Original Paper

Preparation and properties of nitrided phosphate glasses

Luis Pascual and Alicia Durán
Instituto de Cerámica y Vidrio (CSIC), Madrid (Spain)

Nitrided phosphate glasses with the composition (in mol%) of 25 R_2O · 20 BaO · 3 Al_2O_3 · 52 P_2O_5 (R = lithium, sodium, potassium) have been prepared by remelting at 650 to 800 °C in a flowing dry ammonia atmosphere. The chemical durability of the glasses increases strongly with the nitrogen addition, as well as the glass transition and dilatometric softening temperatures and microhardness; whereas the thermal expansion coefficient diminishes with rising nitrogen contents. The kinetics of nitridation and the structural changes produced by nitrogen incorporation are also studied in these glasses.

Herstellung und Eigenschaften nitridierter Phosphatgläser

Es wurden nitridierte Phosphatgläser einer molaren Zusammensetzung von 25 R_2O · 20 BaO · 3 Al_2O_3 · 52 P_2O_5 (R = Lithium, Natrium, Kalium) durch Aufschmelzen bei Temperaturen von 650 bis 800 °C in einer trockenen Ammoniakatmosphäre hergestellt. Mit der Stickstoffzugabe steigen die chemische Beständigkeit, die Transformations- und die dilatometrische Erweichungstemperatur sowie die Mikrohärte dieser Gläser deutlich an. Im Gegensatz hierzu verringert sich der Wärmeausdehnungskoeffizient mit zunehmendem Stickstoffgehalt. Die Kinetik der Nitridierung und die strukturellen Veränderungen, erzeugt durch den Einbau von Stickstoff, wird in diesen Gläsern untersucht.

1. Introduction

In recent years, oxynitride glasses have been largely studied, because of the great research activity in nitrogen ceramic and the specific properties enhanced by the presence of nitrogen in the glass network [1 to 3]. In most of these glasses nitrogen has been incorporated by melting the base composition with different nitride compounds. However, nitrided phosphate glasses have also been prepared by melting in ammonia atmosphere [4], high contents of nitrogen being incorporated in alkaline phosphate glasses [5 to 7] as well as in alkaline earth oxides containing ones [8].

In this work, phosphate glasses of the system $R_2O-BaO-Al_2O_3-P_2O_5$ (R = lithium, sodium, potassium) have been nitrided by remelting at 650 to 800 °C in dry ammonia atmosphere incorporating high contents of nitrogen to the network. The kinetics of N_2 incorporation is studied as a function of temperature and time. Moreover, changes produced by nitrogen relating to structure and to chemical, thermal and mechanical properties are also investigated.

2. Experimental

2.1. Preparation of the glasses

The base glasses, with the composition (in mol%) 25 R_2O · 20 BaO · 3 Al_2O_3 · 52 P_2O_5 (R = lithium, sodium, potassium), were prepared from reagent grade H_3PO_4, $AlPO_4$, $BaCO_3$, Li_2CO_3, Na_2CO_3 and K_2CO_3. The batches, calcined at 450 °C for 24 h, were melted at 1100 °C in a gas-fired furnace using porcelain crucibles. The glasses, quenched on brass plates in air, resulted clear and colorless. Table 1 presents the theoretical and analyzed compositions of the three glasses. SiO_2 and B_2O_3 impurities probably proceed from crucible attack.

About 10 g of each base glass were remelted in graphite crucibles in anhydrous ammonia. The powdered glasses were inserted into an air-tight tube furnace flushed with dry nitrogen to remove air. The furnace was heated up to 900 °C in N_2 atmosphere, held at this temperature for 30 min and then cooled to treatment temperature, whereupon the nitrogen was replaced with anhydrous ammonia. The melts were maintained at each chosen temperature with constant flow for different times between 3 and 44 h; at selected times the atmosphere was changed again by nitrogen, the furnace being slowly cooled to room temperature and the samples removed and annealed in air. The three base glasses were heat-treated together to ensure the same conditions for each treatment.

