Structural Features and Properties of the Vitreous Part of the System
50P₂O₅-25CaO-(25-x)Na₂O-xCoO (with 0 ≤ x ≤ 25; mol%)

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Abstract
The glass series 50P₂O₅-25CaO-(25-x)Na₂O-xCoO (with 0 ≤ x ≤ 25; mol%), has been prepared by direct melting at 1080°C ± 20°C. The introduction of cobalt in calcium phosphate glasses is used to compare its effect with calcium in inhibition corrosion. The dissolution rate has been investigated. It indicated an improvement of chemical durability when the cobalt oxide increases in the network glass at the expense of Na₂O content. Both, IR spectroscopy and X-ray diffraction have confirmed the structure changes when the CoO content increases in the glass. This change results in the disappearance of isolated orthophosphate groups followed of a polymerizing of the structure from isolated orthophosphate towards pyrophosphate chains (Q¹) by promoting the formation of olygophosphates (mixed Q¹-Q²) rich in pyrophosphates. Analysis of the density values, showed an increase of density with the increase CoO content. The covalent radius values of oxygen r_cal (O²⁻) indicate a significant decrease and therefore a relatively high reinforcement of the metal-oxygen-phosphorus (Co-O-P) bonds. SEM micrograph confirms the evolution of the glass structural morphology. The sample having a maximum CoO content confirms a homogeneous glass phase with quite crystalline particles. This property is prerequisite for many interesting industrial applications.

Keywords
Chemical Durability Phosphate Glasses, Cobalt Oxide, Density, DTA, DRX,
1. Introduction

Due to their poor chemical durability, phosphate glasses have rather limited technological application despite their investigation so far conducted by many researchers [1] [2]. However, several phosphate glasses with high aqueous corrosion resistance have been reported [3] [4] [5] [6] [7]. Their properties (low melting point, high thermal expansion coefficient, bioactivity, optical properties etc.) make these glasses serious potential candidates for many technological applications. It has been found that the introduction of oxides, such as ZnO, Fe2O3, Al2O3, PbO, CaO and Cr2O3, results in the formation of Zn-O-P, Fe-O-P, Pb-O-P, Al-O-P, Ca-O-P and Cr-O-P bonds, leading to improvement of phosphate glasses chemical durability [5] [7] [8] [9] [10] [11]. The synergy of phosphate glasses with some types of nuclear waste has indicated the possibility of a form of waste with a lower corrosion rate than borosilicate glasses [8] [12]. As a result of high chemical durability, iron phosphate glasses have been considered as better candidates for the vitrifying of some type of nuclear wastes when compared with borosilicate glasses [4] [5] [6] [8]. The aim of the present work is to synthesize and select phosphate glasses in the system 50P2O5-25CaO-(25−x)Na2O-xCoO (with 0 ≤ x ≤ 25; mol%) for two reasons:

• the first reason is to analyze glasses, with low cobalt content, by different techniques arranged for further studies in the biomedical field [13] [14] [15];
• the second reason is to compare the effect of cobalt with that of iron in inhibition of corrosion [3] [6] [16]. The studied series indicated the structural change when cobalt content increases and causes an important tendency polymerization from orthophosphates to pyrophosphate groups which are at the origin of the improvement of chemical durability.

2. Experimental Section

Phosphate glasses are prepared by direct melting of the (NH4)2HPO4 (98,99% pure), CaCO3 (99.5% pure), Na2O (99% pure), CoCO3, xH2O (Co 43% - 47% pure) mixtures with suitable proportions. The reagents are intimately crushed then introduced into a porcelain crucible. They were initially heated at 300˚C for 2 h and then kept at 500 ˚C for 1 h to complete the decomposition. The reaction mixture was then heated at 850˚C for 1 h and finally at 1080˚C for 30 minutes. The homogeneous liquid was poured in aluminum plate previously heated to 200˚C to avoid thermal shock. They were initially heated at 300˚C for 2 h and then kept at 500˚C for 1 h to complete the decomposition. The reaction mixture was then heated at 850˚C for 1 h and finally at 1080˚C for 30 minutes. The homogeneous liquid was poured in aluminum plate previously heated to 200˚C to avoid thermal shock. Pellets about 5 to 10 mm in diameter and 1 to 3 mm thick were obtained. 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 21 consecu-
tive days. The dissolution rate was evaluated from the mass loss as a function of
time. The IR spectra of the studied phosphate glasses were determined in the
frequency range between 400 and 1600 cm$^{-1}$ with a resolution of 2 cm$^{-1}$ using a
Fourier transform infrared spectrometer (IR AFFINITY-1S). The samples were
finally ground and mixed with KBr (potassium bromide), which is transparent
in the IR and serves as a template. The ratio of the matter/KBr in the pellets was
10% by weight. The vitreous state was first evidenced from the shiny and trans-
parency aspect, which was confirmed by X-ray diffraction patterns (XRD type
BRUKER D8 ADVANCE). The glasses $S_0$, $S_2$ and $S_4$ were annealed at 540˚C,
551˚C and 660˚C, respectively, for 72 hours. Differential thermal analysis (DTA)
was performed using a DTG-60 SUMULTANEOS DTA-DTG Apparatus, at a
heating rate of 10°C/min in atmospheric air with alumina crucibles. The Archi-
medes method was used to measure the density of glasses using orthophthalate
as a floating medium. The microstructures of the sample glasses were charac-
terized by scanning electron microscopy (SEM), equipped with a full system micro-analyser (EDX-EDAX).

