Study and characterisation of the alteration and devitrification of CaO-MoO_3-P_2O_5 bio-glasses for clinical applications

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Abstract. Bio-glasses with the composition yCaO-(1-y)[xMoO₃-(1-x)P₂O₅] ($0 \leq y \leq 30$; x = 50, 67 mol%) were produced. These materials are used in surgery for applications such as bone replacement in orthopaedics, and dental filling. After insertion, they become covered with a layer of carbonated hydroxyapatite, promoting chemical bonds with bone cells that ensure strong adhesion. An in-depth study of their biological and mechanical properties is planned for medical applications. Our study aims to examine in detail the chemical durability and devitrification process of yCaO-(1-y)[0.5MoO₃-0.5P₂O₅] oxide glasses, while establishing a correlation between their structure and properties. This study analyses the evolution of the dissolution rate D_R as a function of CaO content at variable pH and constant temperature, revealing that the dissolution rate does not vary proportionally with the CaO content. It decreases until it reaches a minimum at 10 mol% CaO, after which any further addition causes an increase in D_R. We studied chemical compositions with constant P/Mo ratios and presented the results of X-ray diffraction analyses of the associated glasses. The diffractograms of the crystalline glass for the composition (x = 67; y = 30 mol%) show the formation of crystalline phases: $CaMoO_4$ (JCPDF.08-0144), CaP_4O_{11} (JCPDF.70-2085), MoP_2O_{11} (JCPDF.82-1965) and $Mo(PO_3)_3$ (JCPDF.09-0106).

1 Introduction

Discovered by Hench around 1970 [1], Bio-glasses are amorphous substances with low bio-functionality, mainly used as prosthetic coatings. Initial clinical use has stimulated interest in various sectors, including surgery and the pharmaceutical industry, thanks to their remarkable biological characteristics for bone regeneration [2]. The chemical structure and atomic arrangement of bio-glasses promote the development of a layer of carbonated hydroxyapatite (CHA) on their surface [3], crucial for processes such as osteo-induction [4], bone reconstruction [5], osteo-conduction [5], osseointegration [5] and neovascularisation [6].

Bioactive glasses are composed of 46.1% SiO_2, 24.4% Na_2O, 26.9% CaO and 2.6% P_2O_5 [2] in terms of their molar chemical composition. These glasses were named 45S5 by L. Hench, indicating a composition of 45% SiO_2 and a calcium/phosphorus (Ca/P) molar ratio of 5. The atomic arrangement and chemical composition affect bioactivity, biocompatibility and bio-functionality, which influences their application in the biomedical and pharmaceutical fields.

Calcium plays a vital role in bioactivity by interacting with H^+ ions and impacting bone cells. Research compiled by Marie [7] shows that calcium-sensitive receptors on bone cells control the recruitment, differentiation and longevity of osteoblasts and osteoclasts. Furthermore, research by Maeno et al. [8] indicates that osteoblast activity is influenced by calcium concentration, with low levels of Ca^{2+} stimulating their multiplication and differentiation, while excessive concentrations can be harmful.

Salinas and his colleagues [9] found that glass composed solely of silicon and calcium has higher reactivity than glass in which SiO_2 is substituted by P_2O_5. However, glasses containing P_2O_5 demonstrate faster apatite crystallization in the calcium phosphate layer. However, thanks to binary glass, apatite develops faster and generates a thicker layer. It is not essential to incorporate phosphorus into sol-gel bioactive glasses, which explains the emphasis on researching glasses composed mainly of silicon and calcium.

The study of glass leaching processes, particularly those involving phosphate glass, has become a major scientific and environmental challenge. Although research has been conducted on silicate glasses, the

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study of the stability and degradation of phosphate glasses remains limited, highlighting the need to examine their reaction to various factors.
Glass, once considered a chemically stable material, has been re-evaluated thanks to Lavoisier's work, which proved that it is not inert. Although numerous reactions occur when immersed in aqueous solutions, these reactions are very slow and solubility thresholds remain low, giving glass seemingly endless resistance [10-11].
Chemical durability refers to the ability of glass to resist corrosion caused by water, environments, and various chemical compounds [10-11]. It depends on its composition, exposure conditions, the nature of the corrosive agent, as well as the temperature, pH and ambient pressure. This research addresses these elements that have an impact on the chemical resistance of glass. Studies, particularly those by Morey concerning silicate glasses, have shown that their dissolution in an aqueous medium goes beyond simple solubility and is more akin to decomposition. Several studies subsequently examined glass corrosion in various contexts and suggested mathematical equations to describe the dissolution processes.

