Review Paper

Oxynitride glasses[1)]

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The present work is a review of the numerous nitridation experiments which have been carried out in different glass forming systems. After a brief introduction to the topic of the solubility of nitrogen in glass melts, the nitridation procedures and the different ways of incorporating nitrogen into the glass network are described. Also considered is the increasing cross-linking structure due to the incorporation of nitrogen. This involves a rise of the transition temperature, a decrease of the thermal expansion coefficient, and an improvement of the mechanical properties as well as of the chemical durability of the oxynitride glasses, depending closely on the nitrogen content. Some experiments on preparation of oxynitride glasses via the sol-gel procedure are also described.

Due to their properties the oxynitride glasses have been employed in several specific technical fields.

Oxynitridgläser

Die vorliegende Arbeit stellt in einem Überblick die vielfältigen Nitridierungsversuche dar, die an unterschiedlichen Glassystemen durchgeführt worden sind. Nach einer kurzen Einführung in die Thematik der Stickstofflöslichkeit in Glasschmelzen werden die Nitridierungsverfahren und die möglichen Einbauarten des Stickstoffs in das Netzwerk verschiedener Gläser betrachtet. Desgleichen wird auf die zunehmende Vernetzung eingegangen, die der strukturelle Stickstoffeinbau bewirkt. Dies führt wiederum zu einer Erhöhung der Transformationstemperatur, einer Erniedrigung des thermischen Ausdehnungskoeffizienten und einer Verbesserung der mechanischen Eigenschaften sowie der chemischen Beständigkeit der nitridierten Gläser, die stark vom Stickstoffgehalt abhängen. Einige Versuche, stickstoffhaltige Gläser nach dem Sol-Gel Verfahren herzustellen, werden ebenfalls beschrieben.

Aufgrund ihrer Eigenschaften finden die Oyxnidridgläser Anwendung in einigen besonderen technischen Bereichen.

1. Introduction

The interest in the solubility of nitrogen in glass melts has varied during the course of time. First, this interest was focused on the influence which nitrogen might have on bubble formation, in order to throw light on the mechanisms of refining. Later, it was widely directed towards improving the properties of glasses by incorporating nitrogen into the structure of glasses.

Mulfinger and Meyer [1], the first investigators, showed that nitrogen can not only be dissolved physically in melted glasses, but also chemically by a factor of 10 000 times larger. This explained why bubble formation in glass melts is not attributable to gases dissolved physically under normal pressure, because their saturation pressure is too low to create new internal surfaces.

The purely physical solubility of nitrogen in glass melts of binary alkaline silicates and of calcium sodium silicate is of the same order of magnitude as that of noble gases (between 4 and 12 per 10^{-4} cm^3 of nitrogen per cm^3 glass at 1 bar and at 1480 °C) and changes only slightly with the alkaline content of the glass, while the solubility of the noble gases helium and neon depends on composition to a larger extent [2].

More in-depth studies of the chemical solubility of nitrogen in glass melts [3 and 4] have led to the fact that, when glasses are melted under reducing conditions, nitrogen can be introduced into the glass structure in the form of groups $-NH_2$ or $=NH$ in the presence of hydrogen, where $=N-$ groups can be formed only in the absence of water vapour and of $-OH$ groups.

Somewhat later Elmer and Nordberg [5] nitrided a Vycor porous glass, using ammonia, and introduced about 3 wt% N_2 which was incorporated by forming $B-N-Si$ and $B-NH-Si$ groups replacing the $B-O-Si$ groups. Mulfinger and Kelen [6] used silicon nitride as an alternative to the use of ammonia for dissolving nitrogen in glass melts.

In the seventies the studies on the incorporation of nitrogen seemed to be forgotten. However, at the beginning of the eighties, interest in the subject was renewed and since then research in this field has multiplied. The main reasons why interest in oxynitride glasses increased so much are as follows:

- the increasing development of oxynitride ceramic materials (Si_3N_4, AlN);
- to learn more about the intergranular vitreous phases of $Si-Al-O-N$ ceramics (SIALON) and silicon nitride [7 and 8] in order to enhance their mechanical properties with respect to their possible use in structural applications [9 and 10];
- to increase the availability of glasses for joining nitrides with other materials [11, 12 and 13]; and

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- to develop new families of glasses with more favourable properties to prepare vitroceramic materials based on nitrides and oxynitrides [14].

Complete sintering of silicon nitride requires the addition of oxides which lead to the formation of an eutectic intergranular vitreous phase that favours the diffusion of the nitrogen. When an oxidic glass is used as a binding agent for sintering particles of silicon nitride at high temperatures, the nitrogen diffuses in the vitreous phase forming an oxynitride glass on which the mechanical properties of the material depend largely. During the sintering process part of the silicon nitride is dissolved in the vitreous phase in a relatively large proportion and the generation of internal stresses is reduced. The additives most commonly used in the sintering of silicon nitride are MgO, Y_2O_3 and $Al_2O_3 + Y_2O_3$.

2. Preparation procedures

Nitrogen can be incorporated into glasses by means of several procedures:

- by bubbling dry ammonia or atomic nitrogen through the glass melt in reducing conditions,
- by dissolving nitrides in the glass melt,
- by the sol-gel process,
- by implanting nitrogen ions.

The first procedure, which was used in the first nitriding experiments, is not efficient for incorporating nitrogen for the following reasons:

- the nitrogen reacts slowly with the melted glass,
- the ammonia dissociates at high temperatures,
- the melted glass has insufficient reducing power to maintain the nitrogen in the form of nitride.