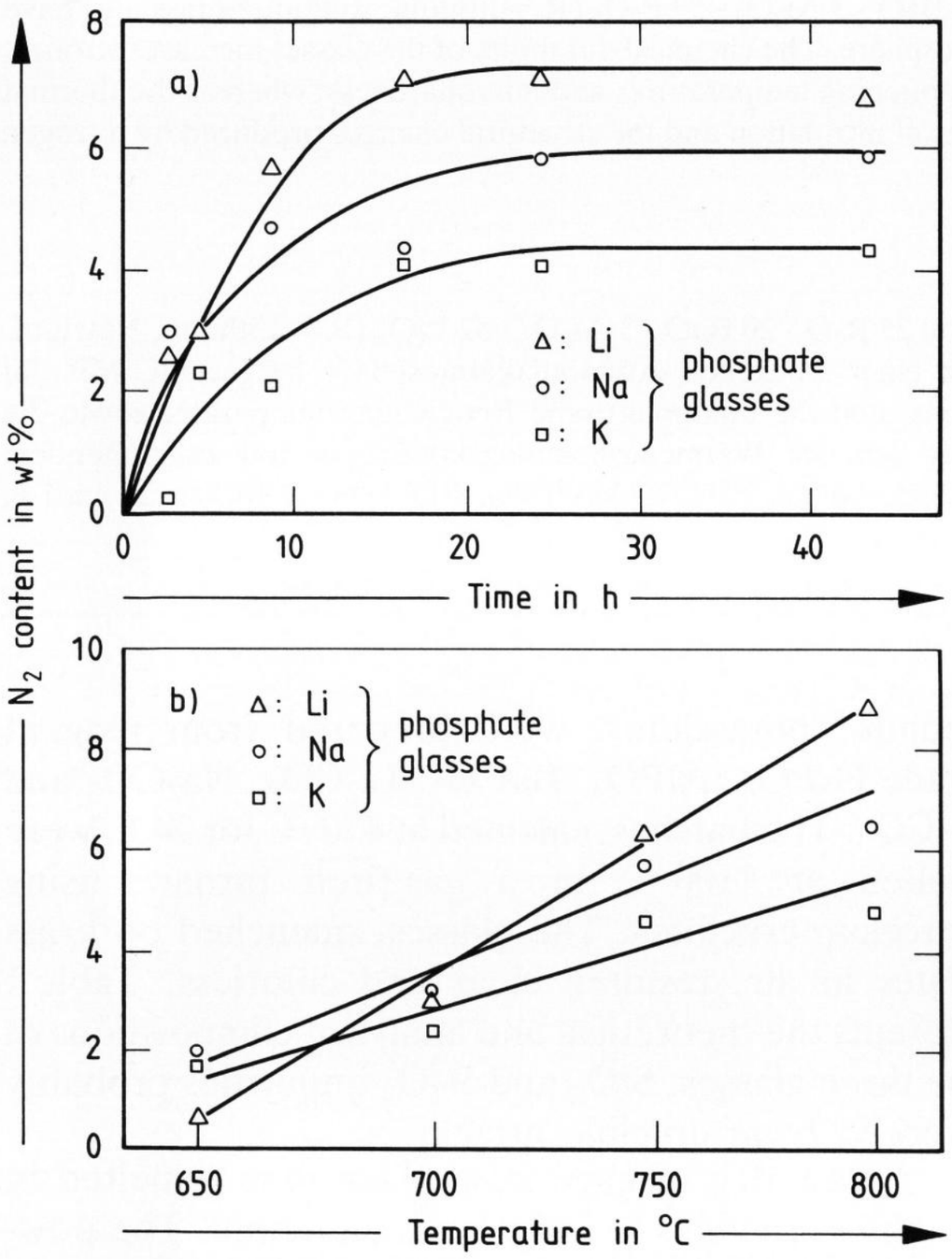
2.2. Sample characterization

After the treatments, the glasses were weighted and the nitrogen content was calculated from the weight loss, supposing that during the nitridation process three divalent oxygen ions are replaced by two

Received 31 July 1990.

Table 1. Theoretical and experimental composition of the base glasses (in mol %)

glass components	lithium phosphate glass		sodium phosphate glass		potassium phosphate glass	
	theoretical	experimental	theoretical	experimental	theoretical	experimental
P_2O_5	52	51.4	52	51.5	52	51.0
BaO	20	19.7	20	19.2	20	19.9
Al_2O_3	3	2.3	3	2.1	3	2.3
Li_2O	25	24.0	–	–	–	–
Na_2O	–	0.7	25	26.1	–	1.2
K_2O	–	0.1	–	0.1	25	24
B_2O_3	–	0.3	–	0.3	–	0.3
SiO_2	–	1.6	–	0.7	–	1.4



Figures 1a and b. Nitrogen content as a function of time (figure a) and temperature (figure b) for lithium, sodium and potassium phosphate glasses remelted for 5 h in ammonia at 700 °C with a flow rate of 350 cm^3/min.

trivalent nitrogen ones in the phosphate network. These nitrogen contents are in good agreement with those measured by inert gas fusion with a nitrogen analyzer (TC 436, Leco Co., St. Joseph, MI (USA)), as reported in [8].

The glass density, ϱ, has been measured by the Archimedes method using toluene.

The hydrolytic resistance of the glasses was measured in deionized water at 70, 80 and 98 °C using prismatic samples polished to 600-grit with silicon carbide paper and cleaned with acetone. After measuring the surface area, the samples were weighted ($\pm 10^{-4}$ g), placed into a plastic bottle filled with 100 ml deionized water and maintained at constant temperature for different times. The dissolution rate,

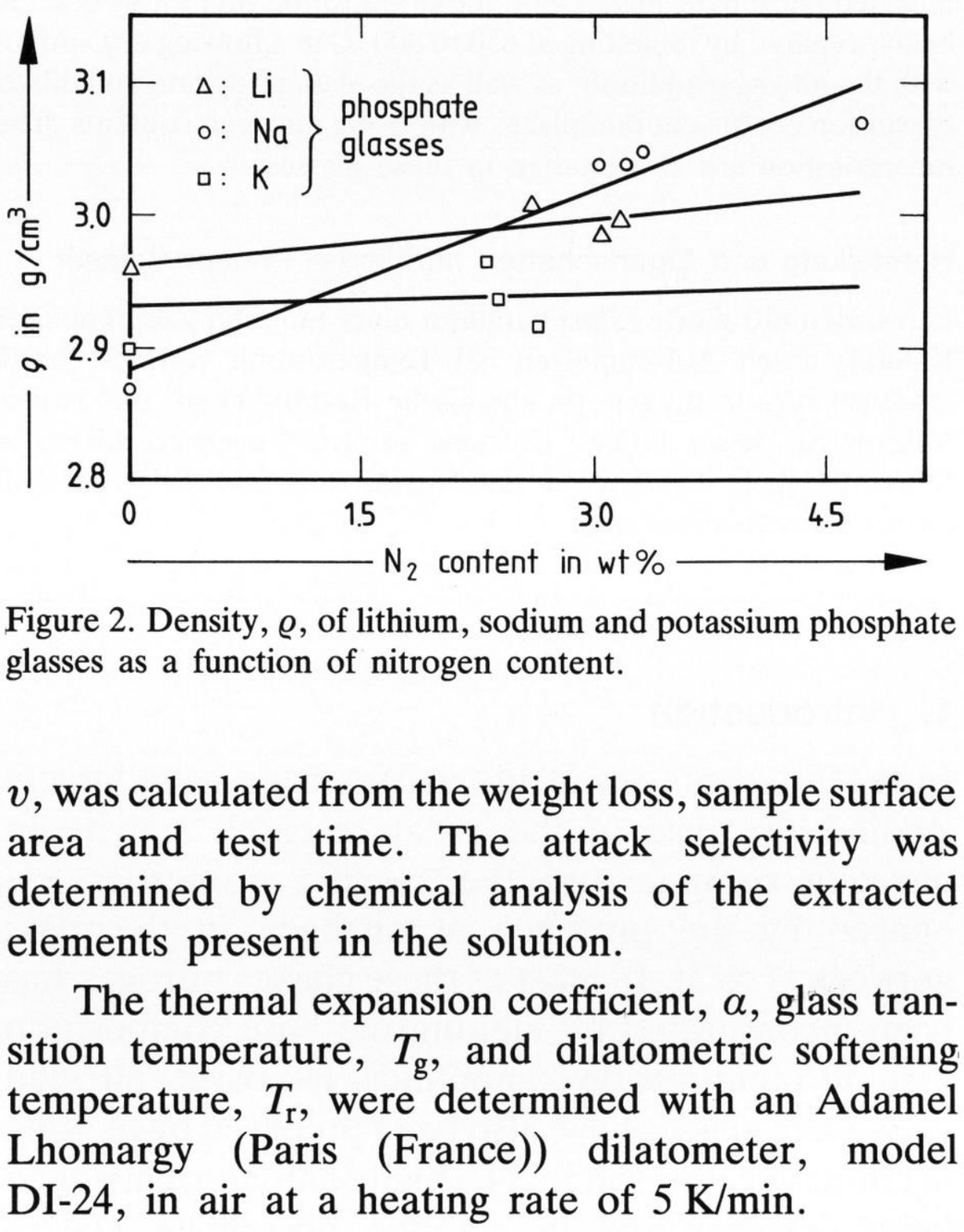


Figure 2. Density, ϱ, of lithium, sodium and potassium phosphate glasses as a function of nitrogen content.

v, was calculated from the weight loss, sample surface area and test time. The attack selectivity was determined by chemical analysis of the extracted elements present in the solution.

