

Leaching and devitrification of lead, molybdenum and phosphorus oxide glasses

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Abstract. Morocco has established a prominent industry focused on the transformation and development of its abundant phosphate deposits, valued for their diverse properties. Numerous physic-chemical studies focus on the leaching and devitrification of oxide glasses characterized by the composition $y\text{PbO}-(1-y)[x\text{MoO}_3-(1-x)\text{P}_2\text{O}_5]$, with specific parameters of $0 \leq y \leq 0.3$ and x values of 0.5 and 0.67. Measurements indicated that the addition of PbO in phosphate glasses, at concentrations from 0% to 30%, affects chemical durability. This was assessed across various solution pHs and dissolution times, utilizing an ammonium acetate solution and grain sizes between 300 to 500 μm , demonstrating the cross-linking effect of lead on the glass framework. A study indicates that the mass losses from the leaching of glasses occur linearly over time, regardless of their composition, and that glasses containing PbO exhibit increased durability. Studying the devitrification of elaborate glasses, this work presents X-ray diffraction analysis results for two glass families ($x=0.67$; 0.5). The analysis of the crystalline glass composition $0.3\text{PbO}-0.47\text{MoO}_3-0.23\text{P}_2\text{O}_5$ indicates the formation of $\text{Pb}(\text{MoO}_2)_2(\text{PO}_4)_2$.

1 Introduction

The significance of glasses in daily life and technology is immense, with ongoing advancements in lens parameters presenting a critical scientific challenge. While a definitive theory is still developing, numerous models and results effectively describe the glassy state and can predict various properties of glasses, including physicochemical, optical, electrical, and thermodynamic characteristics.

The study aims to enhance the chemical durability of phosphate glasses, which currently suffer from low durability when compared to silicate glasses. It focuses on understanding factors influencing glass leaching, acknowledging the complex interplay of multiple factors that affect weathering behavior. To achieve reproducible results and clarify the influence of

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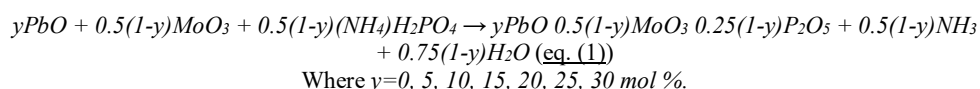
different parameters on dissolution mechanisms and kinetics, a significant number of experiments are required. The study focuses on the complexity of conducting both chemical and structural analyses of phosphate glasses with multivalent oxides (Mo, Pb) known for their good chemical durability. It aims to enhance this durability by modifying the chemical composition, while examining its influence based on several factors: chemical composition, pH of the etching solution, temperature, and immersion time. The study focuses on the chemical durability of phosphate glasses containing multivalent oxides (Mo, Pb), noting that both chemical and structural analyses are necessary for a comprehensive understanding. It emphasizes the potential to enhance durability through modifications in chemical composition, and investigates various influencing factors, such as chemical composition, pH of the etching solution, temperature, and immersion time.

This study focuses on the durability of glasses, assessed through their dissolution rate in water, and involves characterizing the glasses by: (1) chemical analysis via MEB for composition; (2) thermal analysis using DSC to measure glass transition (T_g), crystallization (T_c), and melting (T_f) temperatures; (3) infrared spectroscopy for structural analysis; and (4) X-ray diffraction to examine crystallized phases.

The exploration of new materials with open structures has led to significant research on molybdenum phosphates [1-2], which combine PO_4 tetrahedra and MoO_6 octahedra to create frameworks with tunnels or interlayers for alkaline [3-4] and alkaline-earth cations [5-6]. These materials have applications in heterogeneous catalysis, ion exchange, ion conduction, and as molecular sieves. Recent studies on the devitrification of the compound $yPbO-(1-y)[xMoO_3-(1-x)P_2O_5]$ revealed that the diffractograms for these glasses were completely amorphous at room temperature, with crystallization kinetics assessed through annealing and identification of crystallized phases using ICDD data.

2 Experimental procedures

Glasses $yPbO-(1-y)[0.5MoO_3-0.5P_2O_5]$ are prepared according to the following reaction [7]:



Appropriate amounts of PbO , MoO_3 , and $NH_4H_2PO_4$ are ground and mixed, then subjected to two heat treatments: first at $260^\circ C$ to break down ammonium phosphate and remove moisture, and second at $1000^\circ C$ to fuse the mixture, resulting in glass obtained by air quenching.

The density of the glasses was measured using Archimedes' method, while the amorphous state of the materials was assessed through differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analyses

The chemical durability of the glasses was assessed by calculating the dissolution rate (D_R) from the measured weight loss (ΔW) using a specific equation [8]:

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

Where A is the surface area (cm^2) of the sample and t is the time (min) that the sample was immersed in the test solution at $32^\circ C$.

