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Tuning the Structure and Properties of Potassium-Niobium Phosphate Glasses: A Deep Dive into Thermal and Chemical Behavior

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ABSTRACT

Phosphate glasses in the K_2O-Nb_2O_5-P_2O_5 ternary system were synthesized using the melt-quenching method with precursors K_2CO_3, Nb_2O_5, and $NH_4H_2PO_4$. X-ray diffraction (XRD) confirmed the amorphous nature of the glasses. The density of the glasses increased with Nb_2O_5 content, while the molar volume decreased, indicating a denser glass structure. Differential scanning calorimetry (DSC) showed that the glass transition temperature (T_g) rose with increasing Nb_2O_5 content, implying a stiffer glass network. Fourier transform infrared (FTIR) spectroscopy revealed that the addition of Nb_2O_5 alters the phosphate glass network by promoting the formation of pyrophosphate groups and P-O-Nb bonds, which result in the depolymerization of the glass structure. The chemical durability of the glasses was evaluated by monitoring pH changes in distilled water over time, demonstrating that higher Nb_2O_5 content improved resistance to dissolution. These findings suggest that niobium oxide significantly enhances both the structural integrity and chemical durability of phosphate glasses, making them suitable for applications requiring high-density and durable glass materials.

1. Introduction

Phosphate glasses exhibit diverse structural and thermal properties, which can be tailored by the addition of various oxides. Research has explored their structural characteristics and thermal stability, such as potassium-calcium systems [1] and the effects of molybdenum oxide and alumina [2,3]. Studies have also addressed the optical and dielectric properties of tantalum and bismuth phosphate glasses [4], as well as the role of Li_2O/K_2O ratios and iron oxide [5]. Recently, UV-Vis spectroscopy provided insights into the optical properties of Al_2O_3-containing phosphate glasses [6].

Phosphate glasses containing niobium oxide (Nb_2O_5) have garnered significant attention due to their potential applications in various fields, ranging from optics to biomedical uses. These glasses are of interest as hosts for rare-earth ions in laser applications and as matrices for radioactive waste encapsulation. Niobium also plays a vital role in bioactive glasses, as Nb^{5+} ions have been reported to enhance bone calcification and osteoblast differentiation, making them promising candidates for bone regeneration materials [7,8].

In particular, the addition of niobium to phosphate glasses has been shown to substantially alter their physical, thermal, and structural properties. Studies on several glass systems, such as Li_2O-Nb_2O_5-CaO-P_2O_5 [9], BaO-Nb_2O_5-P_2O_5 [10], and ZnO-Nb_2O_5-P_2O_5 [8], have highlighted the dual role of niobium as both a glass network former and modifier. The incorporation of niobium leads to the formation of NbO_6 octahedral units, which interact with phosphate chains, resulting in increased cross-linking and rigidity within the glass matrix [11]. This structural evolution is often accompanied by improvements in chemical durability and modifications in optical and electrical properties, making niobium-containing glasses versatile materials for advanced technological applications.

Moreover, the introduction of Nb_2O_5 into these glass systems has been shown to enhance ion conduction, particularly in lithium-based glasses, and improve the thermal stability of the glass network [9]. In addition, niobium's role in improving chemical durability has been widely documented, particularly in systems where Nb-O-P bonds contribute to a more stable network. This study investigates the influence of niobium oxide on the structural, thermal, and chemical properties of K_2O-Nb_2O_5-P_2O_5 phosphate glasses. By varying Nb_2O_5 content, we aim to enhance the understanding of its effects, with a focus on potential technological applications.

2. Materials and Methods

2.1. *Glass preparation*

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The synthesis of glasses in the K_2O-Nb_2O_5-P_2O_5 ternary system was carried out using stoichiometric mixtures of potassium carbonate K_2CO_3, niobium oxide Nb_2O_5, and ammonium dihydrogen phosphate $NH_4H_2PO_4$ according to the reaction:

$$xK_2CO_3 + yNb_2O_5 + 2zNH_4H_2PO_4 \rightarrow [xK_2O\text{-}yNb_2O_5\text{-}zP_2O_5] + 2zNH_3\uparrow + 2zH_2O\uparrow + xCO_2\uparrow$$

The starting materials were carefully ground in a quartz mortar to ensure a homogeneous mixture. The prepared blend was then transferred to a porcelain crucible and subjected to precise thermal processing. Preheating at 120°C overnight facilitated the removal of residual moisture, while subsequent heating to 400°C effectively released volatile compounds, including ammonia and carbon dioxide. The mixture was gradually heated to 950°C, with intermittent grinding to maintain homogeneity. The molten product was rapidly quenched in air, a crucial step to ensure glass formation. The resulting glasses were systematically stored in a desiccator to prevent moisture uptake before analysis.