For these reasons, this nitriding procedure is fairly limited, for example to easily fusible glasses (borate and, above all, phosphate glasses), to highly reactive materials (such as those prepared by the sol-gel procedure) or for nitriding very finely powdered materials.

The most commonly used procedure is based on the reaction of the glass melt with nitrides (Si_3N_4, BN, AlN, Ca_3N_2). During melting, up to 50 % of the nitrogen added can be lost. Higher concentrations can be attained in the glasses by using silicon nitride instead of aluminium nitride. In general, oxynitride glasses are prepared in two successive stages: first, the oxidic glasses are obtained by means of the conventional melting process, and later they are finely powdered, mixed with the nitride and melted once more at high temperatures of up to 1750 °C in an argon or – even better – in a nitrogen atmosphere. Graphite, molybdenum or boron nitride crucibles and Tammann or high-frequency furnaces are generally used. As a result of the thermal decomposition of the nitrides atomic nitrogen is formed.

The glasses obtained in this manner often present a greyish colour produced by the fine particles of silicon which deteriorate the optical quality of the glass. The nitrogen content produced can be determined by the well-known Kjeldahl method or by using LECO equipment.

3. Stability of nitridation

The silicon nitride is oxidized at high temperatures by the SiO_2, and SiO and N_2 is formed. The reaction

$$Si_3N_4 + SiO_2(l) + O_2(g) \rightarrow 4\,SiO(g) + 2\,N_2(g)$$

is exothermic ($\Delta G^0_{(1980\,K)} = -335.7$ kJ).

When the partial pressure of O_2 is increased, it favours the breaking of the Si–O–N bonds. Hence, the nitriding reactions have to be carried out under high partial N_2 pressure and in highly reducing conditions. The nitrides are not compatible with all glass melts. Only those oxides which are not reduced by the nitrides make it possible to obtain stable glasses.

The water which is structurally incorporated diminishes the formation of silicon nitride:

$$6\,H_2O + Si_3N_4 \rightarrow 2\,N_2 + 6\,H_2 + 3\,SiO_2\,.$$

The thermal decomposition of the silicon nitride can be prevented by maintaining moderate pressure of SiO(g) in the atmosphere of the furnace. However, an increase of the partial pressure of the nitrogen is ineffective [15].

4. Systems studied

Table 1 summarizes the principal oxynitride glass systems which have been studied by various authors.

4.1 Silica and silicate glasses

Few experiments have been made for nitriding SiO_2 glasses. Wusirika [16] incorporated up to 24 wt% nitrogen through treatment in an ammonia atmosphere at temperatures between 600 and 1200 °C, and found that the quantity of nitrogen dissolved was proportional to the square root of time and to the partial ammonia pressure. When less than 1 wt% nitrogen is incorporated, the glass devitrifies to crystobalite; at contents between 2 and 10 wt% nitrogen it is stable, and between 12 and 29 wt% Si_2N_2O crystallizes.

As the oxides of magnesium, calcium and yttrium and those of rare earths are most frequently used as additives for sintering the silicon nitride, the nitriding ability of the corresponding silicate and silicoaluminate systems has been studied more widely. Silicoaluminate glasses are most suitable for nitridation not only because the tetrahedra (AlO_4) are coupled well with those of (SiO_4), but also because the oxygen ions in both groups can be replaced by nitride ions. Moreover, in glasses containing Al_2O_3 the solubility of the nitrogen is larger, the melting temperature decreases slightly, the area of glass formation is larger [31] and the tendency towards phase separation diminishes [44]. Amongst the alkaline oxides the most compatible one to the formation of nitrides is Li_2O [30].

4.2 Borate glasses

When a current of ammonia is passed through a borate glass melt a small quantity of nitrogen is incorporated into its structure, principally in the form of groups $-NH_2$ or $=NH$ [4]. However, the finely powdered alkaline borate glasses begin to react with the ammonia at 300 °C and this is the more intensive the lower the basicity of the alkaline cation. First, $=NH$ groups are formed in a concentration about three times larger than that obtained by bubbling this gas through the glass melt at 1000 °C, but at 600 °C BN starts to be formed. At about 1200 °C, the lithium borate glasses are transformed almost quantitatively into BN [61].

Frischat et al. [62] found that the final nitrogen content in sodium borate glass melts ($15\,Na_2O \cdot 85\,B_2O_3$), nitrided in a nitrogen atmosphere, was larger than that when BN was introduced. This implies that under the reducing conditions of the melting process additional nitrogen is incorporated from the atmosphere of the furnace, which is possible in the absence of water vapour.

4.3 Borosilicate glasses

The nitriding of borosilicate glasses has been studied to a less extent. The first investigation which should be mentioned is that of Elmer and Nordberg [5]. These authors nitrided a porous Vycor glass with ammonia at 500 to 1100 °C, with care to prevent devitrification to crystobalite induced by the alkali ions in an electric field, and achieved the incorporation of about 3 wt% nitrogen under these conditions. As a result of this treatment, the transition temperature T_g and the electrical resistivity rose above the corresponding values for a pure silica glass.

Fernández Navarro and Oteo [37] treated powdered alkaline borosilicate glasses in an ammonia current and observed that above 1000 °C hexagonal BN starts to form. Jankowski et al. [38] incorporated 2.13 wt% nitrogen by melting a sodium borosilicate glass (in wt%: $14\,Na_2O$, $16\,B_2O_3$, $70\,SiO_2$) at 1600 °C mixed with powdered Si_3N_4, which produced a 45 °C increase in its transition temperature.