The tests involved preparing buffer solutions with pH values ranging from 5.5 to 8.5 using 2.5 vol % glacial acetic acid and concentrated ammonia. The pH was measured with a digital pH-meter. Leaching was conducted by combining 0.2 g of glass with 100 ml of the ammonia acetate buffer in Erlenmeyer flasks at $32^\circ C$ for specific time intervals.

In order to devitrify the glasses studied above, we carried out successive 12-hour anneals at increasing temperatures above T_g , at intervals of 20°C. We found that glassy materials rich in P_2O_5 formative oxide always retain their amorphous character as the temperature rises up to melting temperature.

3 Results and discussion

Figure (1) shows that density of $yPbO-(1-y)[0.5MoO_3-0.5P_2O_5]$ glasses, increases with higher PbO concentration, while molar volume decreases.

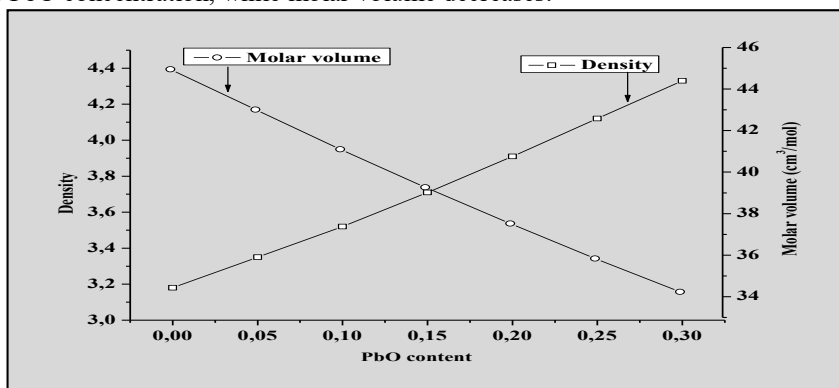


Fig. 1. Changes in density and molar volume (cm^3/mol) depending on the PbO content of the glass $yPbO-(1-y)[0.5MoO_3-0.5P_2O_5]$.

Density increases linearly with PbO content due to glass network cross-linking. The linear density behaviour shows that PbO in the glass matrix contributes to the density evolution with a specific factor [9-12].

Adding PbO to the $0.5MoO_3-0.5P_2O_5$ composition raises glass density due to improved cohesion and more covalent bonds [13].

The study investigates glass network cross-linking through molar volume analysis. This decrease in V_m due to the addition of PbO oxide is confirmed by several studies [14-15].

As shown in Figure (1), molar volume decreases with PbO content. In the glasses studied, the Mo/P ratio is fixed, while the PbO content varies. The evolution of molar volume as a function of PbO insertion in the glass matrix $MoO_3-P_2O_5$, conforms to the decrease in the fraction of ionic character ((FCI (Pb-O)=0.57) (FCI (P-O)=0.36); (FCI (Mo-O)=0.34) and ionic radius ($r(Pb^{2+})=1.21\text{\AA}$; $r(Mo^{6+})=0.41\text{\AA}$; $r(P^{5+})=0.17\text{\AA}$). As a result, the decrease in molar volume in glass is due to the larger ionic radius of lead.

In this section, the measured mass loss method, or leached element release method [16], was utilized to assess the dissolution rate of glasses, with the results illustrated in figure (2), highlighting the relationship between dissolution rate and PbO oxide content.

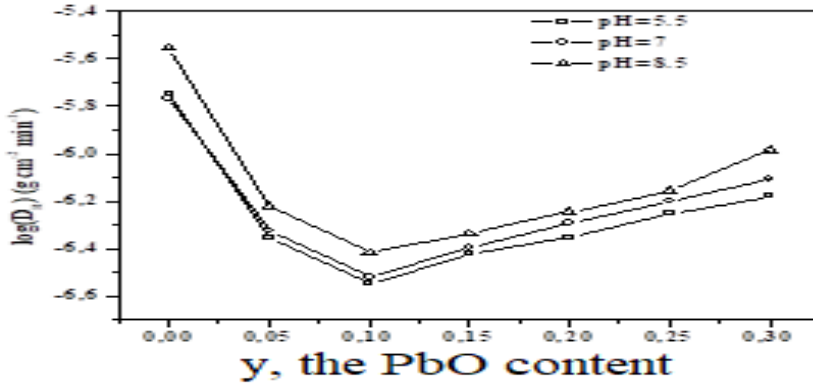
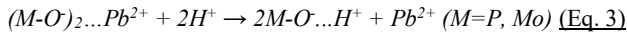