2.2. *Phosphate glasses characterization*

2.2. *1. X-ray diffraction*

X-ray diffraction (XRD) analysis was employed to verify the amorphous nature of the synthesized glass samples. The diffraction patterns were recorded using a Siemens D5000 diffractometer equipped with Cu_λ radiation (λ = 1.5418 Å). Data were collected over a 2θ range of 10° to 70° at a scanning rate of 2° per minute, with all measurements performed at room temperature.

2.2. *2. Density and molar volume*

The density of the synthesized glass samples was measured at room temperature using the Archimedes method, with diethyl phthalate as the immersion liquid. The density (ρ) was calculated using the following equation:

$$\rho = \frac{W_a . \rho_b}{W_a - W_b}$$

…..Where W_a and W_b represent the weight of the glass sample in air and in the immersion liquid, respectively, and ρ_b is the density of the immersion liquid. The difference $(W_a - W_b)$ corresponds to the buoyant force acting on the sample.

The molar volume (V_m) for each glass sample was determined from the density (ρ) and the molecular weight (M) using the equation:

$$V_m = \frac{M}{\rho}$$

2.2. *3. DSC study*

Differential scanning calorimetry (DSC) was used to determine the glass transition temperature (T_g) of the samples. The analysis was carried out using a DSC-SETRAM 121 apparatus, with a heating rate of 10°C/min. The measurements have an estimated error margin of ±5°C.

2.2. *4. Fourier transform infrared spectroscopy (FTIR)*

Fourier Transform Infrared Spectroscopy (FTIR) was employed to investigate the structural phases of the phosphate glasses. The spectra were recorded using a Jasco 4600 FT/IR spectrometer, with a frequency range spanning from 4000 to 400 cm^{-1} and a resolution of 4 cm^{-1}, providing detailed insights into the glass network's vibrational modes.

2.2. *5. Chemical durability*

The chemical durability of phosphate glasses in aqueous environments has been less studied than that of silicate glasses, and the mechanisms behind phosphate glass dissolution remain debated [12,13].

Dissolution occurs via two primary reactions:

- Hydration, where network-modifying cations (K^+, Na^+) exchange with H^+ ions from the solution.
- Hydrolysis of P-O-P bonds.

This study tracks pH changes over time as an indicator of dissolution. Experiments were conducted at ambient temperature using distilled water (pH = 6.74) as the solution. The dissolution was monitored at 24 hours, 7 days, 22 days, and 30 days.

3. Results and discussion

Table 1 presents the composition, density (ρ), molar volume (V_m), and glass transition temperature (T_g) of these samples. The results indicate that with increasing Nb_2O_5 content, both the density (ρ) and glass transition temperature (T_g) show a significant increase, while the molar volume (V_m) progressively decreases.

3.1. *X-ray diffraction*

The XRD diagrams of the synthesized compositions, of (60-x/2)K_2O-xNb_2O_5-(40-x/2)P_2O_5 glassy system (where x=7.5, 10, 12.5, and 15 mol%), illustrate a broad boss between 20° and 40° (2 Theta) with the absence of any sharp peaks confirming, therefore, the amorphous nature of these glassy phosphates (Fig. 1).

Table 1

Glasses composition (mol %), density ρ ($g.cm^{-3}$), molar volume V_m ($cm^3.mol^{-1}$) and glass transition temperature T_g (°C) of (60-x/2)K_2O-xNb_2O_5-(40-x/2)P_2O_5 glassy system (where x=7.5, 10, 12.5, and 15 mol%).