The thermal expansion coefficient, α, glass transition temperature, T_g, and dilatometric softening temperature, T_r, were determined with an Adamel Lhomargy (Paris (France)) dilatometer, model DI-24, in air at a heating rate of 5 K/min.

The Vickers Microhardness Number (VHN), H, was measured on plane-parallel and polished samples using a load of 1 N applied for 30 s. The VHN [2] was calculated from equation (1)

$$H = 1854.4 \cdot P/d^2 \qquad (1)$$

where P is the load in N and d the indentation diagonal in μm, averaging about 10 measurings for each sample.

The infrared transmission spectra were recorded with a Perkin Elmer 580B spectrophotometer using KBr pellets between 400 and 4000 cm^{-1}.

3. Results and discussion

3.1. Kinetics of nitridation and structural changes

The glasses obtained after the ammonia treatment were transparent and colorless; those treated at 800 °C presented a lot of bubbles probably provoked by the reduction of phosphorus to phosphine.

The kinetics of nitrogen incorporation was measured as a function of time and temperature. As expected, the nitrogen content increased with increasing time in ammonia, aiming asymptotically to a limit whose value depends on the alkaline oxide present, as shown in figure 1a. For temperature treatment at 700 °C this limit is around 7 wt% for lithium phosphate glass, 6 wt% for sodium phosphate glass and 4.5 wt% for potassium phosphate glass. These values, obtained for 24 h treatments at this temperature, did not significantly change with increasing times of treatment, which provoked, instead, formation of bubbles due to phosphorus reduction to phosphine.

Over the temperature range studied, i.e. 650 to 800 °C, the nitrogen content increased linearly with rising treatment temperature (figure 1b) following the same tendency as other phosphorus oxynitride glasses [6 and 8]. Heat treatments at temperatures higher than 750 °C often originated bubbles appearing.

These data agree with those of thermodynamic and structural compatibility which predict that the maximum nitrogen content incorporated diminishes with increasing alkali ion radius from lithium to sodium to potassium.

Theoretically, in alkali phosphate glasses the PO_4 tetrahedra are linked forming infinitely long chains [9]; actual ones have a finite length of 20 to 40 PO_4 groups since hydroxyl ions act finishing these chains. Nitrogen can enter in different ways into the phosphate structure – replacing terminating hydroxyl groups, substituting bridging and non-bridging oxygen ions or forming NO_3 groups – to increase the crosslinking of the network.

Raman, XPS and NMR spectra have shown that nitrogen mainly enters the structure as N^{3-} ions, which replace not only the bridging oxygen in the PO_4 tetrahedra but also the non-bridging double-bonded oxygen, producing an increase in the crosslinking of the structure [10 and 11]. This stiffening in the network allows to predict an enhancement of different properties in the nitrided glasses, experimentally confirmed, as it is shown in the following.

3.2. Sample properties

In figure 2 the density of nitrided phosphate glasses is depicted as a function of nitrogen content. This property increases linearly with increasing nitrogen content in the sample, as expected if nitrogen enters the structure closing the network.

The nitrogen content of the glass affects also the thermal properties, specially the glass transition and dilatometric softening temperatures, and the thermal expansion coefficient. Figure 3 shows the behavior of T_g and T_r, both temperatures increasing with nitrogen concentration. On the other hand, as illustrated in

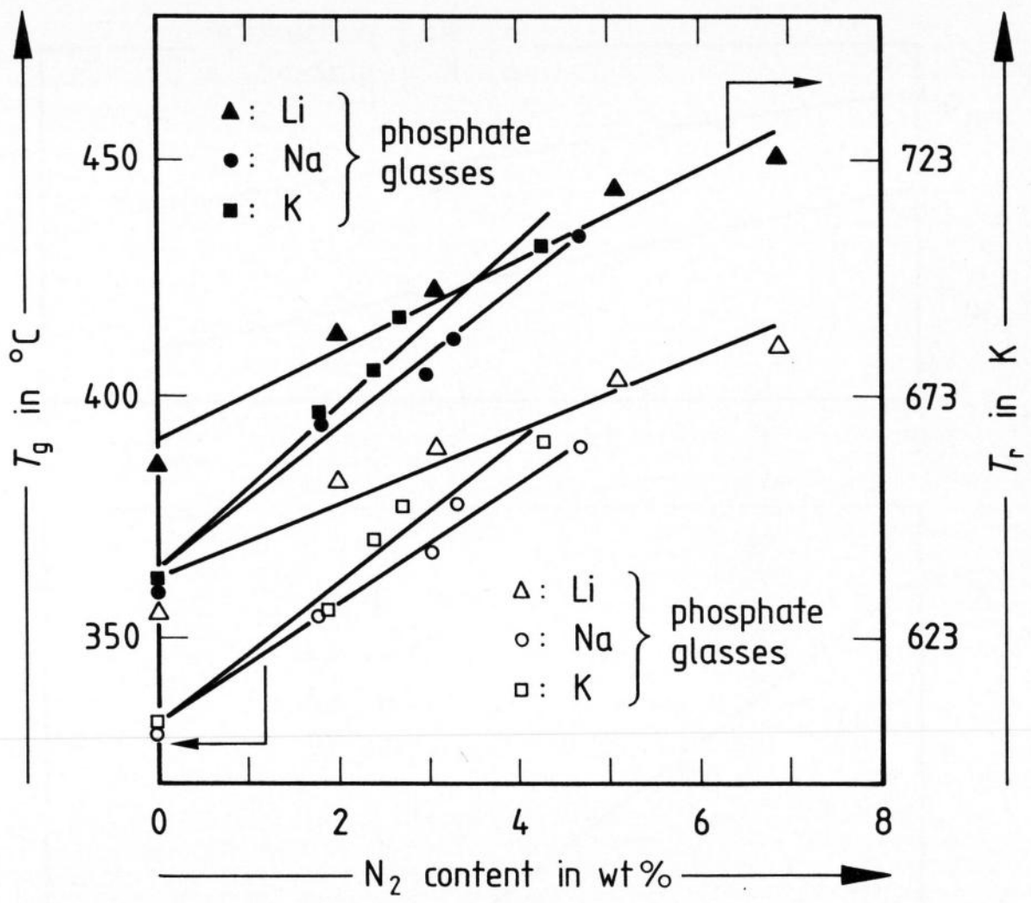


Figure 3. Glass transition temperature, T_g, and dilatometric softening temperature, T_r, of lithium, sodium and potassium phosphate glasses as a function of nitrogen content.