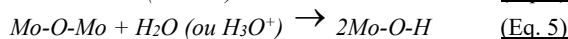
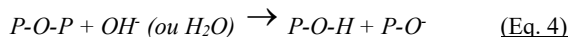
Fig. 2. Evolution of the D_R dissolution rate as a function of the PbO content of glasses $PbO-MoO_3-P_2O_5$

Figure (2) illustrates a non-proportional variation in the dissolution rate (D_R) with respect to PbO concentration. Initially, the D_R decreases to a minimum at approximately 10-15 mol% PbO, aligning with Peng's findings that PbO reduces D_R [13]. Beyond this point, additional PbO leads to an increase in D_R , highlighting the effect of PbO addition on dissolution rate across different pH levels at a constant temperature. The addition of PbO ($0.05 \leq y \leq 0.15$) reduces the dissolution rate (D_R) of $yPbO-(1-y)[0.5MoO_3-0.5P_2O_5]$ glasses at a fixed pH, whereas higher additions (above 15mol% PbO) lead to increased D_R . The dissolution rate rises as the solution's pH increases. The key distinction between binary $0.5MoO_3-0.5P_2O_5$ and ternary $yPbO-(1-y)[0.5MoO_3-0.5P_2O_5]$ glasses lies in the incorporation of PbO, suggesting their dissolution mechanisms may differ, akin to those of lead silicate glasses [17-18]. The dissolution mechanism in these glasses involves a two-stage process, starting with an ionic exchange between divalent Pb^{2+} ions and H^+ , H_3O^+ , and/or H_2O species from the solution:



The ions diffuse in opposite directions, resulting in a leachate or gel layer on the glass surface that lacks divalent Pb ions and is rich in hydrogen-bearing species. Vibrational spectroscopy confirms the formation of P-OH bonds on the glass surface [19]. The second stage involves the dissolution process, which breaks the network's formative links of P_2O_5 .

From the analysis of P_2O_5 and MoO_3 concentrations in leaching solutions, it is observed that the P/Mo ratio varies with acidity: lower in acidic conditions and higher in basic ones, indicating selective dissolution of $yPbO-(1-y)[0.5MoO_3-0.5P_2O_5]$. The selectivity is attributed to the more covalent Mo-O bond compared to Si-O, suggesting Mo atoms assume lattice-forming positions in the $PbO-MoO_3-P_2O_5$ framework. Thus, the glasses contain two oxide formers, P_2O_5 and MoO_3 , with bridging bonds such as -P-O-P-, -Mo-O-Mo-, and -P-O-Mo- [20]. The oxides exhibit acidic (P_2O_5) and basic (MoO_3) behavior, influencing the stability of P-O-P and Mo-O-Mo units under varying pH conditions.



Consequently, the selective dissolution of glasses can be explained by the occurrence of preferential bond attacks.

To clarify the dissolution mechanisms of binary glasses $MoO_3-P_2O_5$ versus ternary $PbO-MoO_3-P_2O_5$, it is noted that binary glasses primarily consist of forming cations (P^{5+} , Mo^{6+} ,

and/or Mo^{5+}) in their glass matrix. Consequently, the ion exchange reaction is excluded from their dissolution process, with the most likely reactions during dissolution being represented by equations (4) and (5).

In order to interpret the IR absorption spectra obtained from our ternary oxide glasses $\text{PbO}-\text{MoO}_3-\text{P}_2\text{O}_5$, we have compiled some information on the vibrational behaviour of the various entities that may exist in phosphate-based glasses [21-29]

IR spectra of glasses from the $y\text{PbO}-(1-y)[0.5\text{MoO}_3-0.5\text{P}_2\text{O}_5]$ ambient in the $400-4000\text{ cm}^{-1}$ are shown in figure (3). The spectrum of every glass shows several bands centred at $400-500\text{ cm}^{-1}$, 531 cm^{-1} , $690-723\text{ cm}^{-1}$, 900 cm^{-1} , 1005 cm^{-1} , 1130 cm^{-1} and 1220 cm^{-1} .

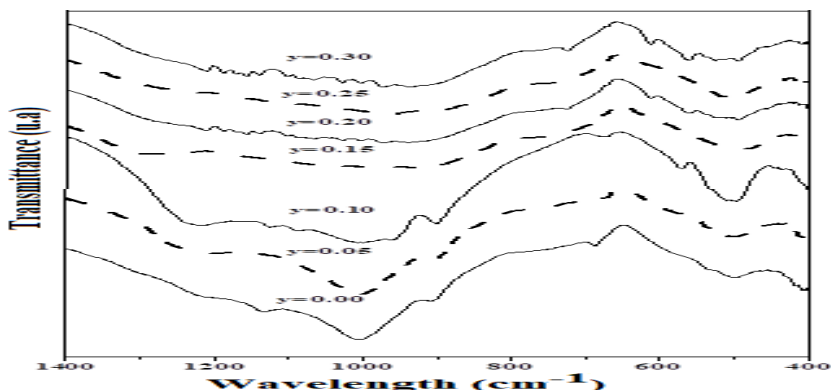


Fig. 3. IR spectra of glasses $y\text{PbO}-(1-y)[0.5\text{MoO}_3-0.5\text{P}_2\text{O}_5]$.