4.4 Phosphate glasses

The ability of phosphate glasses to be nitrided was investigated later. While the main object of nitriding silicate glass melts is to enhance their mechanical properties, in phosphate glasses the aim is to improve their chemical durability without excessively increasing their relatively lower softening temperature or reducing their high thermal expansion coefficient to any extent. In this way, it was possible to reduce the solubility of phosphate glasses in water three- or fourfold. Most nitriding experiments have been carried out with metaphosphate glasses [19, 65, 66, 68, 70 and 71] as the chemically most stable ones.

Table 1. Systems of oxynitride glasses investigated by several authors

system	references
SiO_2	[16]
R_2O-SiO_2	[4, 6, 17 to 25]
$MO-SiO_2$	[23, 26 to 29]
$Me_2O_3-SiO_2$	[26, 27, 30 to 32]
$Na_2O-CaO-SiO_2$	[4, 6, 17 to 20, 33 to 36]
$R_2O-B_2O_3-SiO_2$	[5, 17, 37 to 39]
$R_2O-Al_2O_3-SiO_2$	[22, 23, 30, 40 to 42]
$MO-Al_2O_3-SiO_2$	[23, 30, 31, 42 to 51]
$MO-M'O-Al_2O_3-SiO_2$	[48]
$Me_2O_3-Al_2O_3-SiO_2$	[15, 23, 26, 27, 30, 31, 42, 43, 45, 47, 48, 52 to 59]
$R_2O-TiO_2-SiO_2$	[23]
$MO-Me_2O_3-Al_2O_3-SiO_2$	[43]
$R_2O-B_2O_3-Al_2O_3-SiO_2$	[38]
$MO-Al_2O_3-ZrO_2-SiO_2$	[60]
$Me_2O_3-Al_2O_3-TiO_2-SiO_2$	[53]
$R_2O-MO-Al_2O_3-TiO_2$	[23]
$R_2O-B_2O_3$	[3, 6, 61 to 63]
$TeO_2-B_2O_3$	[64]
$TeO_2-Al_2O_3$	[64]
$R_2O-P_2O_5$	[65 to 68]
$MO-P_2O_5$	[69]
$R_2O-MO-P_2O_5$	[70 to 73]
$R_2O-R'_2O-MO-P_2O_5$	[72 and 73]
$R_2O-MO-Al_2O_3-P_2O_5$	[73 to 75]
$R_2O-SiO_2-P_2O_5$	[39]
$R_2O-B_2O_3-SiO_2-P_2O_5$	[39]

Explanation:
a) R, R' = Li, Na, K, Cs
b) M, M' = Be, Mg, Ca, Ba, Pb, Mn
c) Me = Y, La, Nd, Gd

Due to their low melting temperatures, phosphate glasses can be directly nitrided with ammonia. However, the ammonia should not be bubbled through the glass melt, because the temperature required for this would be too high and the glass could decompose. To speed up the nitriding reaction, it is necessary to increase the area of the glass melt in contact with the ammonia to a maximum. For this purpose Heiberger and Pye [65] treated the glass melt with ammonia in an inclined rotating crucible. Powdered glass can also be treated with a current of ammonia for several hours and immediately melted under the same atmosphere [71, 73 and 75].

The solubility of the nitrogen in the glass melt increases with temperature up to a certain limit, since the viscosity decreases and favours diffusion and decomposition. At temperatures below 650 °C very low nitrogen contents are obtained and above 750 to 780 °C the phosphate can be reduced to elementary phosphorus and even to phosphine [66]. The highest nitrogen concentrations are obtained by treating the glass powder in an ammonia atmosphere at 700 to 725 °C.

Experiments for nitriding in N_2-H_2, N_2-CO and CH_3-NH_2 atmospheres have also been carried out, although in no case were such high nitrogen levels ob-

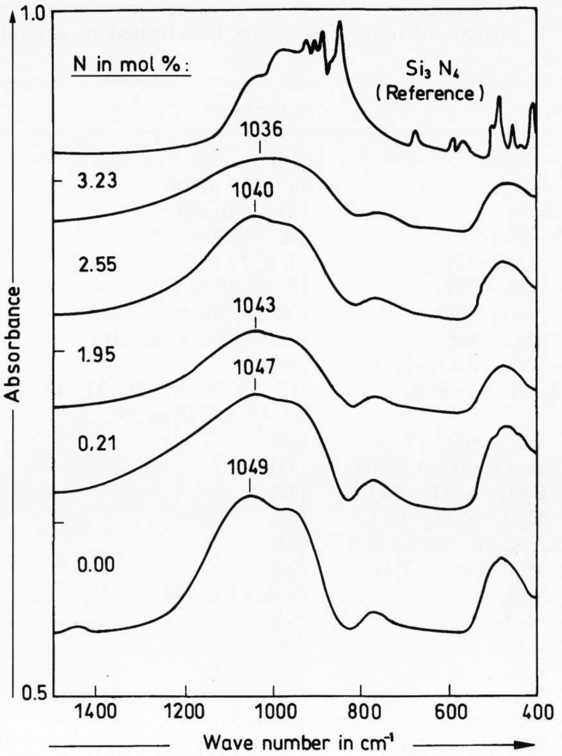
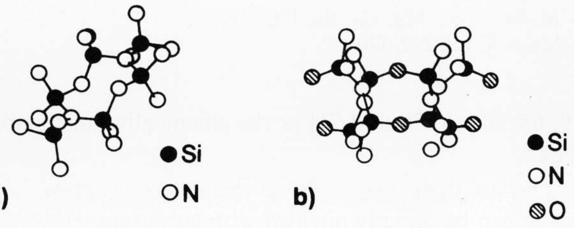


Figure 1. Infrared spectra of oxynitride glasses with different nitrogen contents after Brow and Pantano [18].