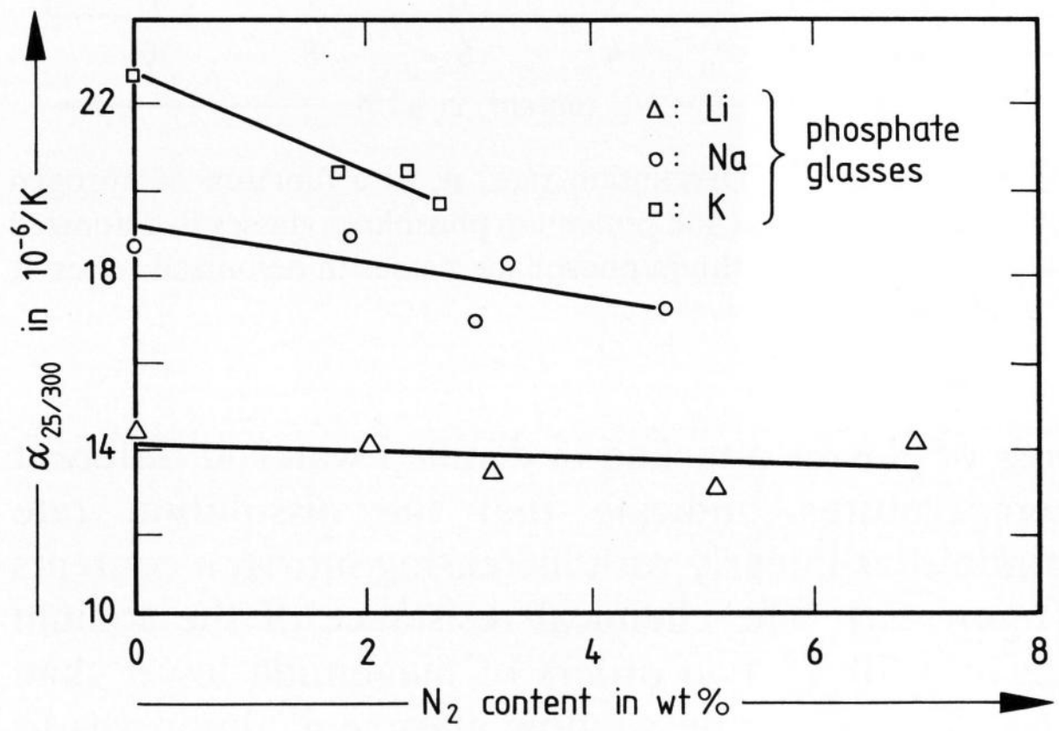
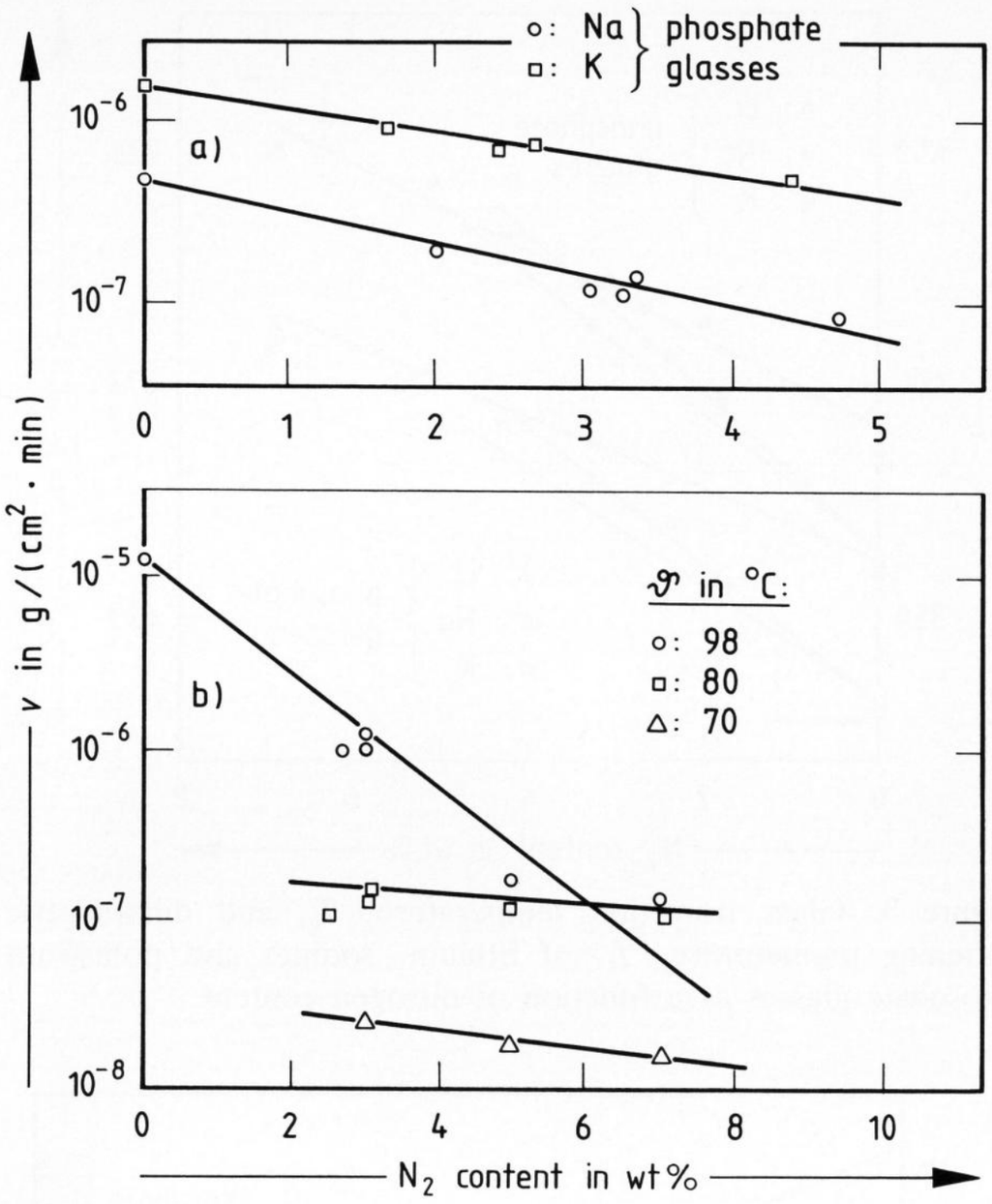


Figure 4. Thermal expansion coefficient, $\alpha_{25/300}$, of lithium, sodium and potassium phosphate glasses as a function of nitrogen content.

figure 4, the thermal expansion coefficient, $\alpha_{25/300}$, decreases with increasing nitrogen content. The resulting coefficient range, $\alpha_{25/300} = (13 \text{ to } 20) \cdot 10^{-6}\,K^{-1}$, coincides with those of some metals and alloys of high technological interest, like copper, special steels, potassium monel, nickel–chromium–molybdenum alloys, etc.