Based on literature data [21-29], The spectra of these glasses exhibit certain general characteristics as illustrated in Figure 3:

In the high-frequency region ($800-1400\text{ cm}^{-1}$), the main modes can be observed:

- The absence of an IR band above 1250 cm^{-1} confirms the lack of very long chains.
 - In the high-frequency region, two bands are observed at 1130 cm^{-1} and 1230 cm^{-1} , attributed to the antisymmetric elongation vibrations of $(\text{PO}_3)^{2-}$ and $(\text{PO}_2)^-$ groups, respectively.
 - Observation of a wide band split at 1000 cm^{-1} is attributed to mode ν_s , which disappears at $y=15\text{ mol}\%$.
 - In the range of $850-1050\text{ cm}^{-1}$, the strong absorption near 900 cm^{-1} is primarily due to the antisymmetric vibrational modes of P-O-P and vibrations of Mo-O bonds in MoO_6 octahedra.
- In the mid-frequency region ($300-800\text{ cm}^{-1}$), features are observed.
- In the field of $690-800\text{ cm}^{-1}$
 - The symmetrical vibrational modes of P-O-P strongly absorb around 720 cm^{-1} , potentially overlapping with the symmetrical elongation vibration mode of Mo-O bonds in MoO_4 .
 - Two centered bands at 570 and 613 cm^{-1} are not present in the glass $0.5\text{MoO}_3-0.5\text{P}_2\text{O}_5$, and their intensity increases with Pb content; these bands are attributed to the vibrations of M-O-Pb (where $M=\text{P}, \text{Mo}$).
 - The deformation modes of the phosphate lattice in glasses are observed between $480-550\text{ cm}^{-1}$, with contributions from the deformation of the phosphate lattice ($\delta(\text{PO}_4)$) and possibly from MoO_4 octahedrons, with intensity decreasing as PbO increases.
 - The observation of a $400-480\text{ cm}^{-1}$ peak, which vanishes upon adding PbO, is linked to the deformation mode $\delta(\text{MoO}_6)$.

Comparison of the dissolution rates of glass with and without divalent oxide PbO indicates that the dissolution rate (D_R) of pure glass is significantly higher than that of glass containing PbO. The incorporation of Pb^{2+} cations into the glass matrix results in a denser cross-linking of phosphate units (PO_4), leading to a reduced dissolution rate. Pb^{2+} facilitates the formation of stronger cross-links between phosphate chains, effectively chelating the metal ions within

the structure, as previously reported by Van Wazer [30]. Irregular change in D_R with increasing cation content Pb^{2+} suggests that there are parameters other than molar volume, such as the rigidity of the structure responsible for the change in the D_R .

IR spectroscopy indicates that the glass ($y=0$) contains metaphosphate units that connect with two neighboring phosphate groups, forming a cross-linked structure, which is altered by the addition of PbO . The strength of the chemical bond [$(E_1 (Pb-O) = 378 \text{ KJ/mol})$; ($E_1 (Mo-O) = 607 \text{ KJ/mol}$) and ($E_1 (P-O) = 596.6 \text{ KJ/mol}$)] in glass depends on the atomic properties of the cation Pb^{2+} and especially its ionic potential (charge/ionic radius). The presence of Pb^{2+} in the $PbO-MoO_3-P_2O_5$ glass is anticipated to lower its durability (D_R). The increased durability of $PbO-MoO_3-P_2O_5$ glass over the glass with $y=0$ is due to the substitution of easily hydrated P-O-P bonds with more corrosion-resistant Pb-O-P bonds.

In this section, we will study the devitrification of oxide glasses $yPbO-(1-y)[0.67MoO_3-0.33P_2O_5]$, with key observations detailed in Table 1 from the annealing at sub-melting temperatures.

