech). In case when sample reacts with water, a suitable inert liquids such as diethyl orthophthalate, xylene, toluene etc, can be selected as the immersion medium.

6. Molar Volume Calculation

The molecular weight of the glass was also calculated as described below and using these molecular weights and

density, the molar volume of the glass samples can be calculated from the following expression:

$$V_m = \frac{M}{\rho} \quad (3)$$

Where, V_m is the molar volume, ρ is the density of the sample and M is the molecular weight of the sample. In the present immersion fluid and the reported density values are the average of at least three independently measured values.

$$V_{\text{OM}} = \frac{M}{\rho_{\text{Na}} \times N_{\text{O}}} \quad (4)$$

$$r_{\text{cal}}(\text{O}^{2-}) = \frac{1}{2} \sqrt[3]{(V_{\text{OM}})} \quad (5)$$

M = molar mass, ρ = density, N_{A} = Avogadro's constant,
 N_{O} = number of atoms of oxygen
 V_{OM} = molar volume of oxygen
 r_{cal} = calculated ionic radius of oxygen

Table 2. Characteristics of the glasses.

N° de série	La composition				molar mass (g/mol)	Density ρ (g/cm ³)	molar volume	Number of oxygen atoms	ionic radius
	Fe ₂ O ₃	Cr ₂ O ₃	Na ₂ O	P ₂ O ₅					
0	26	0	19	55	131,44	2.66	20.22	372	1.4022
1	25	1	19	55	131,36	2.68	20.05	372	1.4018
2	24	2	19	55	131,28	2.70	19.89	372	1.4014
3	23	3	19	55	131,20	2.72	19.73	372	1.4012
4	22	4	19	55	131,12	2.74	19.52	372	1.4010

The evolution of the density of the glasses as a function of chromium rate is shown in Figure 3. We observe a monotonous increase, from 2.66 to 2.74 g / cm³ with y which could translate crosslinking of the network under the effect of the addition of Cr₂O₃. To verify this interpretation, we have chosen to study the evolution of the molar volume deduced from the density by the relation 3:

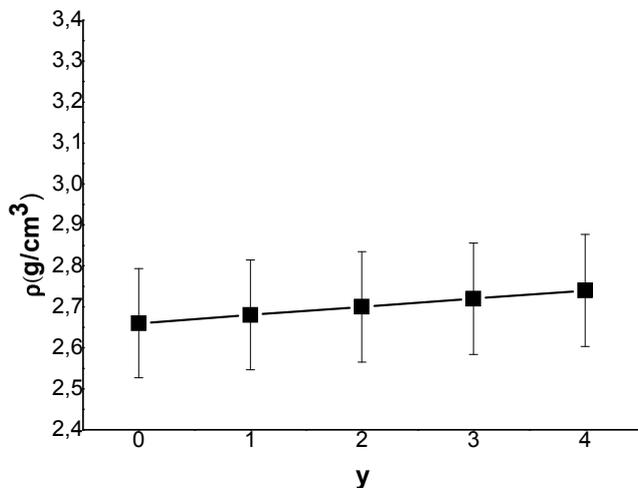


Figure 3. Evolution of the density (ρ) of the glasses $(26-y)\text{Fe}_2\text{O}_3-y\text{Cr}_2\text{O}_3-19\text{Na}_2\text{O}-55\text{P}_2\text{O}_5$ with $0 \leq y \leq 5$ as a function of the chromium (y) content.