The dependence of thermal properties on the nitrogen content is another direct consequence of increased crosslinking that provokes a strengthening and stiffening of the network. On the other hand, at the same nitrogen content, T_g and T_r diminish with increasing alkali ionic size. Instead, the expansion coefficients are directly proportional to the alkali ion radius, i.e. that $\alpha_{25/300}$ increases in the order from lithium to sodium to potassium.

The most important property change linked to nitrogen dissolution in phosphate glasses is undoubtedly the increase in the hydrolytic resistance. The results of durability tests, obtained from the weight



Figures 5a and b. Dissolution rate, v, as a function of nitrogen content of a) sodium and potassium phosphate glasses in deionized water at 70 °C, b) lithium phosphate glasses in deionized water at 70, 80 and 98 °C.

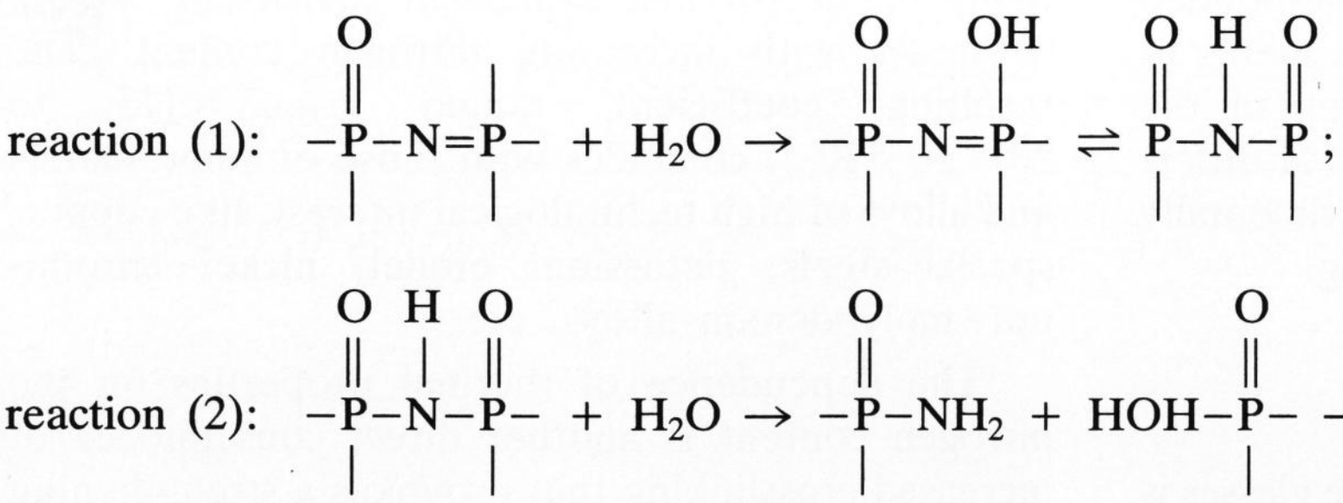
loss of glasses attacked in distilled water at different temperatures, indicate that the dissolution rate diminishes linearly with increasing nitrogen contents (figure 5a). The chemical resistance of the sodium glass at 70 °C, two orders of magnitude lower than that of a soda-lime window glass, e.g., improves to become a fourth of the latter when 4.7 wt% N_2 is incorporated.

Hydrolytic attack on lithium phosphate glasses at 70 and 80 °C caused very small weight losses; the attack was repeated at 98 °C (figure 5b), showing that nitrogen dissolution produces an improvement of two orders of magnitude in the chemical resistance of these glasses at a nitrogen content of 5 wt%. The chemical tests were always duplicated, very similar results being obtained for all the samples.

The difference in chemical durability for different alkaline oxides may be explained taking into account the ionic field strength, F, where $F = z/r^2$ with $z =$ = ionic valence and $r =$ ion radius, which increases for a diminishing ion radius. A lithium ion is more closely associated with a singly bonded oxygen than a sodium or a potassium one. Thus, lithium generates a more densified and consequently strengthened glass network.

The analysis of attack solutions shows that the extracted fraction of each component depends on the nitrogen concentration. In phosphate glasses, water attack provokes a dissolution of the network by hydrolysis of phosphate chains. The plot of the dissolution rate of each component as a function of N_2 content (figure 6) indicates that the principal effect of nitrogen is a significant diminution of the dissolution rate of phosphorus, suggesting that nitrogen is linked to phosphorus ions in the network. On the contrary, extracted aluminum content results independent from N_2 concentration, denoting that nitrogen does not replace the oxygen linked to Al^{3+} ions. Alkaline and barium ions, whose extraction rate depends on the dissolution of the phosphate chains, behave similarly to phosphorus.

The increase in the hydrolytic resistance of these glasses can be explained by the partial substitution of oxygen ions by nitrogen ions in P−O−P bonds, according to the mechanism [12] described in reactions (1 and 2) showing structural changes during nitridation:



Reaction (1) involves the hydrolysis of bonds adjacent to the P−N=P bond followed by the protonation of the nitrogen bridge by the contiguous hydroxyl group to form an imidophosphate (−NH−) bridge, highly resistant to hydrolysis. On the other hand, the hydrolysis of this group described in reaction (2) implicates the formation of a new P−O−P bridge rather than the bond rupture required for dissolution.

The VHN value (figure 7) increases linearly with increasing nitrogen content. The average value for base lithium glass is 3330 enhancing up to 5480 N/mm² for a content of 7 wt% N_2 in the same glass, and thus reaches a VHN value greater than that of soda−lime−silica glass (5140 N/mm²). The lowering values of VHN for sodium phosphate glass and potassium phosphate glass are also explained by the more open and weaker bonding produced by these ions in the glass network.