Table 1. X-ray phase identification of glasses at different temperatures: $yPbO-(1-y)[0.67MoO_3-0.33P_2O_5]$

| y | Temp. °C | Phase identification by RX | y | Temp. °C | Phase identification by RX |
|------|-----------------------|---|------|----------|---|
| 0.05 | 400 | Totally amorphous phases | 0.25 | 400 | Totally amorphous phases |
| | 520 | Merging these phases | | 520 | $Pb(MoO_2)_2(PO_4)_2$ + unidentified phases |
| 0.10 | 400 | Totally amorphous phases | | 600 | $Pb(MoO_2)_2(PO_4)_2$ + unidentified phases |
| | 520 | Merging these phases | | 650 | $Pb(MoO_2)_2(PO_4)_2$ |
| 0.15 | 400 | Totally amorphous phases | | 700 | $Pb(MoO_2)_2(PO_4)_2$ |
| | 520 | $Pb(MoO_2)_2(PO_4)_2$ + unidentified phases | 0.30 | 400 | Totally amorphous phases |
| | 600 | Merging these phases | | 520 | $Pb(MoO_2)_2(PO_4)_2$ + unidentified phases |
| 0.20 | 400 | Totally amorphous phases | | 600 | $Pb(MoO_2)_2(PO_4)_2$ + unidentified phases |
| | 520 | $Pb(MoO_2)_2(PO_4)_2$ + unidentified phases | | 650 | $Pb(MoO_2)_2(PO_4)_2$ |
| | 600 | $Pb(MoO_2)_2(PO_4)_2$ + unidentified phases | | 700 | $Pb(MoO_2)_2(PO_4)_2$ |
| | 650 | $Pb(MoO_2)_2(PO_4)_2$ | | | |
| 700 | $Pb(MoO_2)_2(PO_4)_2$ | | | | |

Analysis reveals that diffractograms of recrystallized glasses from the $PbO-MoO_3-P_2O_5$ system ($Mo/P=1$), when annealed below the melting point, particularly for lead-rich compositions, show the formation of $Pb(MoO_2)_2(PO_4)_2$. An example is illustrated in Figure (4) for the glass composition $0.3PbO-0.47MoO_3-0.23P_2O_5$.

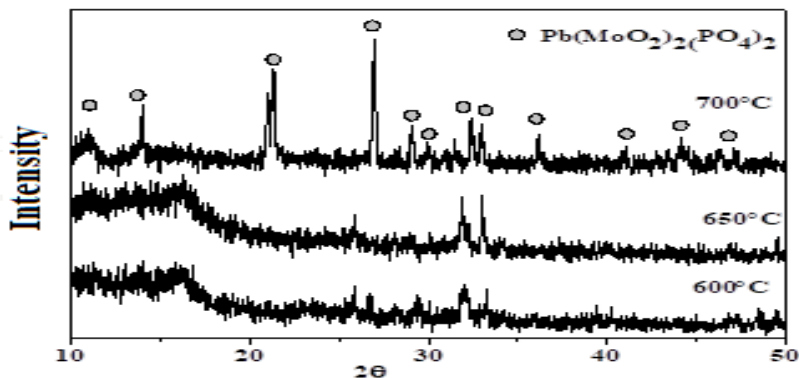


Fig. 4. Diffractograms of glass at different temperatures 0.3PbO-0.47MoO₃-0.23P₂O₅.

Table 2 shows the crystallographic data for the Pb(MoO₂)₂(PO₄)₂.

Table 2. Crystallographic data for Pb(MoO₂)₂(PO₄)₂

| | |
|-------------------------------|--|
| Formula | Pb(MoO ₂) ₂ (PO ₄) ₂ |
| Molar mass | M=653.02 g mol ⁻¹ |
| Crystalline system | Monoclinic |
| Space group | P2 ₁ /c (No. 14) |
| Mesh parameters | a=6.353 Å; b=12.28 Å; c=11.80Å; β=92.56 |
| Mesh volume | V=920.33 Å ³ |
| Group forms | Z=8 |
| Calculated density | D _c =4.713 g cm ⁻³ |
| Powder diffraction file (PDF) | 78-1655 |
| ICSD | 062832 |

The structures consist of a three-dimensional network of monophosphate groups (PO₄) and molybdenum (MoO₂), characterized by polyhedrons. The PO₄ and MoO₆ share their apices, with two oxygen atoms from each MoO₆ bonded to the molybdenum atom.

The crystallographic structure of Pb(MoO₂)₂(PO₄)₂ is monoclinic, belonging to space group P2₁/n. It features chains of PO₄ and MoO₆ groups along the a axis, creating interconnected tunnels along the c axis, forming a rigid network. The structure has two sites for molybdenum (Mo) and two sites for phosphorus (P).

