Chemical Durability and Structural Properties of the Vitreous Part of the System $x\text{CaO}-(40-x)\text{ZnO}-15\text{Na}_2\text{O}-45\text{P}_2\text{O}_5$

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Abstract

The influence of CaO on the glass forming characteristics and properties of $\text{Na}_2\text{O-CaO-ZnO-P}_2\text{O}_5$ glasses has been investigated. According to the studies that we performed on phosphate based glass within system $x\text{CaO}-(40-x)\text{ZnO}-15\text{Na}_2\text{O}-45\text{P}_2\text{O}_5$ ($10 \leq x \leq 30$; mol%), it was found that the increase of CaO and substitution of ZnO can give a good chemical durability. Both Cristallographies X-ray and IR spectroscopy have confirmed the structure change when the CaO content increases in the glass. This change results in the formation of metaphosphate and/or rings of metaphosphate groups at the expense of pyrophosphate. So it indicates the formation of Ca-O-P bonds in the network glass that replaces hydrated P-O-Na and P-O-P bands. The phosphate chains units can be bonded together in rings forming meta-phosphate groups. These rings likely lead to the formation of agglomerates of crystalline phases, which is the main cause of the increase in the chemical durability of the glasses when the CaO content increases. The latter may lead to wider use of these materials, especially in the biomedical field.

Keywords

Phosphate Glasses, Glass Formation, IR Spectroscopy, X-Ray Diffraction, SEM

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1. Introduction

Glass is used before long in aesthetic field. Therefore, this material has never ceased to evolve and diversify as required. Across all continents and most civilizations, glass has always been appreciated for its aesthetic qualities and its physical properties [1]-[6]. These properties, such as low melting point, high thermal expansion coefficient, and optical properties make these glasses potential candidates for many technological applications in the medical field (biomaterials), as solid electrolytes, sealing materials and as alternative methods for the vitrification of nuclear waste, etc. [4] [7]-[10]. The aim of the present study is to investigate the structural change and modification of chemical durability versus composition as the proportion of CaO is varied along the series of phosphate glasses xCaO-(40-x)ZnO-15Na2O-45P2O5 with 10 ≤ x ≤ 30, mol%. So we have explored that the increase of CaO content in the glass network leads to an improvement of chemical durability. The structural change enhanced the formation of metaphosphate and/or rings of metaphosphate groups, with some pyrophosphate groups, that were confirmed by I.R spectroscopy and X-ray diffraction.

2. Experimental Procedures

The synthesis of phosphate-based glasses is carried out by the direct fusion of mixtures of (NH4)2HPO4, CaCO3, Na2CO3 and ZnO in suitable proportions. The reactants are finely ground and then fed into a porcelain crucible. They are heated in a first stage at 300°C for 2 hours and then at 500°C for 1 hour to complete their decomposition. The reaction mixture is then heated to 1060°C - 1100°C for 30 min. The resulting liquid is homogeneous. It is then poured into an aluminium plate previously heated to 200°C to prevent thermal shocks. In our case, pellets about 1 cm in diameter and 2 - 3 mm thick were obtained. The chemical durability of these glasses has been evaluated from the weight loss of sample. The samples were then polished with silica carbon sandpaper (CSI adequate standard), cleaned with acetone and immersed in Pyrex beakers containing 100 ml of distilled water and brought to 90°C. The surface of the sample must be constantly immersed in distilled water for 20 days. Density measurements were made by the method of Archimedes. The glass is immersed in a diethyl orthophthalate solution whose density, depending on the temperature, is known. The precision was 0.05 g/cm³. The infrared spectra of the phosphate glasses studied were determined in the region between 1600 and 400 cm⁻¹ with a resolution of 2 cm⁻¹. The samples were finely ground and mixed with KBr (potassium bromide), which is transparent in the infrared, and whose role was to serve as a matrix. The ratio of material/KBr in the pellets was 10% against 90% by weight. The infrared spectroscopic analysis of our materials was performed on a Fourier transform spectrometer Vertex 70 and saved on a DTGS detector (Tri glucose deuterium sulphate). The glassy state was highlighted by its gloss and transparency, and confirmed by XRD. S1 and S4 annealed glasses were made at 550°C and 650°C, respectively, for 48 hours. The first structural approach was made using X-ray diffraction, which allowed us to follow the structural evolution. The samples were analysed by a X’Pert Pro MPD Panalyti diffractometer. The chemical composition and microstructure of the sample glasses was characterized using a scanning electron microscope (SEM) equipped with a full system of micro-analysers (EDX-EDAX).