3. Results and Discussion

3.1. Analysis of Chemical Durability of Series Glasses

$50P_2O_5$-$25CaO$-$$(25-x)Na_2O$-$xCoO$

The chemical durability ($D_R$) of the glass series $50P_2O_5$-$25CaO$-$$(25-x)Na_2O$-$xCoO$
(with $0 \leq x \leq 25$ mol%) was determined from the dissolution rate ($D_R$) of
the samples immersed in 100 ml of distilled water at 90°C for 21 consecutive days.
The dissolution rate is defined as the weight loss of the glass expressed in
g$\cdot$cm$^{-2}$$\cdot$min$^{-1}$. The values of $D_R$ and of pH of the leaching aqueous solution are
represented respectively, in figures 1 and grouped in Table 1. In Figure 1, the
shape of the $D_R$ curve indicates a progressive improvement of the chemical d ur-
ability of the glass from $5.44 \times 10^{-5}$ to $8.60 \times 10^{-7}$ (g$\cdot$cm$^{-2}$$\cdot$min$^{-1}$) when the CoO
content varies from 0 to 25 mol% [10].

3.2. Density and Molar Volumes

Density measurements allowed us to follow the evolution of the molar volume
depending on the composition of the system 50P₂O₅-25CaO-(25−x)Na₂O-xCoO. The density measurements were completed at room temperature. As can be observed from Figure 2, the variation in density versus CoO content (mol%) indicates an increase of density. On the other hand, it was possible to deduce the value of the molar volume and oxygen radius from density measurements, calculated from the approximate hypothesis of the close packing of oxygen anions, O²⁻, each having \( r_{cal}\) (O²⁻) recapitulated for each composition in Table 2 [4] [10] [16] [17]. The molar volume of oxygen and the radius of anions of oxygen (O²⁻) in the glass have been determined from Equations (1) and (2), respectively.

**Figure 1.** Dissolution rates \((D_{r})\) of the series of 50P₂O₅-25CaO-(25−x)Na₂O-xCoO glasses versus CoO (mol%).

**Figure 2.** Variation of the density \((\rho)\) versus CoO (mol%) along the glasses series 50P₂O₅-25CaO-(25−x)Na₂O-xCoO.
Table 2. Density and related molar data of the \(48\%\text{P}_2\text{O}_5-30\%\text{CaO}-(21-x)\text{Na}_2\text{O}-x\text{TiO}_2\) system.

| Samples | Molar formula Oxygène/Mol (\(N_O\)) | Density \(\rho\) (g cm\(^{-3}\)) | Molar Mass (g/mol) | Molar Volume \(V_m\) (Å) | Calculated oxygen radius \(r_{calr}(\text{O}^{2-})\) (Å) |
|---------|-----------------------------------|-----------------------------------|--------------------|----------------|--------------------------|
| \(S_0\) | \(25\text{Na}_2\text{O}-25\text{CaO}-50\text{P}_2\text{O}_5\) (300) | 2.588 | 10,051.95 | 21.5 | 1.390 |
| \(S_1\) | \(5\text{CoO}-20\text{Na}_2\text{O}-25\text{CaO}-50\text{P}_2\text{O}_5\) (300) | 2.637 | 10,116.615 | 21.2 | 1.384 |
| \(S_2\) | \(10\text{CoO}-15\text{Na}_2\text{O}-25\text{CaO}-50\text{P}_2\text{O}_5\) (300) | 2.709 | 10,181.28 | 20.8 | 1.375 |
| \(S_3\) | \(15\text{CoO}-10\text{Na}_2\text{O}-25\text{CaO}-50\text{P}_2\text{O}_5\) (300) | 2.720 | 10,245.945 | 20.6 | 1.372 |
| \(S_4\) | \(25\text{CoO}-25\text{CaO}-50\text{P}_2\text{O}_5\) (300) | 2.819 | 10,375.275 | 20.3 | 1.364 |

\[
V_{GM} = \frac{M}{\rho N_A * N_0} \quad (1)
\]

\[
r_{calr}(\text{O}^{2-}) = \sqrt[3]{V_{GM}} \quad (2)
\]