In the field of research into materials with high bioactivity, a review of the literature has shown that the crystallochemistry of molybdenum phosphates has been the subject of extensive research [12-13]. These compounds consist of PO_4 tetrahedra and MoO_6 octahedra, resulting in the formation of hybrid structures that create tunnels or the insertion of alkaline earth cations [14]. They are used in heterogeneous catalysis, ion exchange, ion conduction and as molecular sieves. Research into the devitrification of $yCaO$-$(1-y)[xMoO_3$-$(1-x)P_2O_5]$ glass systems ($0 \leq y \leq 30$ mol%; x = 50 or 66.67 mol%) was conducted with a view to developing new open-structure materials. At room temperature, these glasses from both systems exhibit a diffractogram that demonstrates their entirely amorphous nature. Annealing made it possible to understand their crystallization kinetics and determine their structure. Using ICDD data made it possible to identify the crystallized phases.
Previous research [15] has demonstrated that glasses composed of phosphate and molybdenum exhibit interesting characteristics. This project will study oxide glasses of the $yCaO$-$(1-y)[0.50MoO_3$-$0.50P_2O_5]$ system (P/Mo = 2) for values of $0 \leq y \leq 30\%$ by mole, using CaO as a stabilizing agent. The study will include examination of physical characteristics, chemical resistance, and the use of structural characterization methods such as IR. We will also consider linking structural assumptions to physicochemical characteristics and examine glasses with the composition $yCaO$-$(1-y)[xMoO_3$-$(1-x)P_2O_5]$ ($0 \leq y \leq 30$ mol%; x = 50 or 66.67 mol%) (P/Mo= 2 or 1) to observe recrystallisation.

2 Experimental procedures

Glasses derived from the ternary system $yCaO$-$(1-y)[xMoO_3$-$(1-x)P_2O_5]$ are prepared according to the following reaction:

$$yCaO + x(1-y)MoO_3 + (1-x)(1-y)(NH_4)H_2PO_4 \rightarrow yCaO\ x(1-y)MoO_3\ {}^{1}/_{2}\ (1-x)(1-y)P_2O_5 + (1-x)(1-y)NH_3 + {}^{3}/_{2}\ (1-x)(1-y)H_2O \quad \text{(Eq. 1)}$$

Where y = 0, 5, 10, 15, 20, 25, 30 mol %.
The appropriate quantities of CaO, MoO_3 and $NH_4H_2PO_4$ are ground and mixed in a mortar. The contents are placed in an open platinum crucible and introduced into a muffle furnace. The mixture is then subjected to two heat treatments. The first treatment is at 533 K, which allows the ammonium phosphate to decompose and moisture to be removed. The second treatment is at 1173 K. It allows the reaction mixture to fuse. Finally, the glass is obtained by air quenching.
The amorphous nature of the elaborated samples was confirmed by employing XRD and differential Thermal Analysis (DTA) techniques.
The IR spectra of the samples was measured from 400 to 1400 cm^{-1} (wave number) by the standard KBr pellet method using a Fourier transform infrared (FT-IR) spectrometer (Genesis).

The chemical durability of the glasses was estimated in term of the dissolution rate (D_R). This later was calculated from the measured weight loss (ΔW) using the equation [16]:

$$D_R = \Delta W(g) / [A(cm^2) \times t(min)] \quad \text{, (Eq. 2)}$$

In the experiment, leaching tests were conducted to measure the surface area (A in cm^2) of a sample immersed in ammonia acetate buffer solutions at different pH levels (5.5 to 8.5) and a constant temperature of 305 K. The buffer solutions were prepared with 2.5 vol % glacial acetic acid supplemented with concentrated ammonia to achieve the desired pH. A digital pH-meter (micro pH 2000 Crison) was used for pH measurement. The tests involved 0.2 g of glass in 100 ml of the buffer solution during specified time intervals.

To devitrify the glasses, we performed 12-hour anneals at increasing temperatures above T_g, in 293 K intervals. Glassy materials with high P_2O_5 content maintained their amorphous nature even as temperature approached the melting point.

3 Results and discussion

3.1 Density and molar volume

The density ρ of glasses with a P/Mo ratio of 2 increases with CaO concentration, leading to a

decrease in molar volume Vm.