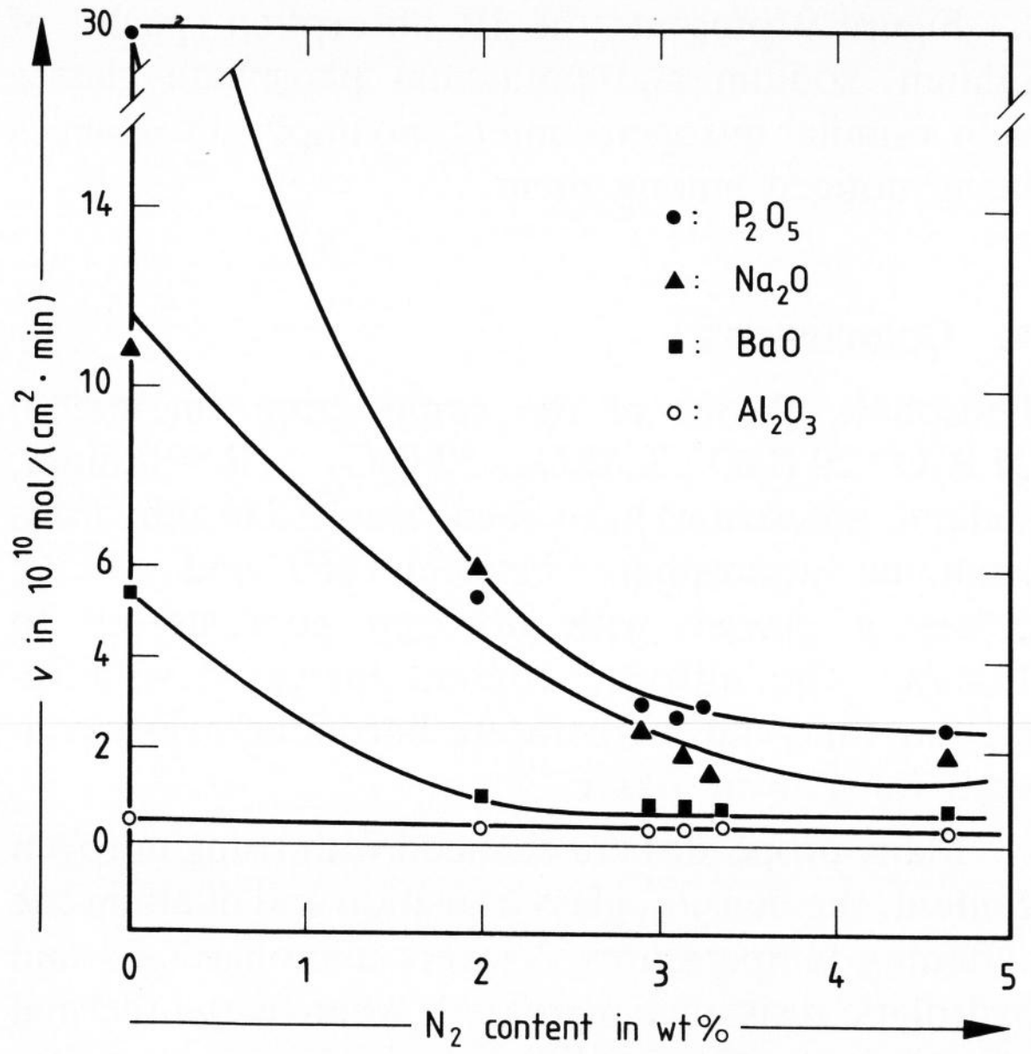


Figure 6. Dissolution rate, v, of each component in a sodium phosphate glass after hydrolytic attack in deionized water at 70 °C as a function of nitrogen content.