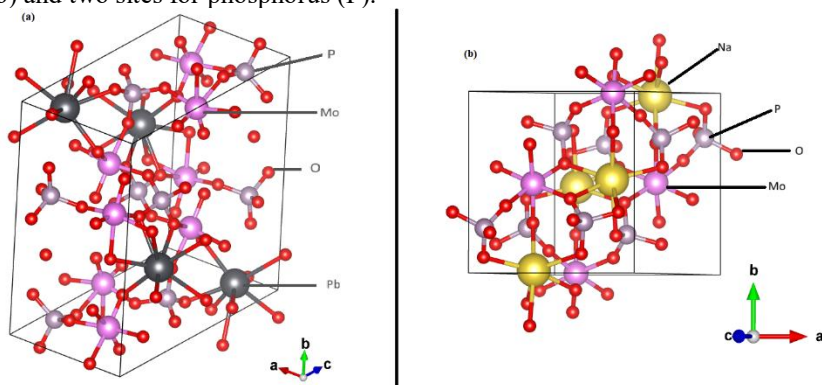


Fig. 5. Projection of the Pb(MoO₂)₂(PO₄)₂ along axis b on plane ac.

The three-dimensional structure of Pb(MoO₂)₂(PO₄)₂ monophosphate features chains of MoO₆ octahedra and PO₄ tetrahedra, located at x = 0.25 and x = 0.75. These elements are

arranged to form chains running along the *a* axis, with PO₄ tetrahedra sharing oxygen atoms with MoO₆ octahedra. The schematic representation omits phosphorus and molybdenum atoms, highlighting the tunnels formed by this framework (Fig. 5a and 5b). The structure around the Pb atom in the tunnels, occurring at $x \approx 0$, consists of eight oxygen atoms forming a deformed antiprism. This resembles the monophosphate NaMoO₂PO₄ described by Kierkegaard [1]. A comparison of the cell parameters shows that Pb(MoO₂)₂(PO₄)₂ can be aligned with NaMoO₂PO₄ ($P2_1/n$, $a = 12.08 \text{ \AA}$ [31], $b = 11.96 \text{ \AA}$ [31], $c = 6.359 \text{ \AA}$ [2], $\beta = 91^\circ 19'$ [32], $Z = 8$) where the (*a*, *c*) projection of NaMoO₂PO₄ is similar to the (*b*, *a*) projection of Pb(MoO₂)₂(PO₄)₂.

Glasses yPbO-(1-y)[0.5MoO₃-0.5P₂O₅] annealed below melting temperatures show specific characteristics based on the annealing conditions:

- At 400 °C, there is no change in glass particle size or color observed.
- At 600 °C, Glasses with compositions greater than 15 mol% melt, whereas those with compositions of 15 mol% or lower exhibit different properties.
- At 640 °C, glasses with compositions of 10 and 15 mol% melt, whereas the glass with a composition of 5 mol% remains amorphous.
- At 660 °C, glass with a composition of 5 mol% begins to melt, accompanied by a change in color.

Glass from the PbO-MoO₃-P₂O₅ (Mo/P=0.5) retains its amorphous character until melting.

4 Conclusion

All results from this study on PbO-MoO₃-P₂O₅ glasses lead to conclusive insights:

- Glasses yPbO-(1-y)[0.5MoO₃-0.5P₂O₅] exhibit a variety of phosphate and molybdate units. IR spectra indicate that the O/P ratio significantly influences the phosphate chain length, with MoO₃ units playing a key role in the structural network. This leads to depolymerization of phosphate units, which reduces V_m , increases density, and enhances chemical durability. The addition of PbO delocalizes the P=O bond, increases glass network cross-linking, reduces mobility, and strengthens the molybdenum phosphate glass network through stronger P-O-Pb bonds, replacing weaker P-O-P bonds.
- Results from the chemical durability study of glasses yPbO-(1-y)[0.5MoO₃-0.5P₂O₅] indicate that substituting PbO enhances the chemical durability of molybdenum phosphate glasses, particularly with small additions ($0.05 \leq y \leq 0.15$). The dissolution rate is primarily influenced by the glass network's cross-linking, while the dissolution mechanism involves simultaneous hydration reactions of anions and cations, leading to their release into solution.
- Molybdenum in the PbO-MoO₃-P₂O₅ glasses exhibits two coordination types: MoO₄ (dominant) and MoO₆ [33].
- X-ray diffraction crystallography of PbO-MoO₃-P₂O₅ glasses (Mo/P=1) with high PbO content ($y \geq 15 \text{ mol\%}$) has identified a new monoclinic material, Pb(MoO₂)₂(PO₄)₂, characterized by an open framework and lack of symmetry center. In contrast, glasses with low PbO concentration ($y < 15 \text{ mol\%}$) remain amorphous until melting.
- Glasses PbO-MoO₃-P₂O₅ (Mo/P=0.5) maintain their amorphous structure until melted.
- Glass is defined as an amorphous material with a glass transition temperature (T_g), no crystallization temperature (T_c), and maintains its amorphous nature despite annealing during devitrification.

References

1. P. Kierkegaard, Crystal structure of NaWO₂PO₄ and NaMoO₂PO₄, Ark. Kemi, **18**, 553 (1962). DOI: [https://doi.org/10.1016/0022-4596\(85\)90229-4](https://doi.org/10.1016/0022-4596(85)90229-4).