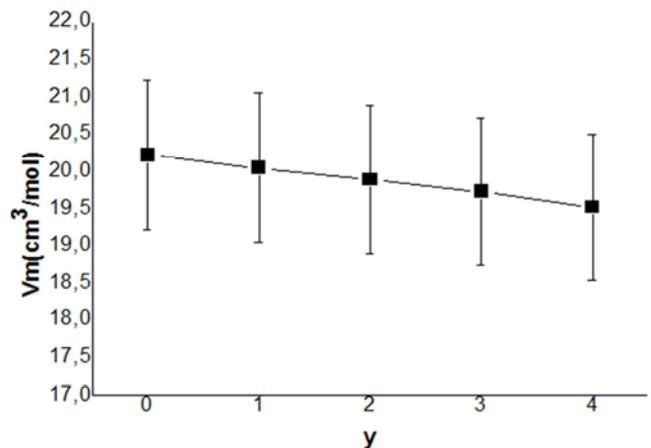


Figure 4. Evolution of the molar volume of the glasses $(26-y)\text{Fe}_2\text{O}_3-y\text{Cr}_2\text{O}_3-19\text{Na}_2\text{O}-55\text{P}_2\text{O}_5$ with $0 \leq y \leq 4$ as a function of the chromium (y) content.

Figures 2 and 3 shows respectively the variation of the density and the molar volume of the glasses of compositions $(26-y)\text{Fe}_2\text{O}_3-y\text{Cr}_2\text{O}_3-19\text{Na}_2\text{O}-55\text{P}_2\text{O}_5$, with $0 \leq y \leq 4$. We note in the case of this glass system that the density increases and the molar volume decreases continuously as the chromium oxide level increases.

The evolution of the density is due to the molar masses of Cr₂O₃ (151.99 g / mol) and Fe₂O₃ (159.69 g / mol) which are

higher than that of Na_2O (61.9789 g / mol). The decrease in the molar volume shows that the glasses become more and more compact.

Indeed, the evolution of the molar volume (V_M) (or the molar volume occupied by an oxygen atom), as a function of the oxide content introduced into the glass, reflects the effect of this oxide within the vitreous network. If the molar volume remains constant, it can be said that the introduced cation is placed in the cavities of the network, this phenomenon is well observed when ZnO is introduced into NaPO_3 [16]. A decrease in V_M shows that the cations introduced reinforce the network with one contraction of the oxygen ion stack. Conversely, an increase in V_M is indicative of an expansion of the network. This case was observed by Delahaye *et al.* by studying the glasses of the system $50\text{P}_2\text{O}_5 - (50-y)\text{Na}_2\text{O} - y\text{CaO}$ [17].

The value of the O / P ratio of the studied glasses is also calculated and grouped in Table 3.

Table 3. Glasse composition and the with the (O/P) ratio.

Composition initial du matériau (mol %)				[O/P]
Fe_2O_3	Cr_2O_3	Na_2O	P_2O_5	
26	0	19	55	3,3818
25	1	19	55	3,3818
24	2	19	55	3,3818
23	3	19	55	3,3818
22	4	19	55	3,3818

7. Results and Discussion

(a) XRD study

The X-ray diffraction analysis was used to confirm the amorphous state of the samples. The annealing of the glasses was realized at 650°C for 48 hours. The first structural approach was made using X-rays diffraction.

XRD studies were carried out in order to get an idea about the structure of $(26-y)\text{Fe}_2\text{O}_3 - y\text{Cr}_2\text{O}_3 - 19\text{Na}_2\text{O} - 55\text{P}_2\text{O}_5$ (mol%) with $(0 \leq y \leq 4)$ glasses and to investigate the amorphous state of the prepared glasses before annealing.