Glasses	Batch composition			ρ	V_m	T_g
	P_2O_5	K_2O	Nb_2O_5			
Nb7.5	36.25	56.25	7.5	2.578	48.24	360
Nb10	35	55	10	2.620	48.87	395
Nb12.5	33.75	53.75	12.5	2.712	48.58	408
Nb15	32.5	52.5	15	2.833	47.86	428

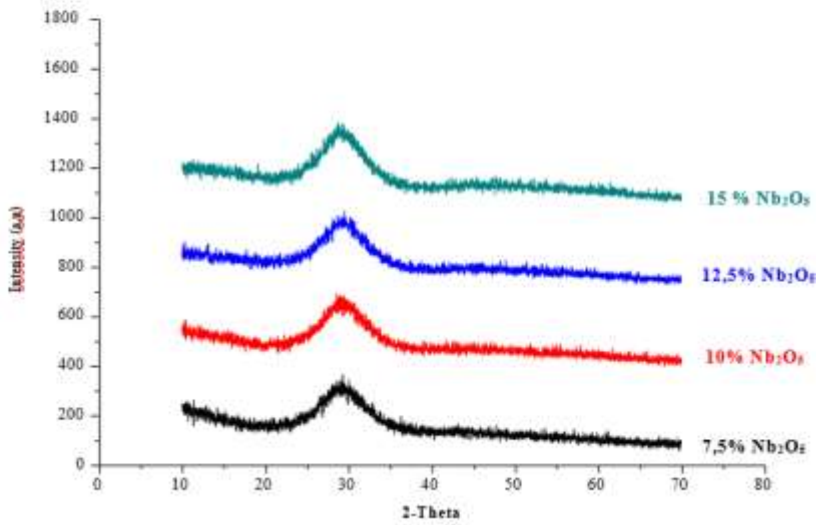

Fig. 1. X-ray diffraction patterns for the compositions studied of (60-x/2)K_2O-xNb_2O_5-(40-x/2)P_2O_5 glassy system (where x=7.5, 10, 12.5, and 15 mol%).

3.2. *Density and molar volume*

Density is a fundamental parameter that provides insights into the structural compactness of glass networks. Both density (ρ) and molar volume (V_m) are influenced by several factors, including atomic structure, coordination number, cross-linking density, and the size of interstitial spaces.

The molar volume (V_m) was calculated from the density (ρ) and molar mass (M) using the relation: $V_m = \frac{M}{\rho}$.

Density measurements were taken with an uncertainty of ±0.4 g/cm³. The results, presented in Table 1 and plotted in Fig. 2 reveals significant compositional dependencies.

The glass density increases with the substitution of potassium and phosphorus by niobium, while the molar volume decreases progressively. This trend can be attributed to the replacement of the lighter elements K and P with the heavier Nb, which leads to a denser packing of the glass matrix. The incorporation of Nb ions strengthens the glass network by forming Nb-O bonds, which are more covalent in nature, thereby reducing the available free volume. These results suggest that Nb not only increases the structural compactness but also plays a critical role in reinforcing the network's rigidity, as observed in other glass systems [14].

Interestingly, Fig. 2 (b) shows a slight increase in molar volume when the Nb_2O_5 content reaches between 7.5% and 10%. This deviation could be explained by the unique dual functionality of Nb^{5+} ions, which can act both as network formers and modifiers, disrupting the glass network to some extent at higher concentrations, resulting in a slight expansion of the molar volume.

When the Nb_2O_5 content exceeds 10%, the molar volume decreases, highlighting the compaction of the oxygen ion network within the glass structure.

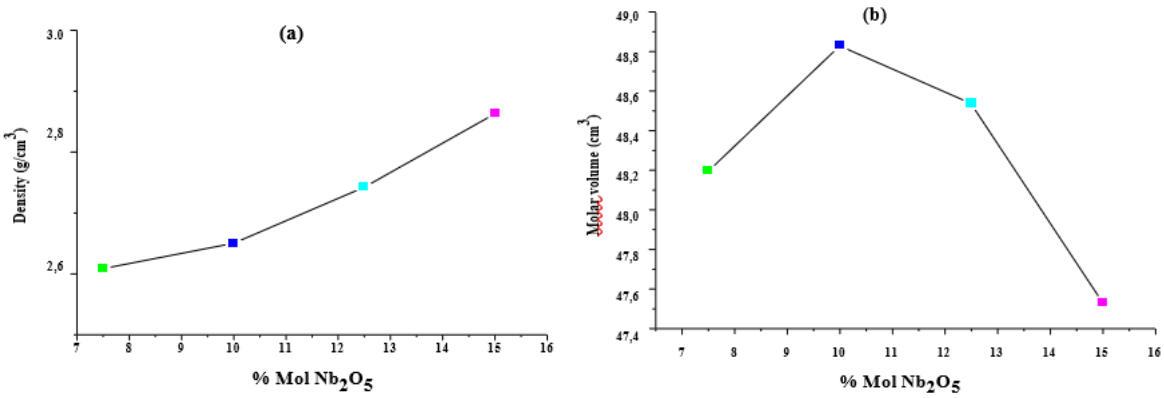

Fig. 2. Density and molar volume as function of Nb_2O_5 content of (60-x/2)K_2O-xNb_2O_5-(40-x/2)P_2O_5 glasses.