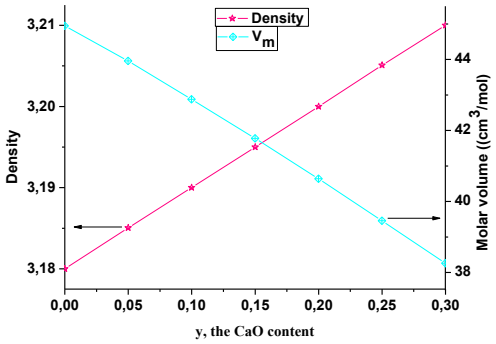

Fig. 1. Dependence of ρ and V_m on the CaO content of glasses with a P/Mo ratio of 2.

The linear increase in density with CaO content is related to cross-linking of the glass network, indicating that CaO contributes to the evolution of density with a specific factor [17]. The addition of CaO to the $0.5MoO_3$-$0.5P_2O_5$ composition increases the density of the glass with a P/Mo ratio of 2. This increase is due to the ability of calcium oxide to strengthen the cohesion of the glass network by creating cross-links and cross-linking the phosphate chains. Ca^{2+} cations, with their partial ionic character, also promote the formation of more covalent bonds between non-bridging oxygen atoms, which increases the density of the glass [18]. We will examine the significance of the molar volume (V_m) of glasses in order to analyze the cross-linking of the glass network, based on density and chemical composition. It highlights that the decrease in V_m observed when calcium oxide (CaO) is introduced is corroborated by various studies [19]. In glasses where the P/Mo ratio = 2 remains constant, the molar volume decreases with increasing CaO content. This change is consistent with the decrease in the ionic character fraction ((ICF (Ca-O) = 0.77) (ICF (P-O) = 0.36); (ICF (Mo-O)=0.34) and the ionic radius ($r(Ca^{2+})$=1 Å; $r(Mo^{6+})$=0.41Å; $r(P^{5+})$=0.17Å), mainly attributed to the increase in the ionic radius of calcium. Consequently, the reduction in molar volume in glasses with a P/Mo ratio of 2 is induced by the influence of CaO in the MoO_3-P_2O_5 glass matrix.

This paragraph explores the influence of CaO content on the chemical stability of glasses with a P/Mo ratio of 2, using either the measured mass loss technique or the technique based on the quantities of leached elements released. We will examine the effect of divalent CaO oxide on the chemical durability of glasses with a P/Mo ratio of 2, by analyzing the dissolution rates. Measurements show that the dissolution rate initially decreases, reaching a minimum at 10 mol% CaO, a result that corresponds to Peng's conclusions on the impact of CaO in the glass matrix [18]. Beyond this minimum, any additional CaO added results in an increase in D_R.

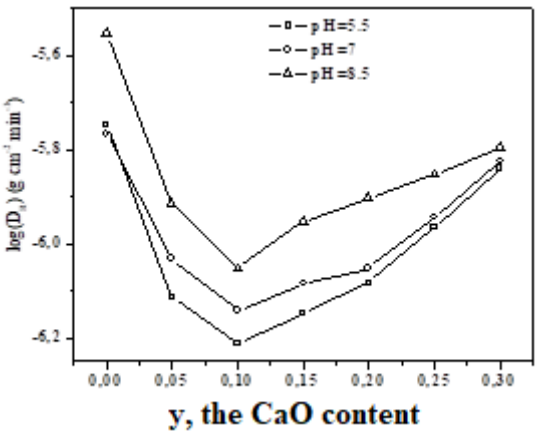

Fig. 2. Variation in dissolution rate D_R against of CaO content in glasses with a P/Mo ratio of 2.

Figure (2) indicates that CaO incorporation has an impact on the dissolution rate D_R, depending on variable pH and a fixed temperature. For additions of 5 to 10% CaO, the proportion of dissolution of glasses with a P/Mo ratio of 2 decreases. However, the increase in the D_R dissolution rate accompanies the addition of more than 10 mol% of CaO with the increase in the pH of the solution.