With \(M\) = molar mass, \(\rho\) = density, \(N_A\) = Avogadro number; \(*N_0\) = number of oxygen atoms in the molecular formula. A detailed analysis of the data in Table 2 shows that the molar volume decreases increasing of the CoO content. The covalent radius value of the oxygen atom (O\(^{2-}\)), calculated by the molar volume using the Equation (2) for each composition, decrease, also, indicating a reinforcement of the metal-oxygen-phosphorus (Co-O-P) bond with increasing of CoO content.

3.3. Structural Approach by Infrared Spectroscopy

Infrared spectra of glass series \(50\%\text{P}_2\text{O}_5-25\%\text{CaO}-(25-x)\text{Na}_2\text{O}-x\text{CoO}\) (0 ≤ \(x\) ≤ 25; mol\%) are shown in Figure 3. The assignments of the vibration bands are given in Table 3. All vibration bands of treated phosphate glasses are shown in the range of frequencies between 400 and 1600 cm\(^{-1}\). The band at 490 - 510 cm\(^{-1}\) is attributed to skeletal deformation \(\delta_{sk}\) (P-O-P) [3] [4] [5] [6] [18]. The frequency band located at 770 - 786 cm\(^{-1}\) is attributed to the symmetrical mode of vibration \(\nu_{sym}\) (P-O-P) of the pyrophosphate groups (Q1) [4] [18] [19] [20] [21], while the bands at 880 - 910 are assigned to the asymmetric vibration mode \(\nu_{asym}\) (P-O-P) [4] [8] [22] [23] [24] [25] [26]. The band that appears around 1015 cm\(^{-1}\) is attributed to the asymmetric vibration mode \(\nu_{asym}\) (P-O-P) of the isolated orthophosphate groups (Q\(^{\prime}\)) [5] [19] [21] [23]. The band at 1280 cm\(^{-1}\) is attributed to asymmetric stretching of two non-bridging oxygens \(\nu_{sym}\) PO\(_2\). Analysis of the IR spectra obtained (Figure 3) indicates that the vibration band \(\nu_{asym}\) P-O-P at 1015 cm\(^{-1}\) attributed to the isolated orthophosphate groups decreases with increasing cobalt oxide at the expense of Na\(_2\)O content. This band disappears completely when the CoO content reaches 15 mol\%. On the other hand the shift, at the
Figure 3. IR spectra of the series of 50P₂O₅-25CaO-(25−x)Na₂O-xCoO glasses, (with 0 ≤ x ≤ 25; mol%).

Table 3. The assignments of different vibration bands of the IR spectra of the quaternary 50P₂O₅-25CaO-(25−x)Na₂O-xCoO.

| Régions de fréquence (cm⁻¹) | assignements | Références |
|-----------------------------|--------------|------------|
| 490 - 510                   | Vibration mode δ₁₆₅ (P-O-P) | [3] [4] [5] [6] [14] [19] [20] [21] [22] [23] |
| 777 - 786                   | Vibration mode υₙₛₚₜ (P-O-P) in unit Q¹ | [14] [18] [19] [20] |
| 880 - 910                   | Vibration mode υₙₛₜ (P-O-P) in unit Q¹ | [5] [18] [19] |
| 1015                        | Vibration mode υₙₛₚₜ (P-O-P) in unit Q⁰ | [5] [23] [27] |
| 1078 - 1093                 | Vibration mode υₙₛₚₜ (PO₃) / υₙₛₚₜ (PO₄) in units Q¹ + Q² | [20] |
| 1280                        | Vibration mode υₙₛₚₜ (PO₄) in unit Q² | [3] [4] [5] [19] [26] [27] |

same time, of the vibration band υₙₛₚₜ P-O-P, located at 777 cm⁻¹, towards the high values and the decrease in the intensity of the vibration band υₙₛₚₜ PO₂, located at 1280 cm⁻¹, added the shift of the vibration band υₙₛₚₜ (PO₃) / υₙₛₚₜ (PO₄) toward low values, confirms the increase in the number of pyrophosphate groups to the detriment of metaphosphate groups, when the CoO content increases in the glass network. As for the vibration bands at approximately 1078-1093 cm⁻¹ and 1280 cm⁻¹ are assigned, respectively, to the stretching vibration mode υₙₛₚₜ (PO₃) / υₙₛₚₜ (PO₄) attributed of the pyrophosphate groups and to the vibration mode Vₙₛₚₜ (PO₄) attributed to metaphosphate groups (Q²) [3] [4] [9] [20] [21] [26] [27]