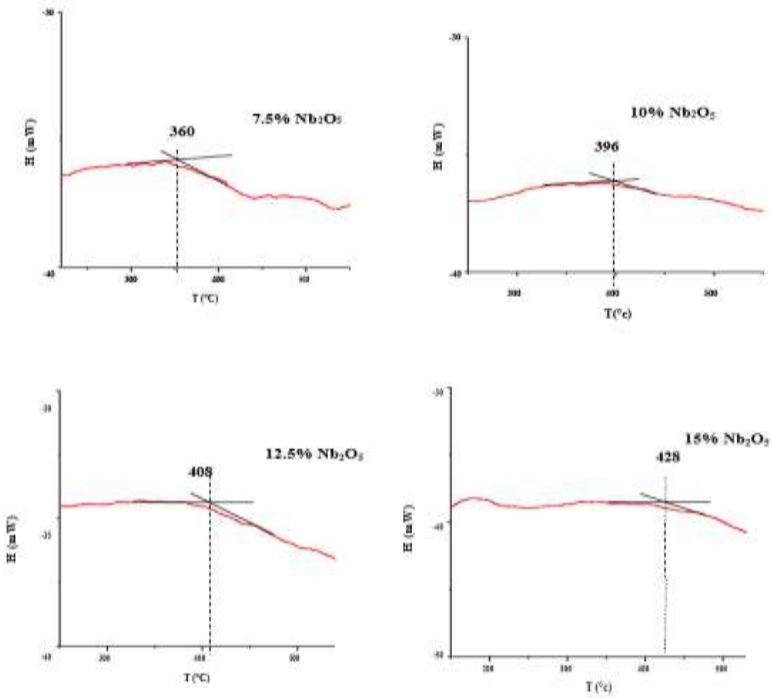

Fig. 3. DSC thermograms of the glasses with the four synthesized compositions of $(60 - x/2)K_2O - xNb_2O_5 - (40 - x/2)P_2O_5$.

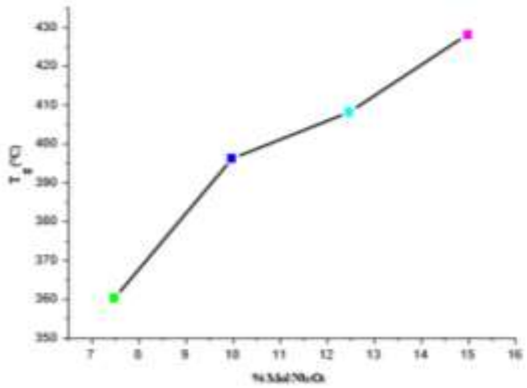

Fig. 4. Variation of T_g as a function of Nb_2O_5 content.

3.4. *FTIR spectroscopy study*

Fig. 5 presents the IR spectra of glasses with the composition $(60 - x/2)K_2O - xNb_2O_5 - (40 - x/2)P_2O_5$ ($7.5 \leq x \leq 15$ mol%), recorded in the frequency range between 400 and 1400 cm^{-1}. The vibrational frequencies and their corresponding assignments are summarized in Table 2.

The spectra of these glasses closely resemble those of potassium metaphosphate glasses, as observed in earlier studies. Key vibrational features include:

- The symmetric vibration of PO_2 groups, typically found at 1160 cm^{-1} ($\nu_s PO_2$) [15].
- The antisymmetric and symmetric vibrations of end-chain PO_3 groups, appearing at 1060 cm^{-1} ($\nu_{as} PO_3$) and 960 cm^{-1} ($\nu_s PO_3$) [16].
- The two distinct antisymmetric and symmetric bands characteristic of P–O–P linkages at 865 cm^{-1} (ν_{as}POP) [17] and 690 cm^{-1} (ν_sPOP) [18].
- The deformation mode of phosphate groups $P{-}O^-$ (δPO_3^-) near 520 cm^{-1} [15,16,19].