The addition of CaO in ternary glasses, unlike binary glasses, is the main distinction between the two with a P/Mo ratio of 2. This results in a change in the dissolution process of molybdenum phosphate glasses. A suggested process for ternary glasses evokes the corrosion of calcium silicate glasses [20]. The dissolution process in glasses where the P/Mo ratio = 2 occurs in two phases, beginning with ion exchange between Ca^{2+} and various entities in the solution such as H^+, H_3O^+ and/or H_2O :

$$(M\text{-}O^-)_2\ldots Ca^{2+} + 2H^+ \rightarrow 2M\text{-}O^-\ldots H^+ + Ca^{2+}\ (M=P, Mo) \quad (Eq.\ 3)$$

The ions move in opposite directions, causing the formation of a leachate or gel layer on the glass, depleted in Pb^{2+} ions and enriched in hydrogenated species. The formation of P-OH bonds on the surface of the glass is validated by vibration spectroscopy. In the second phase, dissolution involves breaking the bonds in the P_2O_5 network.

Based on the analysis of P_2O_5 and MoO_3 concentrations in the leaching solution, it is observed that the P/Mo ratio is less than two in an acidic environment and higher in a basic environment, indicating selective dissolution of glasses. This can be explained by the covalence of the Mo-O bond, suggesting that Mo atoms occupy positions in the glass network. Thus, these glasses combine P_2O_5 and MoO_3, forming P-O-P, Mo-O-Mo and P-O-Mo bonds. The oxides act as acids and bases, promoting the modification of P-O-P units in an alkaline environment and the breaking of Mo-O-Mo bonds in an acidic environment, respectively.

$$P\text{-}O\text{-}P + OH^- \text{ (or } H_2O) \rightarrow P\text{-}O\text{-}H + P\text{-}O^- \quad (Eq.\ 4)$$

$$Mo\text{-}O\text{-}Mo + H_2O \text{ (or } H_3O^+) \rightarrow 2Mo\text{-}O\text{-}H \quad (Eq.\ 5)$$

An explanation of the selective dissolution of glasses must take into account the preferential attacks on bonds. The dissolution of binary MoO_3-P_2O_5 glasses differs from that of ternary CaO-MoO_3-P_2O_5 glasses in that the former only include cation formers (P^{5+}, Mo^{6+} and/or Mo^{5+}) in their glass matrix. Consequently, the ion exchange reaction does not contribute to their dissolution; the reactions dominating this mechanism are described by equations (4) and (5).

To interpret the IR absorption spectra of CaO-MoO_3-P_2O_5 ternary oxide glasses, information on the vibrational behavior of entities present in phosphate-based glasses was gathered [21-23]. The IR spectra of glasses with a P/Mo ratio of 2, measured at room temperature in the range of 400–4000 cm^{-1}, are shown in Figure 3.

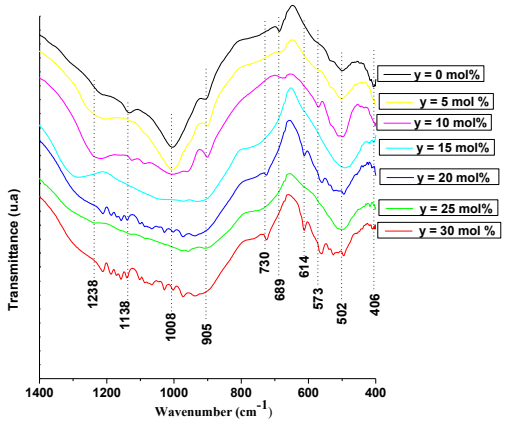

Fig. 3. IR spectra of glasses with a P/Mo ratio of 2.

The spectra of glasses with a P/Mo ratio of 2 show general characteristics based on data from the literature [21-23] :

In the high frequency range from 800 to 1400 cm^{-1}, the modes observed are essentially those mentioned:

- The absence of IR bands beyond 1250 cm^{-1} indicates the absence of very long chains.
- In the high frequency region, two bands at 1138 cm^{-1} and 1238 cm^{-1} are observed, attributed to the antisymmetric stretching vibrations of the PO_3^{2-} group and PO_2^- groups.
- A broad split band in the region of 1008 cm-1 is observed, attributed to a υ_s mode, but this disappears from y=10 mol%.
- The antisymmetric vibrations of P-O-P cause strong absorption around 905 cm^{-1} in the 850-1050 cm^{-1} range, also attributed to Mo-O bonds in MoO_6 octahedra.