3. Results

3.1. Chemical Durability

The chemical durability of the series of glasses xCaO-(40-x)ZnO-15Na2O-45P2O5 with 10 ≤ x ≤ 30, mol% was approached by measuring the dissolution (Dr) rate, which was defined as the weight loss of the glass expressed as g·cm⁻²·min⁻¹. The values of Dr reported in Table 1 show dissolution decreased versus the CaO content of our samples after their immersion in 100 ml of distilled water heated at 90°C for 20 consecutive days (Figure 1) [11].

| Glass Sample | Starting Oxide mixtures mol% | [O/P] ratio | Dr (g·cm⁻²·min⁻¹) | ρ, (g/cm³) |
|--------------|------------------------------|-------------|-------------------|------------|
|              | CaO | ZnO | Na₂O | P₂O₅ |              | (2.84 ± 0.20) × 10⁻⁷ | (2.80 ± 0.05) |
| S₁           | 10  | 30  | 15   | 45   | 3.11         | (2.10 ± 0.20) × 10⁻⁷ | (2.81 ± 0.05) |
| S₂           | 15  | 25  | 15   | 45   | 3.11         | (9.68 ± 0.20) × 10⁻⁶ | (2.69 ± 0.05) |
| S₃           | 25  | 15  | 15   | 45   | 3.11         | (6.84 ± 0.20) × 10⁻⁶ | (2.73 ± 0.05) |
3.2. Density and Molar Volume

The density of the glass was measured at room temperature. As can be deduced from the plots in Figure 2, density (more precisely the specific mass) decreased with increasing CaO content [11]. This behaviour can be explained by the decrease in the glass weight as the Ca replaces Zn, which has a smaller atomic weight. The oxygen molar volume and the oxygen anion radius in the glass were determined from Equations (1) and (2), respectively:

\[ V_{OM} = M \left( \frac{\rho N_A \cdot N_o}{N_a} \right) \]  

(1)

\[ r_{rel}(O^{2-}) = \frac{\sqrt{3}VOM}{2} \]  

(2)

with \( M \) = molar mass; \( \rho \) = density; \( N_A \) = Avogadro number; \( N_o \) = number of oxygen atoms in the molar formula.

A detailed analysis of the data in Table 2 shows that the molar volume remained almost constant while the CaO content increased. The value of the relative oxygen radius \( r_{rel}(O^{2-}) \), calculated from the molar volume Equation (2) [12] and recapitulated for each composition in Table 2, also did not change.

3.3. X-Ray Diffraction

The X-ray crystallography confirmed the single glassy character of all investigated samples. Indeed, the records of the X-ray diffraction (XRD) patterns were found to be typical of amorphous substances [12]. As expected, it is also worth noting that the annealing of the samples led to their crystallization as evidenced by their new XRD patterns given in Figure 3. Annealed glasses in the series with composition xCaO-(30-x)ZnO-25Na2O-45P2O5 were prepared at temperatures between 550°C and 650°C for 48 hours. Counting the RX spectra obtained shows (Figure 3) that the S4 composition 30CaO·10ZnO·15Na2O·45P2O5 tended to crystallize as a mixture of metaphosphate and pyrophosphate, with metaphosphate and/or rings metaphosphate chains majorities, while S1 belonging to oligophosphate field samples is expected to contain a mixture of meta-and pyrophosphate networks related to those of calcium and zinc [13].

3.4. Infrared Spectra

The infrared spectra of glasses in the series xCaO-(40-x)ZnO-15Na2O-45P2O5 are shown in Figure 4. All vibration bands in the phosphate-treated samples are presented in the field between frequencies of 1400 and 599 cm\(^{-1}\). The band at 1300 - 1200 cm\(^{-1}\) is assigned to asymmetric vibration modes \( \nu_{as}(PO_2) \) [12] [14], comprising two non-bridging oxygen atoms of phosphorus in a \( Q^2 \) phosphate tetrahedron. The vibration bands at around 1100 and 1000 cm\(^{-1}\) are characteristic of terminal \( PO_3^- \) groups [12]. In addition, the band at 884 - 890 cm\(^{-1}\) shifts to a low wavenumber due to the asymmetric vibration \( \nu_{as}(P-O-P) \) while the band at 753 cm\(^{-1}\) is attributed to symmetric vibration vs (P-O-P) groups bridging oxygen atoms bonded to a phosphorus atom in a \( Q^2 \) phosphate tetrahedron [12] [14] [15]. The spectrum of \( C_4P_6O_{19} \) shows a strong vibration in the region around 696 - 733 cm\(^{-1}\) [5] [10] with a CaO content \( \leq 15 \) mol%. This vibration shifts to low frequencies when the CaO content increases, whereas the same band disappears from the spectrum when the CaO content is \( \geq 25 \) mol%. The band
Figure 2. Variation of the Density ($\rho$) versus CaO mol% along the Glass series $x$CaO-(40-$x$)ZnO-15Na$_2$O-45P$_2$O$_5$.