3.4. X-Ray Diffraction and DTA Analysis

As expected, X-ray diffractions have confirmed the vitreous character of all of
the investigated glass samples (see Figure 4). DTA analysis of the phosphate glass 50P$_2$O$_5$-25CaO-(25−x)Na$_2$O-xCoO (with 0 ≤ x ≤ 25; mol%), shown in Figure 5, indicates both an increase in the glass transition temperature and the crystallisation temperature versus the CoO content. When the CoO content increases from 0 to 25 mol%, the glass transition temperature (T$_g$) increases in the 399°C - 477°C range, whereas the crystallisation temperature (T$_c$) increases in the 502°C - 657°C range (Table 1). The T$_c$-T$_g$ difference is significant, which explains the high thermal stability [13] [28]. The heat treatments of the S$_0$, S$_2$ and S$_4$ glasses at 540°C, 551°C and 660°C for 72 h, respectively, give the XRD patterns shown in Figure 6. These spectra show a structural evolution from orthophosphate (O/P = 4) and olygophosphate phases (3 ≤ O/P ≤ 3.5) to olygophosphate phase with majority of pyrophosphates phases (Q$^1$). When the S$_0$ sample was thermally treated at 540°C, the amorphous phase partially disappeared and major Ca$_3$PO$_4$ [JCPDS file N°: 00-009-0340], NaCaPO$_4$ [JCPDS file N°: 00-029-1193] and Na$_3$PO$_4$ [JCPDS file N°: 00-031] occurred in the sample, with minor NaPO$_3$ [JCPDS file N°: 00-002-0776], Ca(PO$_3$)$_2$ [JCPDS file N°: 00-017-0500], CaP$_2$O$_6$ [JCPDS file N°: 00-015-0204], and Ca$_2$P$_2$O$_7$ [JCPDS file N°: 00-009-0346] phases. When the CaO content increased in the S$_2$ glass, the heat treatment at 551°C...
caused the formation of Na$_2$P$_2$O$_7$, [JCPDS file N°: -], Ca$_3$P$_2$O$_7$ [JCPDS file N°: 00-009-0346] and Co$_5$P$_2$O$_7$ [JCPDS file N°00-052-1470] with some traces of metaphosphate and isolated short orthophosphates phases. However, when the CoO content increased to 25 mol%, the heat treatment, at 660°C, indicated the disappearance of the isolated ortho-phosphate phases, while the CaP$_2$O$_6$ phases [JCPDS file N°: 01-015-0204], Ca(PO$_3$)$_2$ [JCPDS file N°: 00-009-0363], Co$_5$P$_4$O$_{12}$ [JCPDS file N°: 00-040-0068], Co(PO$_3$)$_2$, [JCPDS file N°: 00-027-1120], Ca$_2$P$_2$O$_7$ [JCPDS file N°: 00-009-0346], and Co$_2$P$_2$O$_7$ [JCPDS file N°: 00-040-0068] appeared largely in the sample with very high intensities that confirms the results obtained by IR [13].

3.5. SEM Micrograph Analysis

SEM images in Figure 7 illustrate the morphology of the glasses considered in this work. The glass form of S$_1$ shown in Figure 7(a), exhibit the presence crystalline phases with different form and size [5] [9] [10] [23]. When the CoO content increases in the glass, the number of crystallites decreases. Hence, SEM analysis confirms a homogenous vitreous phase with feeble crystalline particles in the S$_4$ sample (Figure 7(e)) which has the maximum CoO content. Some different crystalline phases were identified by XRD and it seems that a decrease of crystallisation tendency is enhanced and Co(PO$_3$)$_3$, Ca$_3$P$_2$O$_7$ and Co$_5$P$_2$O$_7$ phases are crystallized in the last sample (S$_4$) [13]. This probably explains the structural change towards more short pyrophosphates at the detriment of shorter isolated

![Figure 6](image-url). X-ray diffraction spectra, after heat treatment at crystallization temperatures 508°C, 560°C and 680°C for 72 h, respectively, for S$_0$, S$_2$ and S$_4$. 