Figures 2a and b. Structure of β-silicon nitride (figure a) and of silicon oxynitride (figure b) after Sakka et al. [46].

tained as in an ammonia atmosphere. During very long treatments or at temperatures above 780 °C [65], the weight losses measured in these experiments are larger than the theoretical losses, which is partly due to the volatilization of the glass melt itself and partly to the reduction of the phosphate. If the sodium oxide is replaced by an alkaline-earth oxide, the solubility of nitrogen is reduced [70], which may be attributable to the double electrostatic bond of the alkaline-earth ions with two nonbridging oxygen ions from two adjacent phosphate chains.

4.5 Tellurite glasses

Tellurite glasses and vitroceramic materials have also been prepared from binary compositions of the $TeO_2-B_2O_3$ and $TeO_2-Al_2O_3$ systems mixed with AlN [64] and melted at 800 to 1200 °C.

5. Structure

When glass melts are bubbled with nitrogen in a reducing atmosphere of nitrogen in the presence of water vapour, $-NH_2$ or $=NH$ groups are formed, which can be identified by the wide absorption band, situated at 2.95 μm, due to valency vibration. The lower the partial water vapour pressure, the more is the quantity of the nitrogen favoured as nitride groups. Thus, nitrogen can be incorporated in the glass structure in three different ways.

The notable densification and reinforcement of oxynitride glasses, which is the result of the creation of a more rigid and more cross-linked structure, suggested that the nitrogen is incorporated preferably in the form of nitride groups, with three oxygen ions being replaced by every two nitride ions incorporated and with each nitride ion joining three silicons. This replacement involves a weight loss during the nitriding process. The values calculated theoretically agree very well with those determined experimentally [65].

5.1 Silicate glasses

The infrared spectra (figure 1) of nitrided silicate glasses with different nitrogen contents show that the characteristic absorption band at $1050\ cm^{-1}$ shifts towards lower wave numbers. At the same time this band becomes more asymmetrical [18, 19, 27, 35, 40 and 49]. For the majority of the glasses this band appears at about $930\ cm^{-1}$, i.e. at the same position as in the silicon nitride, which means that it can be attributed to the formation of Si–N–Si bonds. The broadening of this band can be explained by the angular deformation of the Si–O–Si bonds provoked by the incorporation of the nitrogen.

There are two crystalline compounds with a similar structure: silicon nitride and silicon oxynitride [46] (figures 2a and b). In the silicon nitride, each silicon is tetrahedrally coordinated with nitride ions, while in the silicon oxynitride it is surrounded by three nitrogens and one oxygen. The distance between the silicon and the nitrogen is 0.174 nm in the silicon nitride and 0.172 nm in the oxynitride, in both cases larger than the Si–O distance, which is 0.162 nm. However, around the nitride ions the structure may be more compact, because each nitrogen is bonded to three silicon tetrahedra. Sakka [46] compared the experimentally measured density values of nitrided calcium silicoaluminate glasses with the values calculated theoretically on the basis of molar volumes and found that they agree very well with the proposed structures based on Raman spectra [58].

As the criterion for establishing the most likely means of incorporating nitrogen into the structure of sodium-calcium silicate glasses, Schrimpf and Frischat [35] used the values of the Young's modulus, since it changes to a great extent with the concentration of nitrogen in the glass. For this purpose they calculated the theoretical values of the Young's modulus, E, for the three possible ways of incorporating nitrogen and compared them with the experimental values. The most acute slope which corresponds to the linking of three nitride ions to one silicon is that which agrees closest with the experimental values.

Investigations using nuclear magnetic resonance (NMR) technique in nitrided sodium silicate binary glasses [20] showed that there are three different types of nitrogen in all compositions. The addition of nitrogen produces the increasing replacement of bridging oxygen ions by nitrogen ions, which can bond with up to three silicon tetrahedra. The same conclusions were reached by molecular dynamics calculations [21 and 25] and by neutron diffraction [24]. All of these investigations confirm that nitrogen can be bonded to three, two or single atoms of silicon. According to the values calculated for sodium silicate binary glasses [21 and 25], each nitrogen is bonded to 2 to 2.3 atoms of silicon on average. Sakka [22] found that 58 % of nitrogen ions are bonded to two silicons and 42 % to three silicons. In yttrium silicoaluminate glasses [SiO_3N] and [SiO_2N_2] groups are formed. The XPS spectra of the nitrided glasses are similar to those of Si_3N_4 [19].

Another issue to be clarified was whether the nitrogen could also directly be bonded to aluminium ions in silicoaluminate glasses, since the presence of aluminium favours the nitriding process. However, it has been shown that the incorporation of nitrogen does not change either the tetrahedric or the octahedric aluminium coordinations, and the results achieved in [20 and 44] exclude the existence of N−Al bonds.