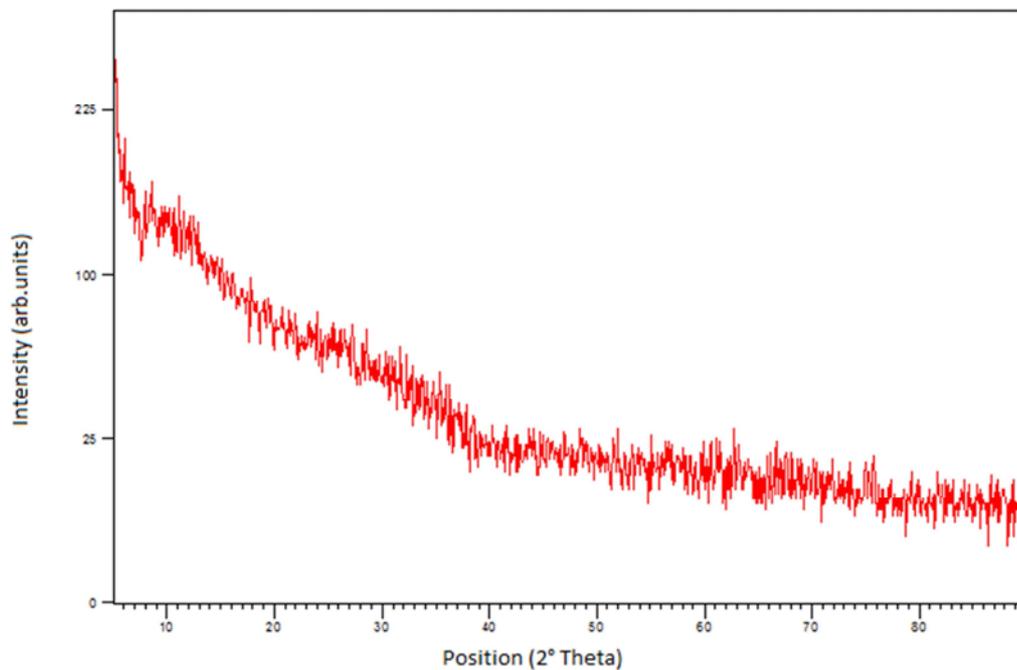


Figure 5. XRD of the $(26-y)\text{Fe}_2\text{O}_3 - y\text{Cr}_2\text{O}_3 - 19\text{Na}_2\text{O} - 55\text{P}_2\text{O}_5$ sample (before annealing).

No crystalline phase was detected by X-ray in the glass composition $(26-y)\text{Fe}_2\text{O}_3 - y\text{Cr}_2\text{O}_3 - 19\text{Na}_2\text{O} - 55\text{P}_2\text{O}_5$ (mol%) with $(0 \leq y \leq 4)$ before annealing (Figure 3). Whereas after annealing at 650°C , we notice the existence of crystalline micro domain in the samples (Figure 4) which means that the crystallization of the glass was just starting [18]. This observation comes from the appearance of some peaks related to the $\text{Na}_2\text{FeP}_2\text{O}_7$ phase, and some non-identified peaks.

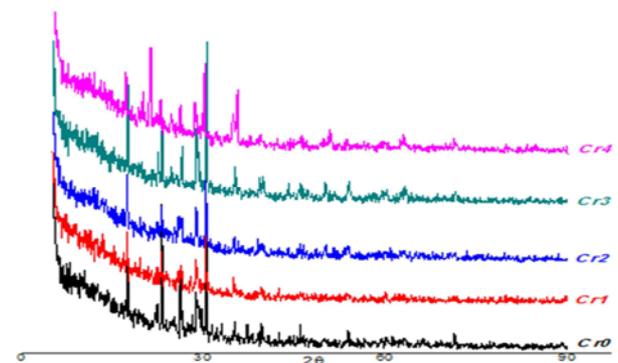


Figure 6. The XRD diffractograms of the elaborated glasses (after annealing).

(b) IR spectroscopy

Figure 5 represents the IR spectra of $(26-y)\text{Fe}_2\text{O}_3-y\text{Cr}_2\text{O}_3-19\text{Na}_2\text{O}-55\text{P}_2\text{O}_5$ (mol%) with $(0 \leq y \leq 4)$ glasses.