In the mid-frequency range from 300 to 800 cm^{-1}, various spectroscopic modes can be observed:
- In the range of 690–800 cm^{-1}, strong absorption around 730 cm^{-1} is caused by the symmetric P-O-P vibration modes, which could overlap with a symmetric stretching vibration mode of the Mo-O bonds of the MoO_4 entities.
- Two bands at 573 and 614 cm^{-1} appear with increasing CaO content, whereas they are absent in the binary glass $0.5MoO_3$-$0.5P_2O_5$. These bands could correspond to vibrations of M-O-Ca entities, with M being P or Mo.
- The deformation modes of the phosphate network manifest themselves between 480-550 cm^{-1} in these glasses, including deformations of the phosphate network $\delta(PO_4^{3-})$ and possibly MoO_4 octahedra, with an intensity that increases with increasing CaO content.
- The vibration mode located at 406 cm^{-1}, attributed to the deformation mode $\delta(MoO_6)$, disappears with the addition of CaO.

The dissolution of glass with Ca^{2+} cations is significantly reduced compared to glass without cations, indicating that Ca^{2+} increases the density of cross-links between phosphate (PO_4) units. The bonds formed by Ca^{2+} are more robust, and the chelate structure of the metal has been observed by Van Wazer. Furthermore, irregular variations in the dissolution rate (D_R) with increasing Ca^{2+} cations suggest the influence of other factors, such as structural rigidity, in addition to molar volume.

IR spectroscopy of the glass (y = 0) reveals that the metaphosphate unit, bonded to two phosphate groups, creates cross-links that are disrupted by the addition of CaO. The strength of the chemical bonds [(E_l (Ca-O) = 464 kJ/mol); (E_l (Mo-O) = 607 kJ/mol) and (E_l (P-O) = 596.6 kJ/mol)] in ternary glass is influenced by the atomic properties of Ca^{2+} and its ionic potential. The addition of Ca^{2+} to the ternary glass (P/Mo = 2) is expected to reduce durability, while the improvement in durability of this glass compared to binary glass (y = 0) is attributed to the replacement of hydrated P-O-M bonds with Ca-O-M bonds (M = P, Mo), which are more resistant to corrosion.

This paragraph examines the devitrification of oxide glasses in the ternary system with a P/Mo ratio of 1, annealed between 400 °C and 740 °C. Ternary glasses low in CaO (y ≤ 15% mol) remain amorphous at all temperatures, while those rich in CaO (15 < y ≤ 30% mol) recrystallize, forming the phases $CaMoO_4$ (JCPDF.08-0144), CaP_4O_{11} (JCPDF.70-2085), MoP_2O_{11} (JCPDF.82-1965) and $Mo(PO_3)_3$ (JCPDF.09-0106) phases. An example of a diffractogram for a ternary glass with a composition of 25CaO-50.25MoO_3-24.75P_2O_5 is shown (Figure 4).

Table 1. Results of the analysis of the diffractograms of glasses (P/Mo = 1) recrystallized at different temperatures.

% mol	Temp. K	Formed phases
5	673	Amorphous
	753	Amorphous
10	673	Amorphous
	753	Amorphous
15	673	Amorphous
	753	Amorphous
20	673	Amorphous
	753	Amorphous
	793	$CaMoO_4$ + CaP_4O_{11} + $MoOPO_4$ + ΦUI
	833	Amorphous
25	673	Amorphous
	753	Amorphous

	793	$CaMoO_4 + CaP_4O_{11} + MoOPO_4 + \Phi$ UI
	833	$CaMoO_4 + CaP_4O_{11} + MoPO_4 + Mo(PO_3)_3$
	873	$CaMoO_4 + CaP_4O_{11} + MoPO_4 + Mo(PO_3)_3$
	913	Amorphous
30	673	Amorphous
	753	Amorphous
	793	$CaMoO_4 + CaP_4O_{11} + MoOPO_4 + \Phi$ UI
	833	$CaMoO_4 + CaP_4O_{11} + MoPO_4 + Mo(PO_3)_3$
	873	$CaMoO_4 + CaP_4O_{11} + MoPO_4 + Mo(PO_3)_3$
	953	$CaMoO_4 + CaP_4O_{11} + MoPO_4 + Mo(PO_3)_3$
	1013	Amorphous

Φ UI: unidentified phases.