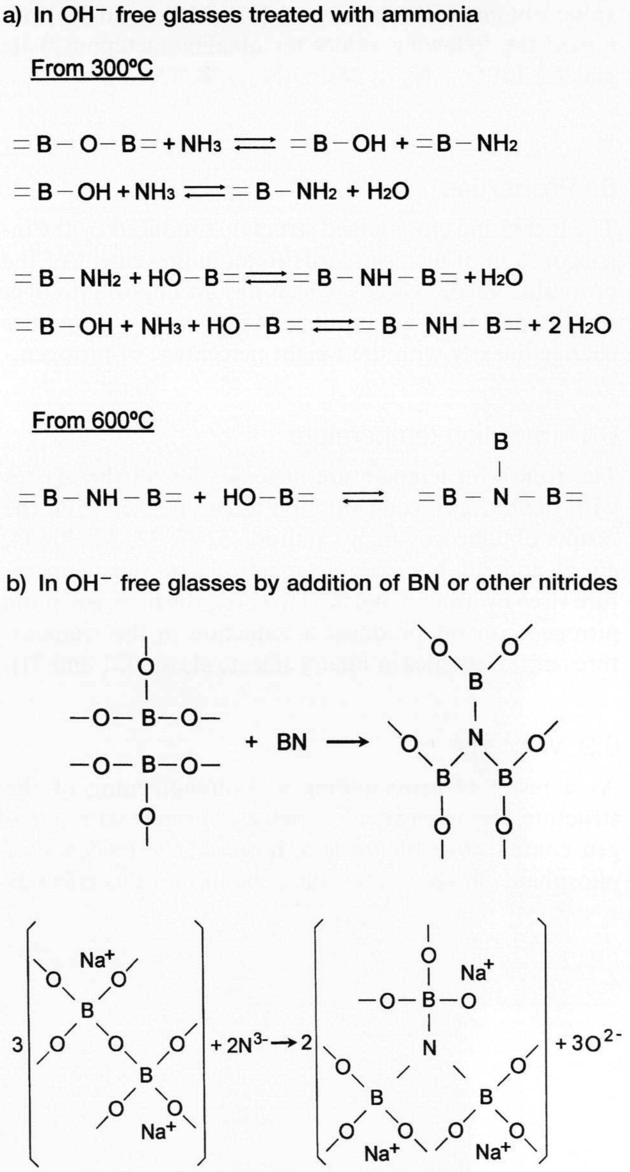
5.2 Borate glasses

Amino and imido groups are formed from 300 °C on when borate glasses are nitrided with ammonia and nitride groups are formed additionally at temperatures exceeding 600 °C. However, when nitrides are used, the nitrogen is incorporated in the structure exclusively as nitride (figures 3a and b).

5.3 Phosphate glasses

The structure of nitrided phosphate glasses presents a more complicated feature since these glasses have several possibilities of incorporating nitrogen. Figures 4a and b show the different groups which can be formed. When nitrogen is incorporated into the structure of a metaphosphate glass, $P(O,N)_4$ groups are formed. The trivalent nitride ions can replace both, the bridging and nonbridging oxygens. In the second case, they give rise to the formation of a cross-linked structure (figures 5a to c). With low nitrogen content PO_4 groups and linear chains of metaphosphate predominate. When the concentration of nitrogen is increased, pyrophosphate chains begin to be formed, together with [PO_3N] and [PO_2N_2] groups at the expense of the PO_4 groups.

The study on the structure of nitrided phosphate glasses has been approached through several procedures.



Figures 3a and b. Structural incorporation of nitrogen in borate glasses [61 and 62]; a) in OH^- free glasses treated with ammonia, b) in OH^- free glasses by addition of BN or other nitrides.

NMR and Raman spectroscopy [68] confirm that the nitrogen, no matter what its content, can be bonded to two or three phosphates. The oxygen bonds in nitrided lithium and sodium metaphosphate glasses were studied and it was found that the ratio of the number of bridging oxygens to nonbridging oxygens decreases when the nitrogen content is increased. This implies that the ammonia reacts with both types of ions, with no preference for either of them. This procedure makes it possible to calculate the maximum nitrogen content which can be incorporated into a metaphosphate glass. This value agrees very well with the $PO_{1.67}N_{0.89}$ ratio which corresponds to 13.4 wt% nitrogen, consistent with the top value obtained in experiments [71]. Marchand [66] obtained the following values for alkaline metaphosphate glasses: $LiPO_{2.15}N_{0.57}$, $NaPO_2N_{0.67}$, $KPO_2N_{0.67}$.

6. Properties

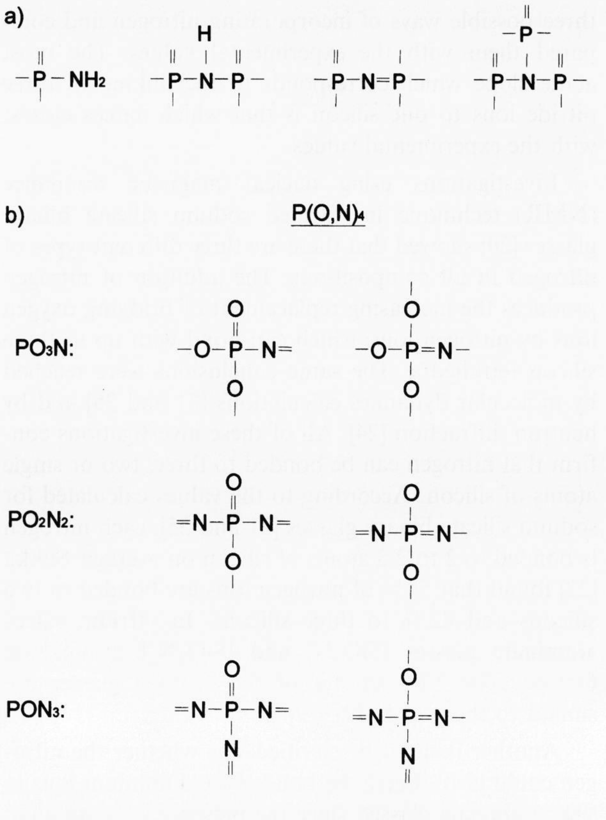
The increasing cross-linked structure produced by the incorporation of nitrogen leads to an improvement of the properties of the glasses, which has an important effect on their technical application. Many physical properties change linearly with the weight percentage of nitrogen.