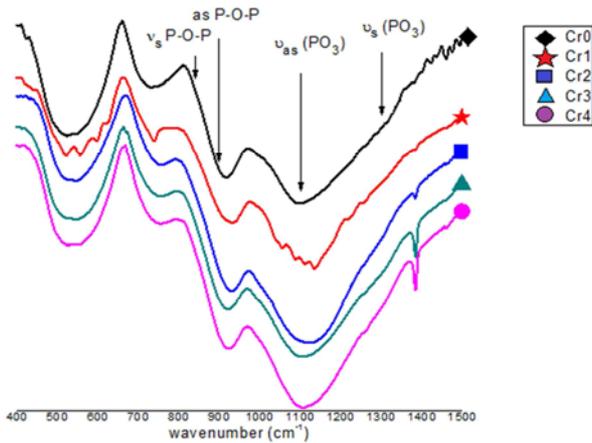


Figure 7. IR spectra of the samples.

In Figure 5 the bands at 1368 cm^{-1} , 1329 cm^{-1} and 1260 cm^{-1} are a characteristic feature of the symmetric stretching

vibration of the $\nu_s(\text{PO}_3)$. The bands at, 895 cm^{-1} , 934 cm^{-1} , 952 cm^{-1} , are attributed to the asymmetric stretching vibration of the $\nu_{as}\text{P-O-P}$ [20] and 880 cm^{-1} was assigned to symmetric stretching vibration of $\nu_s\text{P-O-P}$ [18,19].

While the bands at 703 cm^{-1} and 694 cm^{-1} are attributed to the symmetric stretching vibration of P-O-P linkages, $\nu_s\text{P-O-P}$. The absorption band at 640 cm^{-1} may be due to the bending mode of PO_4 units.

(c) Differential Scanning Calorimetry (DSC)

T_g (glass transition temperature) and T_c (crystallization temperature) were determined by DSC 121 SETRAM instrument. Data acquisition and processing was done using SetSoft software, using a heating rate of $10^\circ\text{C}/\text{min}$ (20°C to 800°C).

A mass of 28 mg of crushed sample were placed in a platinum crucible then heated from 20°C to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$ under an argon atmosphere.

The DSC thermograms of the $(26-y)\text{Fe}_2\text{O}_3-y\text{Cr}_2\text{O}_3-19\text{Na}_2\text{O}-55\text{P}_2\text{O}_5$ (mol%) with $(0 \leq y \leq 4)$ glasses compositions are shown in Figure 6.

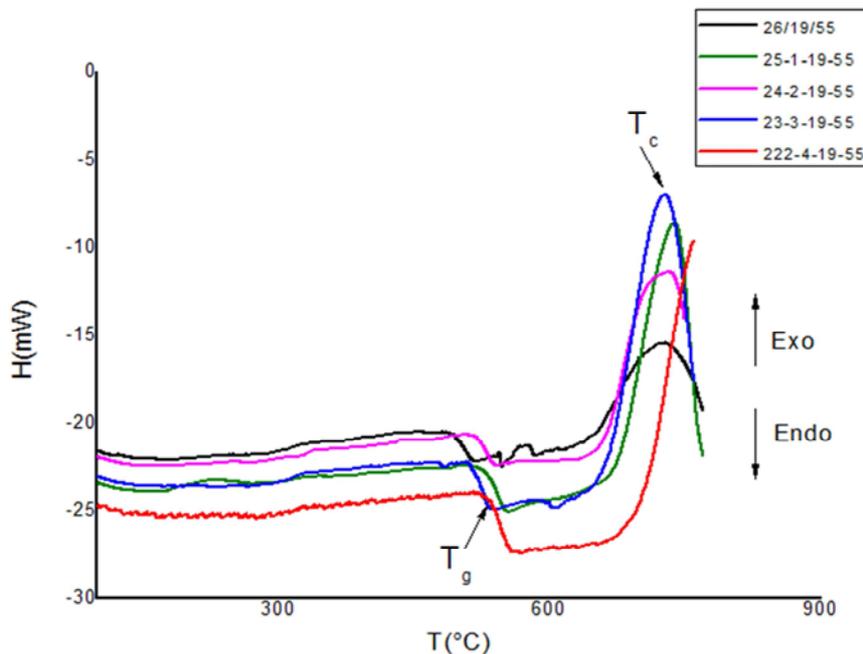


Figure 8. DSC thermograms of the glass composition $(26-y)\text{Fe}_2\text{O}_3-y\text{Cr}_2\text{O}_3-19\text{Na}_2\text{O}-55\text{P}_2\text{O}_5$ (mol%) with $(0 \leq y \leq 4)$.