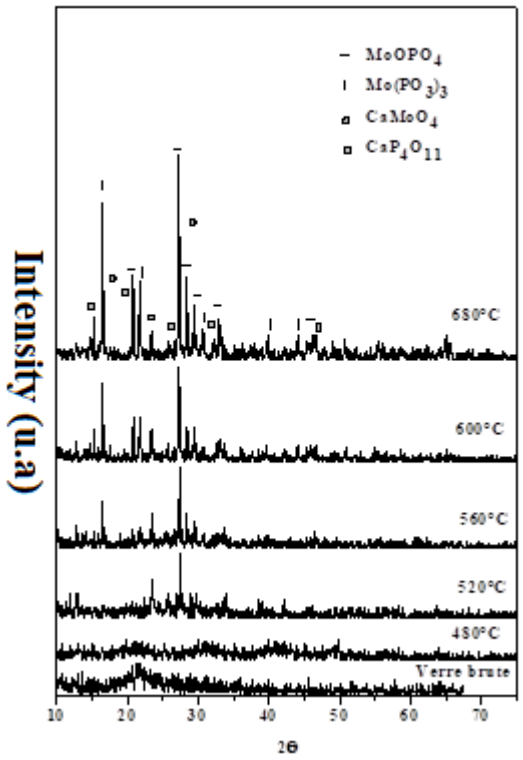

Fig. 4. Diffractograms obtained for $25CaO\text{-}50.25MoO_3\text{-}24.75P_2O_5$ glass recrystallized at different temperatures.

In the case of glasses with a P/Mo ratio of 2, recrystallisation did not result in the formation of crystalline phases, with the resulting phases remaining amorphous after annealing. On the other hand, glasses with a P/Mo ratio of 1 promote crystallization during annealing, suggesting that the nature of the crystalline phases depends heavily on the P/Mo ratio.

4 Conclusion

This study on second series glasses, prepared with increased CaO content, contain various types of phosphate and molybdate units. IR spectra indicate that the O/P ratio affects the length of the phosphate chain, incorporating MoO_3 units into the lattice. The results show depolymerization of phosphate units, a decrease in V_m and an increase in density and chemical durability. The addition of CaO strengthens the glass network by delocalizing the P=O bond and promoting the formation of more resistant P-O-Ca bonds, while reducing P-O-P bonds. It has been demonstrated that the formation of glasses with a P/Mo ratio of 2 occurs near MoO_3 and P_2O_5, confirming their role as formers in the system.

The results of the study on the chemical durability of glasses with a P/Mo ratio of 2 indicate that their dissolution in aqueous ammonium acetate buffer media is congruent and follows a linear law. The addition of CaO to the glass network improves chemical durability, particularly for substitution rates of 5 to 10 mol%. Dissolution is mainly influenced by the cross-linking of the glass network, and the dissolution mechanism appears to result from simultaneous hydration of anions and cations, followed by their departure into solution.

In second series glasses, molybdenum exhibits dominant MoO_4 coordination and MoO_6 coordination. These orthophosphate glasses (O/P>4) exhibit pyro and orthophosphate groups, confirmed by infrared spectroscopy (IR). IR analysis reveals a band at 920–940 cm^{-1} for the Mo-O bond of MoO_6 and a band between 1080–1330 cm^{-1} for the metaphosphate groups. A pyrophosphate characteristic is observed at 1080–1130 cm^{-1}, with a splitting related to CaO. IR comparisons show that the bands associated with P-O-M bonds decrease with the addition of CaO, indicating a break in the P-O-M bonds and the formation of Ca-O bonds.

Based on the IR spectral investigations carried out, a hypothesis concerning the formation of the glass network in the ternary system P/Mo = 2 is proposed. The existence of several structural units [MoO_4], [MoO_6], [PO_4], [P_2O_7], [CaOn] (n=4,6) has been proven, with the fraction of each unit varying according to their composition. The simultaneous presence of CaO and P_2O_5 in glass leads to the transformation of [MoO_6] groups into [MoO_4] groups. And the simultaneous presence of CaO and MoO_3 leads to the transformation of pyrophosphate [P_2O_7] groups into orthophosphate [PO_4] groups.

The devitrification of first and second series glasses is influenced by MoO_3, which acts as a modifier or network former. The second series glasses remain amorphous at all annealing temperatures, while those first series, rich in CaO, favor crystalline phases. MoO_3 contributes to amorphousness at P/Mo = 2, whereas at P/Mo = 1, CaO and MoO_3 concentrations above 15% generate crystalline phases, unlike low concentrations, which maintain amorphousness.

Glassy materials rich in network formers retain their amorphous character regardless of the annealing temperature. A network trainer is therefore defined as a component with this property. As an amorphous material, glass exhibits a glass transition temperature (T_g), has no crystallization temperature and retains its amorphous character at all annealing temperatures.

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