6.1 Transition temperature

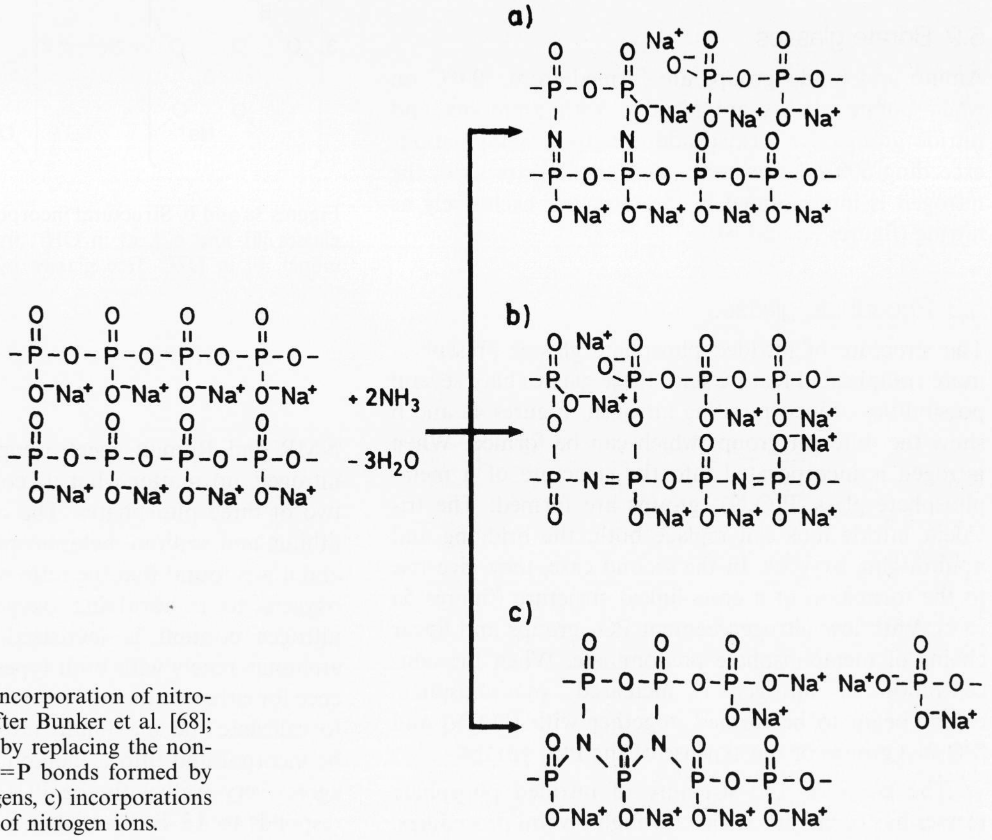
The transition temperature increases for all the glasses with the nitrogen concentration as can be seen from the results obtained by many authors [5, 27, 32, 34, 40, 44, 46, 51 and 80]. For metaphosphate glasses this temperature rises by around 100 °C. However, the increase in the nitrogen content produces a reduction in the temperatures of the eutetics in binary silicate glasses [31 and 71].

6.2 Viscosity

As a result of cross-linking and strengthening of the structure, the viscosity also increases usually with nitrogen content. For this reason, however, the tendency of phosphate glasses to crystallize diminishes this effect as



Figures 4a and b. Different possibilities of bonding nitrogen to phosphorus (figure a) and $P(O,N)_4$ groups that theoretically can be formed (figure b)).



Figures 5a to c. Structural incorporation of nitrogen in phosphate glasses after Bunker et al. [68]; a) P–N=P bonds formed by replacing the nonbridging oxygens, b) P–N=P bonds formed by replacing the bridging oxygens, c) incorporations of increased concentration of nitrogen ions.

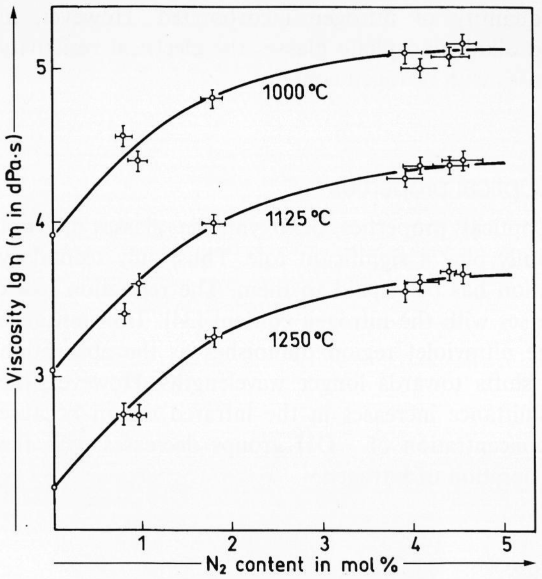


Figure 6. Viscosity curves of nitrided $Na_2O-CaO-SiO_2$ glasses versus nitrogen content after Schrimpf and Frischat [34].

the proportion of nitrogen incorporated is increased. The activation energy of the viscous flow does not depend on the nitrogen content and remains constant [35] (figure 6).