2. P. Kierkegaard and M. Westerlund, The crystal structure of MoOPO₄, *Acta Chem. Scand.*, **18**, 2217 (1964). DOI : [10.3891/acta.chem.scand.18-2217](https://doi.org/10.3891/acta.chem.scand.18-2217).
3. C. Gueho, M. M. Borel, A. Grandin, A. Leclaire, and B. Raveau, A Mo (V) monophosphate with an intersecting tunnel structure: K₂Mo₂P₂O₁₁, *J. Solid State Chem.*, **104**, 202 (1993). DOI: <https://doi.org/10.1006/jssc.1993.1154>.
4. T. Hoareau, A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, A mixed valent molybdenum monophosphate with a layer structure: CsMo₂O₃(PO₄)₂, *J. Solid State Chem.*, **116**, 87 (1995). DOI: <https://doi.org/10.1006/jssc.1995.1186>
5. M. M. Borel, J. Chardon, A. Leclaire, A. Grandin, and B. Raveau, A molybdenum (V) monophosphate with a layer structure, BaMo₄O₈(PO₄)₂, *J. Solid State Chem.*, **112**, 317 (1994). DOI: <https://doi.org/10.1006/jssc.1994.1311>.
6. S. Ledain, A. Leclaire, M. M. Borel, J. Provost, and B. Raveau, A Mo (V) monophosphate with a chain-like structure: Ba₃Mo₂O₂(PO₄)₄, *J. Solid State Chem.*, **125**, 147 (1996). DOI: <https://doi.org/10.1006/jssc.1996.0277>.
7. L. Abbas, L. Bih, A. Nadiri, Y. E. Amraoui, H. Khemakhem, D. Mezzane, Chemical durability of MoO₃-P₂O₅ and K₂O-MoO₃-P₂O₅ glasses, *Journal of thermal analysis and calorimetry*, **453**, 90 (2007). DOI:[10.1007/s10973-006-7673-4](https://doi.org/10.1007/s10973-006-7673-4).
8. E. K. Chamberlain, M. A. Rao, Effect of concentration on rheological properties of acid-hydrolyzed amylopectin solutions, *Food Hydrocolloids*, **14** (2) 163 (2000). DOI: [https://doi.org/10.1016/S0268-005X\(99\)00063-6](https://doi.org/10.1016/S0268-005X(99)00063-6)
9. M. B. Volf, "Mathematical approach to glass ", *Glass Sciences and Technology* 9, Ed Elsevier, Amsterdam, (1988), <https://lcn.loc.gov/87015703>.
10. T. Cardinal, Nonlinear optical properties of titanium or niobium borophosphate glasses, Thèse, Université de Bordeaux I, 1997.
11. L. Koudelka, P. Mošner, M. Zeyer, C. Jäger, Structure and properties of mixed sodium-lead borophosphate glasses, *J. of Non-Cryst. Solids*, **351**, 1039 (2005). DOI. <https://doi.org/10.1016/j.jnoncrysol.2005.01.015>
12. E. Mansour, Mixed alkali effect in quaternary K₂O-Li₂O-BaO-B₂O₃ glasses containing V₂O₅, *Physica B : Condensed Matter*, **88**, 362 (2005). DOI : <https://doi.org/10.1016/j.physb.2005.01.479>.
13. Y. B. Peng and D. E. Day, High thermal expansion phosphate glasses. Part 1, *Glass Technol.*, **32**(5), 166 (1991).
14. A. Elhadrami, Study of storage conditions of lead and cadmium into zinc-metaphosphate glass matrix; Thèse d'état, Université Cady Ayyad, Marrakech, 2002.
15. L. Koudelka , J. Subčík ; P. Mošner , Glass-forming ability and structure of glasses in the ZnO-WO₃-P₂O₅ system, *J. of Glass Science and Technology* , **53**(3), 79 (2012).
16. P. Baillif and J. C. Touray, Chemical behavior of aluminum and phosphorus during dissolution of glass fibers in physiological saline solutions, *Environmental health perspectives*, **102**(5), 77 (1994). <https://doi.org/10.1289/ehp.94102s577>.
17. M. Christopher , D. Towill, An integrated model for the design of agile supply chains, *Journal of Physical Distribution & Logistics*, **31**(4), 235 (2001). <https://doi.org/10.1108/09600030110394914>.
18. H. Darwish, Investigation of the durability of sodium calcium aluminum borosilicate glass containing different additives, *Materials Chemistry and Physics*, **69** (1-3), 36 (2001). [https://doi.org/10.1016/S0254-0584\(00\)00295-9](https://doi.org/10.1016/S0254-0584(00)00295-9).