Figure 3. XRD patterns for glass samples $S_1$ and $S_4$ after heat treatment for 48 hrs under an air atmosphere at 550°C and 650°C, respectively.

Table 2. Density and related molar data of the $x$CaO-(40-$x$)ZnO-15Na$_2$O-45P$_2$O$_5$ system.

| Sample | Molar Formula | $\rho$, (g/cm$^3$) | Molar mass g·mol$^{-1}$ | Molar volume (Å$^3$) | Calculated oxygen radius (Å) $r_{cal}$(O$^{2-}$) |
|--------|---------------|---------------------|------------------------|----------------------|---------------------------------------------|
| $S_1$  | 10CaO·30ZnO·15Na$_2$O·45P$_2$O$_5$ | (2.80 ± 0.02) | 103.201 | 21.86 | 1.40 |
| $S_2$  | 15CaO·25ZnO·15Na$_2$O·45P$_2$O$_5$ | (2.81 ± 0.02) | 101.935 | 21.51 | 1.39 |
| $S_3$  | 25CaO·15ZnO·15Na$_2$O·45P$_2$O$_5$ | (2.69 ± 0.02) | 99.403 | 21.91 | 1.40 |
| $S_4$  | 30CaO·10ZnO·15Na$_2$O·45P$_2$O$_5$ | (2.73 ± 0.02) | 98.137 | 21.32 | 1.39 |
that appears between 615 and 630 cm$^{-1}$ is attributed to asymmetric vibration modes of the P-O-P skeleton [16]. All characteristic phosphate vibrations show that the bands in phosphate glasses with compositions xCaO-(40-x) ZnO-15Na$_2$O-45P$_2$O$_5$ may have chains and/or rings of metaphosphate structure with some groups of pyrophosphate structure, which is confirmed by the crystalline phases identified by X-ray diffraction. Furthermore, the structure deduced from the vibrational spectroscopy is compatible with the localizations of the analysed compounds (S$_1$, S$_2$, S$_3$, S$_4$) inside the ternary diagram given in Figure 5 and in Table 3.

Figure 4. IR spectra of phosphate glasses of composition xCaO-(40-x)ZnO-15Na$_2$O-45P$_2$O$_5$.

Figure 5. Localization of the investigated glass compositions S$_1$→S$_4$ within the ternary diagram (CaO·P$_2$O$_5$)·(ZnO·P$_2$O$_5$)·(3Na$_2$O·P$_2$O$_5$). The table gives the corresponding compositions within the quaternary system (P$_2$O$_5$·CaO·Na$_2$O·ZnO).
### Table 3. Glass compositions expressed in terms of quaternary systems.

| Glass sample | Chemical composition | Glass compositions inside the ternary diagram |
|--------------|----------------------|---------------------------------------------|
| S1           | 10CaO·30ZnO·15Na2O·45P2O5 | 0.222 (CaO·P2O5). 0.666 (ZnO·P2O5). 0.111 (3Na2O·P2O5) |
| S2           | 15CaO·25ZnO·15Na2O·45P2O5  | 0.333 (CaO·P2O5). 0.555 (ZnO·P2O5). 0.111 (3Na2O·P2O5) |
| S3           | 25CaO·15ZnO·15Na2O·45P2O5  | 0.555 (CaO·P2O5). 0.333 (ZnO·P2O5). 0.111 (3Na2O·P2O5) |
| S4           | 30CaO·10ZnO·15Na2O·45P2O5  | 0.666 (CaO·P2O5). 0.222 (ZnO·P2O5). 0.111 (3Na2O·P2O5) |

#### 3.5. SEM Micrographs

The SEM micrograph shows the existence of two phases, one crystalline and the other glass (Figure 6). It also indicates the formation of agglomerates of crystalline phases amounting to a few tens of micrometres. The presence of the crystalline phase seems to explain the increase in chemical durability [13]. Comparing the SEM results for sample S4 (Figure 7) before and after being attacked by water at 90°C for 20 days, it was found that the percentage of calcium in the glass composition increased while the percentages of sodium and oxygen decreased.