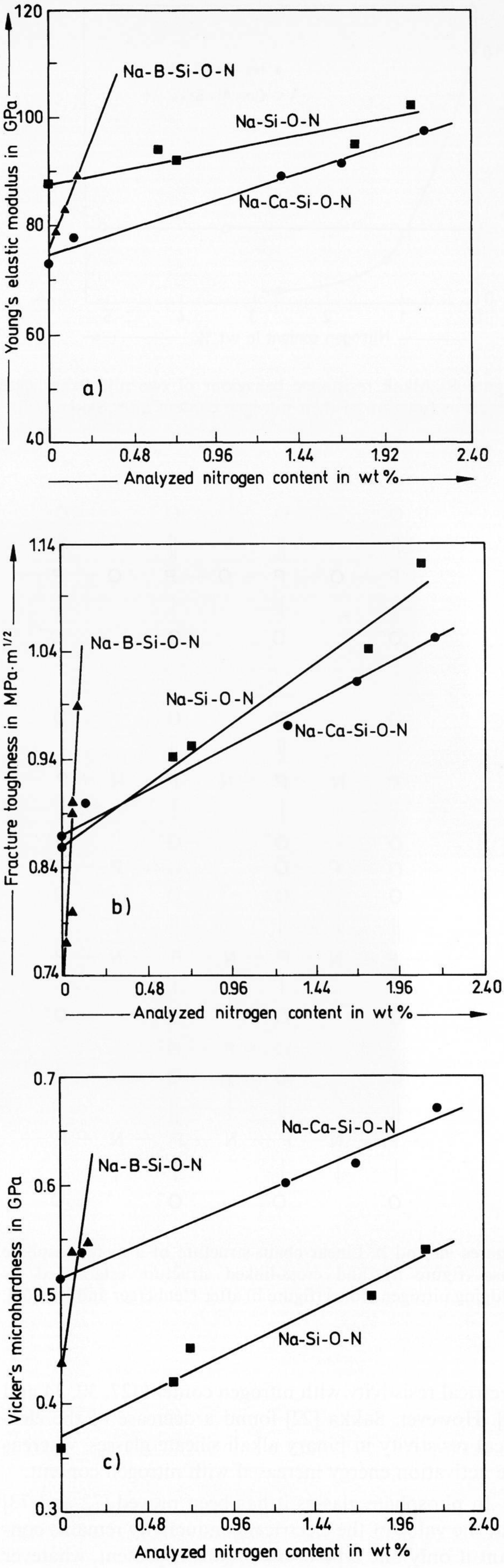
6.3 Mechanical properties

For the same reasons as mentioned above and in section 5, an increase in the nitrogen content produces an increase in the density, Young's modulus, microhardness and toughness (figures 7a to c). The improvement of the mechanical properties can be explained by the more covalent Si$-$N bonds than those of the Si$-$O bonds and by the larger cross-linking effect of N^{3-}. Thus, it is understandable that the Si$-$N$-$Si bonds produce larger resistance to bending. The reduction in the thermal expansion coefficient can be explained in a similar way [27, 36, 43, 44, 47, 51, 64 and 73].

It should be noted that small concentrations of nitrogen produce more pronounced effects on borate glasses than on silicate glasses. Phosphate glasses also show the same trends in their properties as those of silicates or borates.

6.4 Electrical properties

Although one of the objectives of the first nitriding experiments [5] was to increase the electrical resistivity of glasses, the electrical properties of oxynitride glasses belong to those which have been scarcely studied. The majority of oxynitride glasses show an increase in their



Figures 7a to c. Variation of some mechanical properties of ▶ different glasses as function of the nitrogen content after Coon et al. [17]; a) Young's elastic modulus, b) fracture toughness, c) Vicker's microhardness.

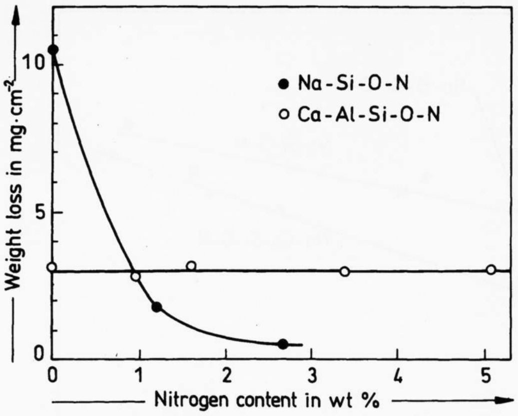
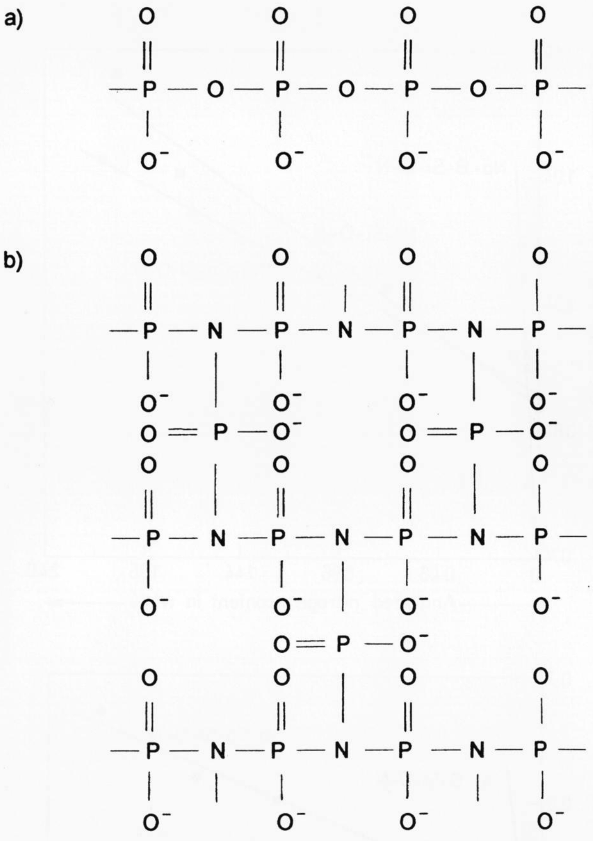