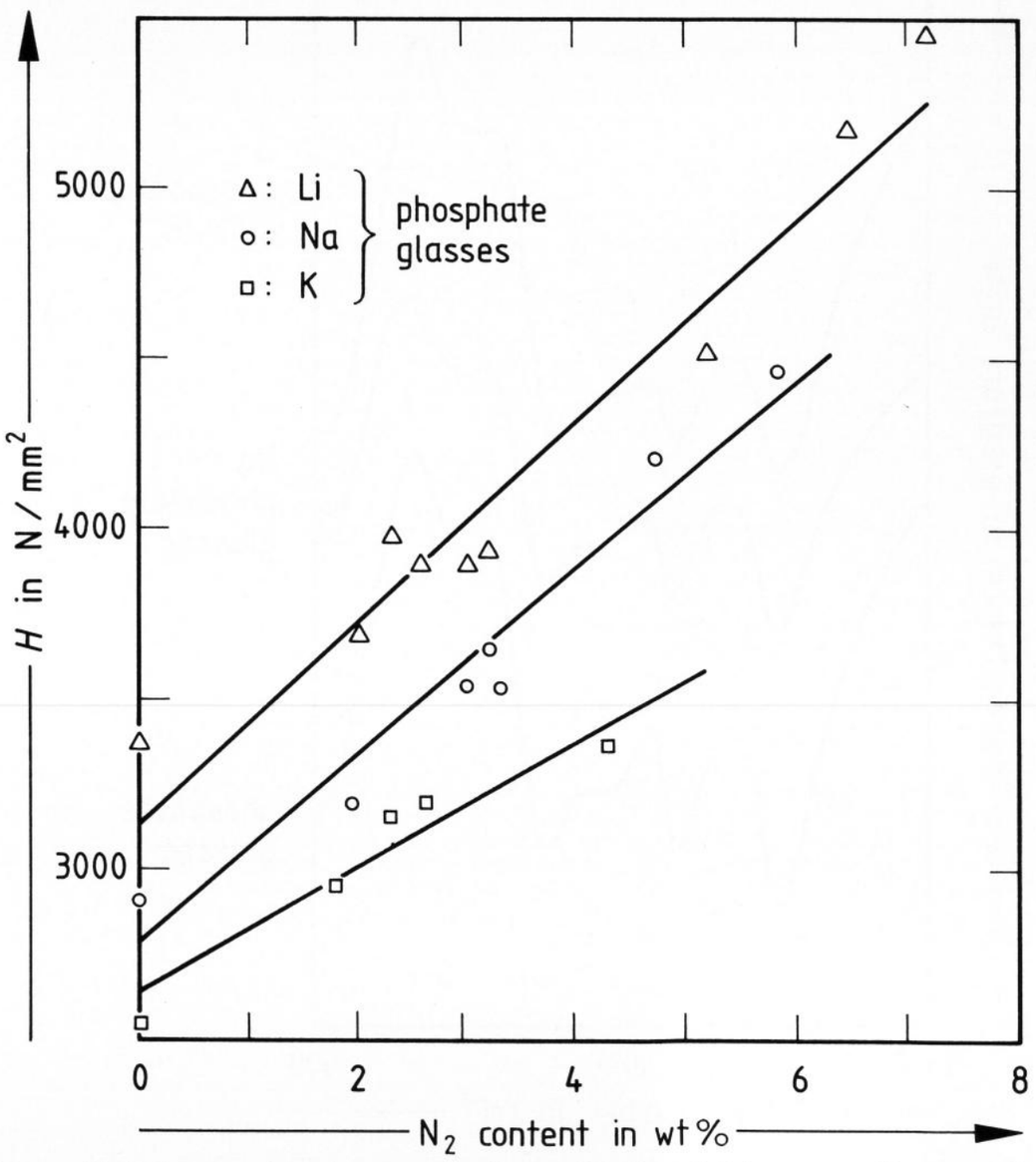
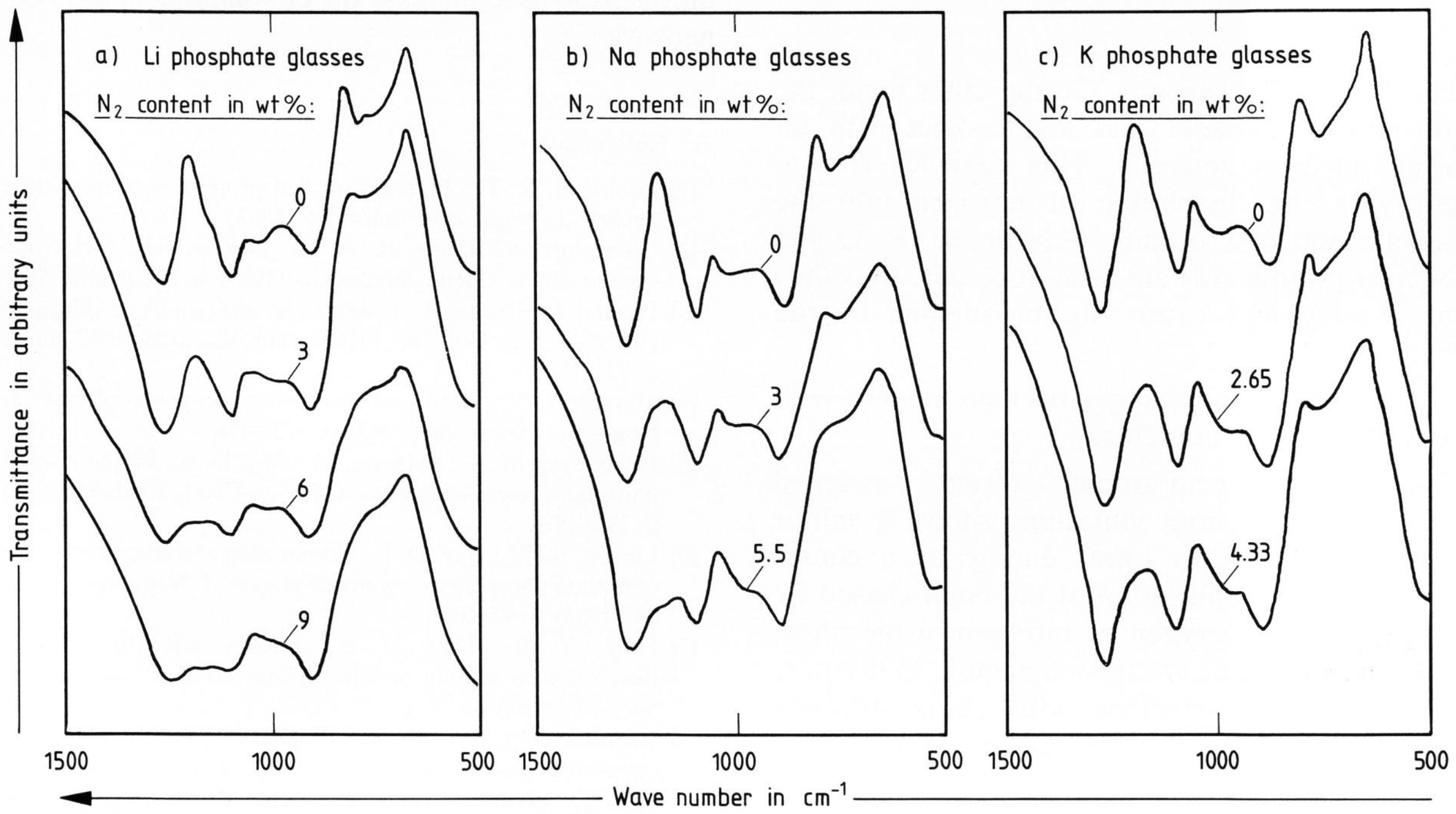


Figure 7. Vickers hardness number, H, for lithium, sodium and potassium phosphate glasses as a function of nitrogen content.



Figures 8a to c. Infrared absorption spectra of the investigated glasses with different nitrogen contents as parameter; a) lithium phosphate glasses, b) sodium phosphate glasses, c) potassium phosphate glasses.

3.3. Structural evolution

IR spectra of lithium, sodium and potassium phosphate glasses with different nitrogen contents are depicted in figures 8a to c, the main bands and their corresponding assignments being presented in table 2. Several absorption peaks are of particular interest. The bands corresponding to P=O and $P-O^-$ absorptions remain strong, suggesting that nitrogen preferentially replaces the bridging oxygen

Table 2. Infrared absorption bands in phosphate glasses

wave number in cm^{-1}	characterization of the bonds
1636	bending H−O−H
1263	stretching P=O
1096	stretching $P-O^-$
903	stretching P−O−P
899	bending P−O−P
790	bending P−O−P
740	stretching P−O−P