19. N. Mouhsine, L. Bih, N. Allali, A. Nadiri, A. Yacoubi, M. Haddad, M. Danot, Elaboration and characterization of glassy cobalt phosphomolybdates, *Solid State Sciences*, **5**, 669 (2003). DOI: [https://doi.org/10.1016/S1293-2558\(03\)00017-7](https://doi.org/10.1016/S1293-2558(03)00017-7).
20. Y. Zhang, Electronegativities of elements in valence states and their applications. 1. Electronegativities of elements in valence states, *Inorg. Chem.*, **21**, 3886 (1982). DOI: <https://doi.org/10.1021/ic00141a005>.
21. A. Belkébir, J. Rocha, AP. Esculcas, P. Berthet, Structural characterization of glassy phases in the system $\text{Na}_2\text{O}-\text{Ga}_2\text{O}_3-\text{P}_2\text{O}_5$ by MAS-NMR, EXAFS and vibrational spectroscopy. I. Cations coordination, *Acta Part A*, **56(3)**, 423 (2000). [https://doi.org/10.1016/S1386-1425\(99\)00279-6](https://doi.org/10.1016/S1386-1425(99)00279-6).
22. S. Muthupari and K. J. Rao, Thermal and infrared spectroscopic studies of binary $\text{MO}_3-\text{P}_2\text{O}_5$ and ternary $\text{Na}_2\text{O}-\text{MO}_3-\text{P}_2\text{O}_5$ ($M = \text{Mo}$ or W) glasses, *J. Phys. Chem. Solids*, **57(5)**, 553 (1996). [https://doi.org/10.1016/0022-3697\(95\)00298-7](https://doi.org/10.1016/0022-3697(95)00298-7).
23. T. Minami, Infrared spectra and structure of superionic conducting glasses in the system $\text{AgI}-\text{Ag}_2\text{O}-\text{MoO}_3$, *J. Non-cryst. Solids*, **29(3)**, 389 (1978). [https://doi.org/10.1016/0022-3093\(78\)90159-X](https://doi.org/10.1016/0022-3093(78)90159-X).
24. S. V. Stefanovsky, O. I. Stefanovsky, M. I Kadyko, FTIR and Raman spectroscopic study of sodium aluminophosphate and sodium aluminum-iron phosphate glasses containing uranium oxides, *J Non-Cryst Solids*, **443**, 192 (2016). <https://doi.org/10.1016/j.jnoncrysol.2016.04.031>.
25. S. V. Pershina, B. D. Antonov, I. I. Leonidov, Effect of MoO_3 on structural, thermal and transport properties of lithium phosphate glasses, *J Non-Cryst Solids*, **569**, 120944 (2021). <https://doi.org/10.1016/j.jnoncrysol.2021.120944>.
26. S. H. Santagneli, J. Ren, M. T. Rinke, S. J. Ribeiro, Y. Messaddeq, & H. Eckert, Structural studies of $\text{AgPO}_3-\text{MoO}_3$ glasses using solid state NMR and vibrational spectroscopies, *J. Non-Cryst Solids*, **358(6-7)**, 985 (2012). <https://doi.org/10.1016/j.jnoncrysol.2012.01.031>.
27. D. F. Toy, *The Chemistry of Phosphorus: Pergamon Texts in Inorganic Chemistry*, Volume 3, Elsevier, (2016).
28. LY. Zhang, H. Li, LL. Hu, Statistical structure analysis of GeO_2 modified Yb^{3+} : Phosphate glasses based on Raman and FTIR study, *J Alloys Compd*, **698**, 103 (2017). <https://doi.org/10.1016/j.jallcom.2016.12.175>.
29. K. Bodiang, Effects of molybdenum in phosphate glasses: structure-property relationships, Thèse d'état, (Doctoral dissertation, Université de Lille (2018-2021)) 2019.
30. J. R. Van Wazer, « Phosphorus and its compound », vol. 1, Interscience, New York, 1958, <https://lccn.loc.gov/58010100>, <https://catalog.hathitrust.org/Record/001113621>.
31. P. Kierkegaard. Studies on some oxide compounds of phosphorus and molybdenum or wolfram (Doctoral dissertation, Kungl. Svenska Vetenskapsakademien) (1962).
32. G. Bukhalova, Phase diagram of the system $\text{Pb}(\text{PO sub 3})\text{ sub 2}-\text{MoO sub 3}$. *Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialy*, **18(6)**, 1057 (1982).
33. J. Swenson, A. Matic, A. Brodin, L. Bfrjesson, W.S. Howells, Structure of mixed alkali phosphate glasses by neutron diffraction and Raman spectroscopy, *Phys. Rev. B*, **58(17)**, 11331 (1998). DOI: <https://doi.org/10.1103/PhysRevB.58.11331>.