Adding Nb_2O_5 to the $60K_2O$-$40P_2O_5$ glass matrix significantly alters the vibrational landscape. Notably, the symmetric vibration band of PO_2 disappears, and the intensity of both antisymmetric ($\nu_{as} PO_3$) and symmetric ($\nu_s PO_3$) PO_3 end-chain groups diminishes. This behavior is attributed to increased non-bridging oxygens (NBOs) within the glass network and the incorporation of cross-linking P–O–Nb bonds.

The persistence of ν_{as} (PO_3) alongside the absence of $\nu_{as}(PO_2)$ [56] suggests the depolymerization of phosphate chains as Nb^{5+} ions are introduced. This also indicates a shift away from metaphosphate chains in these glasses [20].

Moreover, the presence of asymmetric and symmetric ν_{as}POP and ν_sPOP bands, which appear bent and non-linear, provides strong evidence for the existence of pyrophosphate groups.

Overall, the incorporation of Nb_2O_5 modifies the glass structure by depolymerizing the phosphate chains and promoting the formation of pyrophosphate groups, enhancing the cross-linking within the glass network. This structural evolution results from the interplay between non-bridging oxygens and P–O–Nb bonds, fundamentally altering the vibrational modes observed in the spectra.

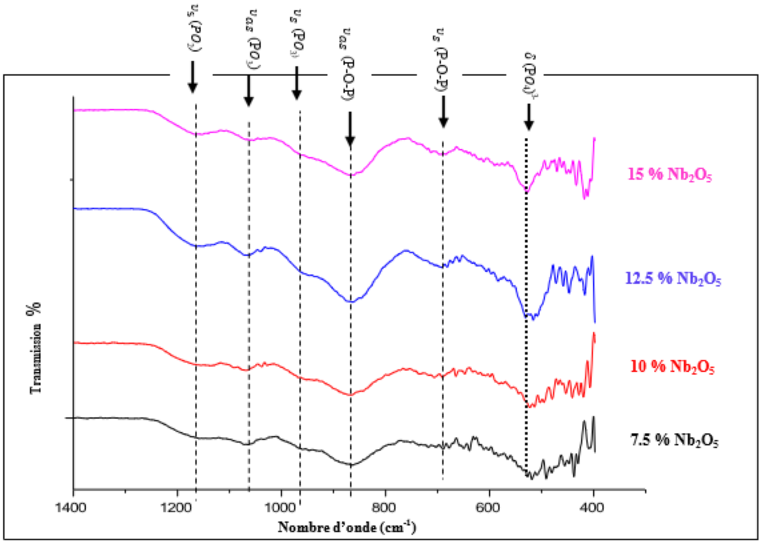

Fig.4. FTIR spectra of the glasses with the four synthesized compositions of $(60 - x/2)K_2O - xNb_2O_5 - (40 - x/2)P_2O_5$.

Table 2.
Frequency and assignment of FTIR bands for glasses with the composition $(60 - x/2)K_2O - xNb_2O_5 - (40 - x/2)P_2O_5$.

Compositions (mol %)	**x=7.5**	**x=10**	**x=12.5**	**x=15**	**Attributions**
Frequencies (cm^{-1})	517	520	523	526	$(\delta PO^{3-})_4$
	689	689	687	689	υ_s (P-O-P)
	868	866	871	865	υ_{as} (P-O-P)
	960	963	967	973	υ_s (PO_3)
	1058	1066	1069	1062	υ_{as} (PO_3)
	1159	1161	1164	1168	υ_s (PO_2)

3.4. *Chemical durability study*

The study examined the four glass samples over varying leaching periods: 24 hours, 7 days, 22 days, and 30 days. The leachate solutions were left unbuffered, allowing the pH to evolve naturally over time. Final pH values for each leaching period are presented in Table 3 and plotted in Fig. 5.

Upon analyzing the results, it is clear that all the glasses exhibit similar pH behavior, regardless of the leaching duration. The pH of the leachates increases with immersion time, showing a continuous rise between 0.5 and 2 units. At longer leaching times, the pH appears to approach an asymptote, likely due to the saturation of the solution.

The pH evolution reveals a significant initial alkalization of the leachate, which occurs almost immediately upon immersion. This increase in pH is attributed to the extraction of alkali ions from the glass network, driven by ion exchange processes between hydrogen ions and mobile network ions.

This exchange leads to the accumulation of residual OH^- ions in the leachate, subsequently raising the pH of the solution. Such pH behavior has been well-documented in previous studies [21,22]. The observed alkalization is due to the interdiffusion of hydronium ions (H^+) from the solution and potassium ions (K^+) from the glass. The dissolution process of the glass is closely linked to the concentration of non-bridging oxygen (NBO) sites within the glass network.