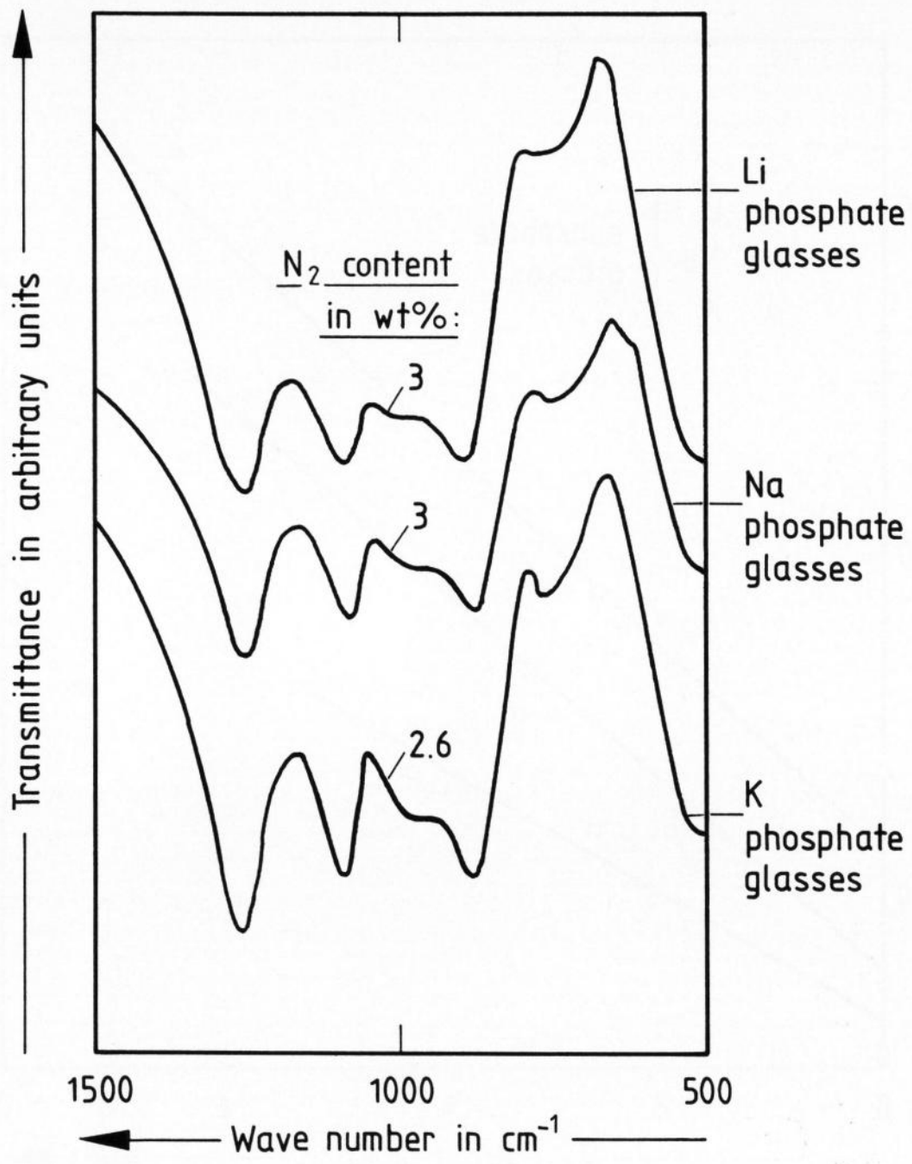


Figure 9. Infrared absorption spectra of lithium, sodium and potassium phosphate glasses with similar nitrogen contents.

P−O−P in the PO_4 groups. On the other hand, the bands become broader and less distinct with increasing nitrogen contents. This behavior is consistent with the dissolution of nitrogen into the phosphate network forming P−N bonds. P−O and P−N absorption bands are close together, thus they could overlap and cause the broadening of the spectra.

Several structural changes become evident with increasing nitrogen contents:

a) The absorption band around 1260 cm^{-1}, assigned to the P=O stretching vibration, shows a minor intensity and shifts to lower energy as a consequence of the destabilization of the bond caused by the substitution of oxygen by nitrogen in the phosphate chains [13]. The absorption band at 1176 cm^{-1}, that appears and develops with rising nitrogen concentrations, may also be related to the P=O stretch.

b) The absorption band at 1096 cm^{-1}, attributed to the $P-O^-$ vibration, does not change appreciably, offering evidence that this bond is not affected by nitrogen incorporation.

c) The characteristic absorption bands around 900 cm^{-1}, associated to the P−O−P linkage, broaden and slightly shift to higher wavelengths. The bands at 790 and 740 cm^{-1}, also assigned to this bond, become broader and diffuse with nitrogen addition. This behavior is probably due to the overlapping with the absorption band corresponding to the P−N vibration, consistent with the substitution of P−O−P for P−N−P bonds.

Figure 9 presents the IR absorption spectra of lithium, sodium and potassium phosphate glasses with a similar nitrogen content, no important changes being noticed among them.

4. Conclusions

Phosphate glasses of the composition (in mol%) 25 R_2O · 20 BaO · 3 Al_2O_3 · 52 P_2O_5 (R = lithium, sodium, potassium) have been remelted in anhydrous ammonia atmosphere between 650 and 800 °C, obtaining glasses with nitrogen contents up to 10 wt%. The nitrogen content increased with remelting time and temperature becoming nearly constant for 12 h at 700 °C.

Many properties are changed with rising nitrogen content: the density, glass transition and dilatometric softening temperatures, Vickers microhardness and hydrolytic resistance increased, whereas the thermal expansion coefficient diminished.

Weight loss data, chemical analyses and IR absorption spectra can be best explained by assuming that three bridging oxygens are replaced by two nitrogens so as to increase the crosslinking in the PO_4 network.

5. References

[1] Loehman, R. E.: Preparation and properties of oxynitride glasses. J. Non-Cryst. Solids **56** (1983) p. 123−134.
[2] Hampshire, S.; Drew, R. A. L.; Jack, K. H.: Oxynitride glasses. Phys. Chem. Glasses **26** (1985) no. 5, p. 182−186.
[3] Pascual, L.; Durán, A.: Oxinitruros: una familia de vidrios de alta resistencia. Bol. Soc. Esp. Ceram. Vidrio **29** (1990) no. 2, p. 73−81.
[4] Marchand, R.: Nitrogen-containing phosphate glasses. J. Non-Cryst. Solids **56** (1983) p. 173−178.
[5] Reidmeyer, M. R.; Rajaram, M.; Day, D. E.: Preparation of phosphorus oxynitride glasses. J. Non-Cryst. Solids **85** (1986) p. 186−203.
[6] Larson, R. W.; Day, D. E.: Preparation and characterization of lithium phosphorus oxynitride glasses. J. Non-Cryst. Solids **88** (1986) p. 97−113.
[7] Peng, Y. B.; Day, D. E.: Factors affecting nitrogen dissolution in sodium metaphosphate glass. J. Am. Ceram. Soc. **70** (1987) no. 4, p. 232−236.
[8] Rajaram, M.; Day, D. E.: Preparation and properties of oxynitride glasses made from 27 R_2O · 20 BaO · 3 Al_2O_3 · · 50 P_2O_5 glass. J. Non-Cryst. Solids **102** (1988) no. 1−3, p. 173−180.
[9] Rawson, H.: Inorganic glass-forming systems. London, New York: Academic Press 1967.
[10] Bunker, B. C.; Tallant, D. R.; Balfe, C. A. et al.: Structure of phosphorus oxynitride glasses. J. Am. Ceram. Soc. **70** (1987) no. 9, p. 675−681.
[11] Marchand, R.; Agliz, D.; Boukbir, L. et al.: Characterization of nitrogen containing phosphate glasses by X-ray photoelectron spectroscopy. J. Non-Cryst. Solids **103** (1988) no. 1, p. 35−44.
[12] Bunker, B. C.; Arnold, G. W.; Rajaram, M. et al.: Corrosion of phosphorus oxynitride glasses in water and humid air. J. Am. Ceram. Soc. **70** (1987) no. 6, p. 425−430.
[13] Graver, C. D. (ed.): The Coblentz Society desk book on infrared spectra. Kirkwood, MO: Coblentz Soc.

91R0012