#### 4. Discussion

The influence of CaO on glass forming characteristics and properties of of xCaO·(40-x)ZnO·15Na2O·45P2O5 (10 ≤ x ≤ 30; mol%) has been investigated. The density measurement shows that the value of relative radius of oxygen anion \( r_{\text{cal}} \) (O\(^{2-}\)), calculated from the molar volume remain almost constant for all the glasses, whereas, the glass composition exhibits a tendency to move from field pyrophosphate to metaphosphate units when the CaO content increases. This structural change enhances the formation of metaphosphate and/or rings of metaphosphate groups, with some pyrophosphate groups, confirmed by X-ray diffraction and IR spectroscopy [15]. The X-ray diffraction patterns of S1 and S4, heated to 550°C and 650°C, respectively, illustrate the formation of crystalline phases Zn\((\text{PO}_3)\)_2, Zn\textsubscript{3}P\textsubscript{2}O\textsubscript{7}, CaZnP\textsubscript{2}O\textsubscript{7}, Ca(PO\textsubscript{3})\textsubscript{2} and the crystalline phase Ca\textsubscript{4}P\textsubscript{6}O\textsubscript{19}. The IR spectra indicate that the vibration bands 696 - 733 cm\(^{-1}\) disappear from the spectrum when the CaO content ≥ 25 mol%. These bands are assigned to vibrations of olygophosphate groups (mixture of Q\(^2\) and Q\(^1\) with majority of Q\(^2\) P\textsubscript{6}O\textsubscript{19}\(^{4-}\) [5]. This also explains that the increase of CaO content, led to the decrease of the phase Ca\textsubscript{4}P\textsubscript{6}O\textsubscript{19}\(^{4+}\) and promotes the formation of metaphosphate and/or rings metaphosphate chains at the expense of olygophosphate groups. Hence, the substitution of zinc oxide by calcium oxide in the glass structure can reduce the non-bridging oxygens and induce an increase in the bonding strength of the glass phosphate. On the other hand, 45% P\textsubscript{2}O\textsubscript{5} is supposed to give a mixture of metaphosphate and pyrophosphate as indicated in Figure 3. When the CaO content increases in the glass network, we see the disappear of the phase Ca\textsubscript{4}P\textsubscript{6}O\textsubscript{19} (mixture of 4(PO\textsubscript{3})\textsuperscript{−} + P\textsubscript{2}O\textsubscript{7}\textsuperscript{4−}) for \( x \geq 25 \) mol%, which indicates the change of olygophosphate units in the form, presumably, of cyclic metaphosphate chains that result in agglomerates of crystallites amounting to a few tens of micrometres. These agglomerates lead to a clear improvement in chemical durability [14].

#### 5. Conclusion

The structure and chemical durability of the phosphate glass series \( x\text{CaO}·(40-x)\text{ZnO}·15\text{Na}_2\text{O}·45\text{P}_2\text{O}_5 \) (10 ≤ x ≤ 30; mol%) have been investigated using various techniques such as IR, XRD, SEM, etc. The structural characteristics of these glasses by I.R spectroscopy show a structural change when the CaO content increases. This change leads to the formation of mostly metaphosphates and/or rings of metaphosphate groups with pyrophosphate chains in low concentration. SEM micrographs indicate the formation of agglomerated crystalline phases, which are units of phosphate chains bonded together in rings (cyclic structures) forming meta-phosphate groups, the main cause of the increase in resistant Ca-O-P bands in the glass network. This change led to an important increase in chemical durability. The dissolution ratio obtained in these glasses is in the order of 10\(^{-9}\) (g/cm\(^2\)·min\(^{-1}\)). This result is promising and can be further improved to lead to wider use of these glasses, particularly in the medical field. The outlook will therefore move in the direction of improving the performance of these glasses for possible technological applications.
Figure 6. (a) SEM optical micrograph showing the structure of sample S4 before aqueous attack; (b) SEM optical micrograph showing the structure of sample S4 after aqueous attack.

Figure 7. EDS spectra of glass sample S4 before and after aqueous attack.

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