In the case of $(26-y)\text{Fe}_2\text{O}_3-y\text{Cr}_2\text{O}_3-19\text{Na}_2\text{O}-55\text{P}_2\text{O}_5$ (mol%) with $(0 \leq y \leq 4)$ glasses, the substitution of Fe_2O_3 by Cr_2O_3 , is manifested by a decrease in glass transition temperatures T_g and increase of the crystallization temperature T_c .

After the examination of the values of T_g , T_c and T_c-T_g (Table 3) we could make the following observations:

Table 4. Values of T_g , T_c and T_c-T_g of the glasses compositions $(26-y)\text{Fe}_2\text{O}_3-y\text{Cr}_2\text{O}_3-19\text{Na}_2\text{O}-55\text{P}_2\text{O}_5$ (mol%) with $(0 \leq y \leq 4)$.

composition	$T_g(\pm 5^\circ\text{C})$	$T_c(\pm 5^\circ\text{C})$	T_c-T_g
$26\text{Fe}_2\text{O}_3-19\text{Na}_2\text{O}_3-55\text{P}_2\text{O}_5$	503	724	221
$25\text{Fe}_2\text{O}_3-1\text{Cr}_2\text{O}_3-19\text{Na}_2\text{O}_3-55\text{P}_2\text{O}_5$	492	726	234
$24\text{Fe}_2\text{O}_3-2\text{Cr}_2\text{O}_3-19\text{Na}_2\text{O}_3-55\text{P}_2\text{O}_5$	486	730	244
$23\text{Fe}_2\text{O}_3-3\text{Cr}_2\text{O}_3-19\text{Na}_2\text{O}_3-55\text{P}_2\text{O}_5$	479	739	260
$22\text{Fe}_2\text{O}_3-4\text{Cr}_2\text{O}_3-19\text{Na}_2\text{O}_3-55\text{P}_2\text{O}_5$	472	-	-

As we can see from the table 3 the glass transition temperature T_g is decreasing when the chromium content increases in the glass series whereas the crystallization temperature T_c is increases.

This study of DSC shows then a good thermal stability that we can deduce from the subtraction $T_c - T_g$ [21].

(d) Chemical durability

The chemical durability of the glasses compositions glasses with approximate size of $1 \times 1 \times 1 \text{ cm}^3$ was evaluated by weight loss measurements from glasses exposed to beaker containing 100 ml of distilled water at 90°C for 30 days. Glasses were polished to 600 grit, finished with SiC paper, and cleaned with acetone.

The measurements were conducted for each glass and the

average dissolution rate (D_R), normalized to the glass surface area and the corrosion time was calculated from the weight loss.

From the two curves below it is noted that the aqueous dissolution rate decreases slightly with increasing rate of Cr_2O_3 in the glass system, but this decrease still very low that can be assumed to remain the same ($D_R \approx 10^{-9}$).

In general the chemical durability for phosphate glasses improves with the increase in Iron and Chromium content, however the indecreasing of chemical durability could be attributed to the replacement of P–O–P bonds by P–O–Fe and P–O–Cr bonds. The presence of P–O–Fe bonds in higher concentration makes the glass more hydration resistant. The P–O–Cr bonds seem to play the same role than P–O–Fe ones.