![Figure 7](image-url). SEM images illustrating the morphology of the glasses considered in this work.
orthophosphate chains as the CoO content increases in the glass network.

4. Discussion

The glasses series 50P$_2$O$_5$-25CaO-(25−x)Na$_2$O-xCoO (with 0 ≤ x ≤ 25; mol%), were prepared by direct melting at 1080°C. The structure and the chemical durability of these glasses have been investigated using various techniques such as density, X-Ray, DTA, diffraction, IR and SEM. The study of the dissolution rate for all the glasses studied indicates an improvement in chemical durability when the CoO content increases to the detriment of Na$_2$O. The variation of transition temperature versus CoO content indicates an increase in Tg from 399°C to 477°C when the CoO content increases from 0 to 25 mol%, elucidating an improvement in the rigidity of the glass [8] [13] [18] [21] [28].

The specific mass (Density) of vitrified phosphates is increasing with molar fraction along the series. The covalent radius values of oxygen calculated from Equation (2) indicate that the minimum value $r_{cal}$ (O$^{2-}$) is observed for x = 20
and therefore a relatively high reinforcement of the metal-oxygen-phosphorus (Co-O-P) bond [4] [12] [17] [28]. On the other hand, Analysis of infrared spectra indicates that the increase of CoO content to the detriment of Na2O, in phosphate glass, leads to the formation of olygophosphate groups (Q1-Q2) [22] [28] with the majority pyrophosphates at the expense of orthophosphates and metaphosphates and or cyclical metaphosphates groups. X-ray diffraction analysis of glasses, annealed between 502˚C to 663˚C for 72 hours, confirms the evolution, with the increase of CoO content, of crystalline phases towards olygophosphate phase’s rich of pyrophosphates. In fact, when the CoO content exceeds 15 mol%, the orthophosphate phases completely disappear in the vitreous network. Analysis of SEM micrograph indicates the evolution of the structural morphology of the glasses. As the CoO content increases in the glass, the number of crystallites decreases, consequently, SEM micrograph expected in Figure 7(e) for S4 sample, having a maximum CoO content, confirms a homogeneous glass phase with low crystalline particles.

This phenomenon is explained by the fact that Na2O (Na+ alkali ion) is a main modifier oxide which easily depolymerizes the vitreous network by creating increasingly short chains going from ultraphosphate chains to metaphosphate, pyrophosphate and shorter isolated orthophosphate chains [3] [5] [29]. This accentuated depolymerization leads to the formation of a large number of easily hydrated Na-O-P bonds which greatly reduce the chemical durability of the glasses. In addition, the effect of the oxide CaO which depolymerizes the glass from ultra-phosphate towards chains mainly of metaphosphate or cyclic metaphosphate, it can be explained that the increases of CoO to the detriment of Na2O has the effect of polymerizing the structure from isolated orthophosphate chains toward the formation of olygophosphates predominantly by pyrophosphate chains. This behavior leads to the replacement of hydrated Na-O-P, P-O-P and possibly Ca-O-P bands, by the covalent and resistant Co-O-P bonds.

Hence, the glasses series studies in the present work can be divided into three categories:

1) Glasses with a low CoO content (0.5 to 3 mol%) can be applied with a slight improvement in the optical field [19] [30] [31].
2) Glasses with CoO content between 5 and 15 mol% can be tested successfully in the biomedical field because they can increase the rigidity of the glass and participate in the osteoinduction of bone tissue [14] [15] [18] [31].
3) Glasses with content between 20 and 25 mole%, can be used, with some improvement, in the electrical conduction range since cobalt can be found under two degrees of oxidation Co2+ and Co3+ which ensures the hopping mechanism of the electrons and therefore oxidation reduction phenomenon [21] [32].

Hence, a better understanding of phosphate glass structure is very relevant to the industry in the development of technical glasses to achieve good performances.
5. Conclusions

The structure and properties of xCoO-(25−x)Na2O-25CaO-50P2O5 phosphate glasses (with 0 ≤ x ≤ 25; mol%) have been investigated in the present paper. Here are some conclusions from this paper:

1) The structure of the Co-Na-Ca-phosphate samples glasses, predominantly, consists of olygophosphate, Q2-Q1 units, and the CoO leads to the conversion of Q0 units to Q1 units.

2) The glass transition temperature is improved by increasing CoO content in the glass network and leads to the increase of thermal stability.

3) Increasing the glass transition temperature leads to improved chemical durability.

4) The SEM Micrograph indicates an obvious decrease in crystallites with the increase in CoO, causing a relatively large equilibrium between the glass bath and the crystallites.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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