As water molecules diffuse into the glass matrix, they become immobilized near NBO sites, initiating the formation of P-O-H^+ bonds. Simultaneously, K^+ ions diffuse out of the glass, accompanied by hydroxide (OH^-) ions at the glass-solution interface [23].

Moreover, the data shows that higher concentrations of niobium in the glass correlate with a greater final pH. This suggests enhanced interdiffusion of hydronium (H^+) ions from the solution via ion exchange mechanisms, further reinforcing the idea that niobium content plays a critical role in altering the glass network and its dissolution behavior.

This comprehensive analysis underscores the importance of NBO sites and niobium content in the leaching behavior of these phosphate-based glasses, offering valuable insights into the mechanisms of glass corrosion and ion exchange processes.

Table 3.
Final ph values of $(60 - x/2)K_2O - xNb_2O_5 - (40 - x/2)P_2O_5$ glass compositions over different leaching durations

Compositions (mol%)	Leaching durations (h)			
	24	**168**	**528**	**720**
	pH			
7.5	7.38	7.38	7.38	7.38
10	6.87	7.58	7.73	7.48
12.5	7.21	7.67	7.52	7.52
15	7.42	8.58	8.78	8.97

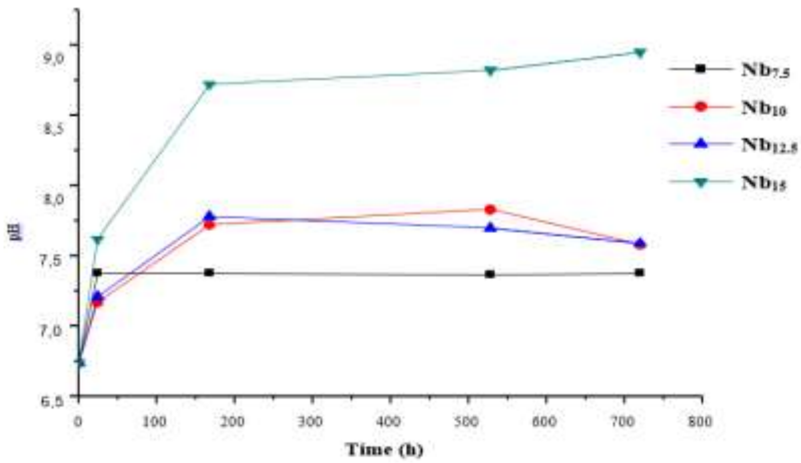

Fig. 5. *pH evolution as a function of immersion time*

4. Conclusion

The study of the K_2O-Nb_2O_5-P_2O_5 glass system revealed significant insights into the role of niobium in influencing structural and thermal properties. As the Nb_2O_5 content increased, the density of the glasses rose, while the molar volume decreased, indicating a more compact and interconnected glass network. This can be attributed to the incorporating of Nb^{5+} ions, which introduce stronger Nb-O bonds and enhance cross-linking within the phosphate glass matrix.

Differential Scanning Calorimetry (DSC) measurements demonstrated that the glass transition temperature (T_g) increases almost linearly with the addition of Nb_2O_5, ranging from 360°C at 5% mol to 428°C at 15% mol. This rise in T_g suggests that niobium enhances the rigidity of the glass network by reinforcing the connections between non-bridging oxygen atoms and cations, leading to a stronger, more resilient structure.

Infrared spectroscopy further supported the structural impact of niobium. The absence of characteristic PO_2 vibrations and the decrease in PO_3 end-group intensity indicated the depolymerization of phosphate chains, likely due to the Nb^{5+} ions cross-linking the glass matrix. The emergence of P–O–Nb bonds suggested that niobium integrates into the glass network, acting as a glass former and modifier.

Leaching experiments also revealed a correlation between Nb_2O_5 content and pH evolution. Over time, all glasses exhibited an increase in pH due to ion exchange between the glass matrix and the leachate solution, but glasses with higher niobium content showed greater final pH values. This indicates a higher inter-diffusion rate of hydronium (H^+) ions and suggests that niobium-enriched glasses are more resilient to aqueous alteration.

In summary, niobium plays a crucial role in enhancing the structural integrity, thermal stability, and chemical durability of K_2O-Nb_2O_5-P_2O_5 glasses, making these materials promising candidates for applications requiring strong, stable, and durable phosphate-based glasses.

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