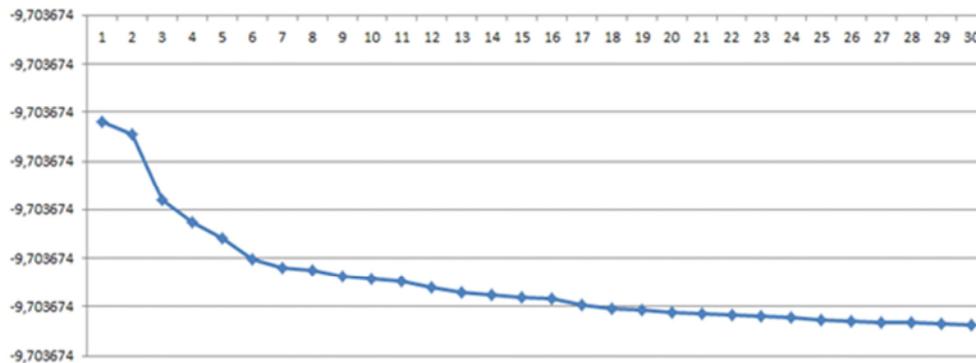


Figure 9. Logarithm of the dissolution rate as a function of the number of days in distilled water:

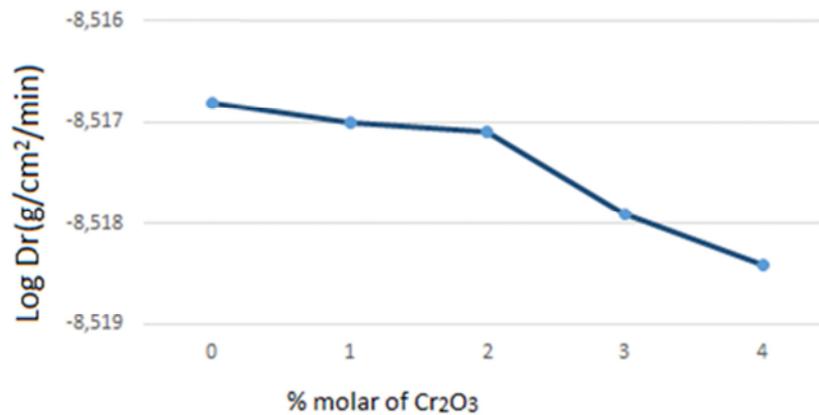


Figure 10. Logarithm of the aqueous dissolution rate as a function of % Cr_2O_3 .

8. Conclusion

The investigations performed on the samples of $(26-y)\text{Fe}_2\text{O}_3 - y\text{Cr}_2\text{O}_3 - 19\text{Na}_2\text{O} - 55\text{P}_2\text{O}_5$ (mol%) with $(0 \leq y \leq 4)$ glass allowed to formulate the following statements:

- The X-ray diffraction investigations revealed that the studied materials were in amorphous state, and probably inform about existence of different amorphous states in samples with various content of chromium and iron. On the other hand many crystalline materials can be formed after annealing.
- Infrared absorption spectra of $(26-y)\text{Fe}_2\text{O}_3 - y\text{Cr}_2\text{O}_3 - 19\text{Na}_2\text{O} - 55\text{P}_2\text{O}_5$ (mol%) (mol %),

with $(0 \leq y \leq 4)$ glasses, have been studied in the region of $400 - 1500 \text{ cm}^{-1}$. The spectra were analyzed to determine the relative intensity of the IR bands responsible for the different phosphate units.

- After washing crucibles containing glass samples with in HCl solution at 200°C , we noticed that the prepared glasses have exceptionally good chemical durability and low dissolution even against acids in high temperature, which make them a good candidate for matrix to immobilization of radioactive waste.
- In the case of the investigated glasses, O/P ratio is equal to 3.38 which means that they are polyphosphate glasses built of PO_4 tetrahedra.

- e. The DSC study shows a good thermal stability of the glass composition with increasing Cr_2O_3 in the sodium chromium-iron phosphate glasses.

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