Figure 8. Alkali resistance behaviour of two nitrided silicate glasses as function of their nitrogen content after Sakka [22].



Figures 9a and b. Linear chain structure of a metaphosphate glass (figure a), and cross-linked structure established by bridging nitrogen atoms (figure b) after Heuberger and Pye [65].

electrical resistivity with nitrogen content [27, 30, 34 and 55]. However, Sakka [22] found a decrease of the electrical resistivity in binary alkali silicate glasses, whereas the activation energy increased with nitrogen content.

In phosphate glasses it has been proved [72 and 73] that the value of the electrical conductivity remains constant if only one type of alkali ions is present, whatever the quantity of nitrogen incorporated. However, in mixed alkali phosphate glasses the electrical resistivity increases with nitrogen content.

6.5 Optical properties

The optical properties of oxynitride glasses do not generally play a significant role. Thus, only secondary attention has been paid to them. The refraction index increases with the nitrogen content [34]. Transmittance in the ultraviolet region diminishes as the absorption edge shifts towards longer wavelengths. However, the transmittance increases in the infrared region because the concentration of $-OH$ groups decreases with the incorporation of nitrogen.

6.6 Chemical properties

The effects produced by the incorporation of nitrogen on the chemical properties of glasses depend on their composition. In binary alkali silicate glasses the incorporation of nitrogen produces a considerable improvement in chemical durability [29 and 41]. A glass with a composition of $30Na_2O \cdot 70SiO_2$ with nitrogen contents of more than 1 wt% behaves better than a calcium silicoaluminate glass against an NaOH solution of c(NaOH) = 0.1 val/l ($\hat{=}$0.1 N) (figure 8) [22]. The chemical resistance of this glass does not change with its nitrogen content. In contrast, nitriding of magnesium silicoaluminate glasses increases their NaOH resistance [50] with increasing nitrogen. Yttrium silicoaluminate glasses [27 and 42] behave extraordinarily well and show a better hydrolytic resistance than that of a pure silica glass.

The improvement of the resistance against acids can be explained by slowing down the kinetics of the ionic change due to the increase of its density, while the increase in alkali resistance must be attributed to the larger covalency of the $Si-N$ bonds, which are more resistant to $-OH$ groups.

The improvement of the chemical durability of the phosphate glasses by the incorporation of nitrogen is due to the increase of cross-linking of the phosphate chains [71 and 73] (figures 9a and b). Hydration of the phosphate chains takes place first during its chemical attack [75]; these later dissolve in the water without breaking and are subsequently hydrolyzed leading to the formation of orthophosphate groups.

According to this model the kinetics of the dissolution takes place in two successive stages (figures 10a and b). For the first of the two relations (figure 10a) the rate of dissolution is determined by the diffusion of water into the glass and its kinetics adjusts to the square root of the time. The second stage evolves proportional to the time (figure 10b).

While in non-nitrided phosphate glasses the dissolution kinetics depends on the concentration and on the radius of the alkaline-earth ions, these do not play an important role in nitrided glasses, since the influence of trivalent nitride ions predominates [70].

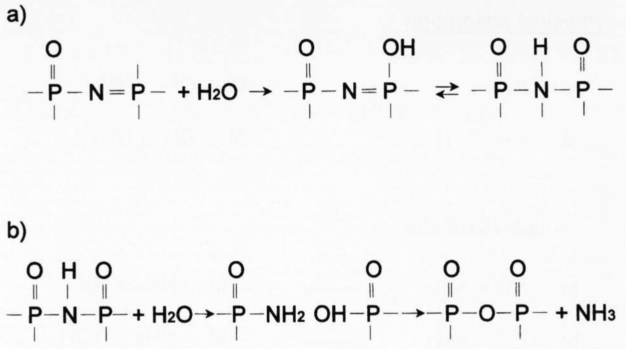
Figures 11a and b show the change of the hydrolytic resistance of some phosphate glasses according to their nitrogen content. The phosphate groups dissolve fastest and the aluminium groups slowest. The fact that the speed of dissolution of the phosphate groups decreases sharply when the nitrogen content is increased is the result of the larger strength of the P=N−P or P−N−P bonds as compared to the P−O−P bonds. The dissolution kinetics of the aluminium groups is independent of the concentration of nitrogen, which proves that there are no Al−N bonds formed as had been confirmed by nuclear magnetic resonance.

7. Sol-gel preparation

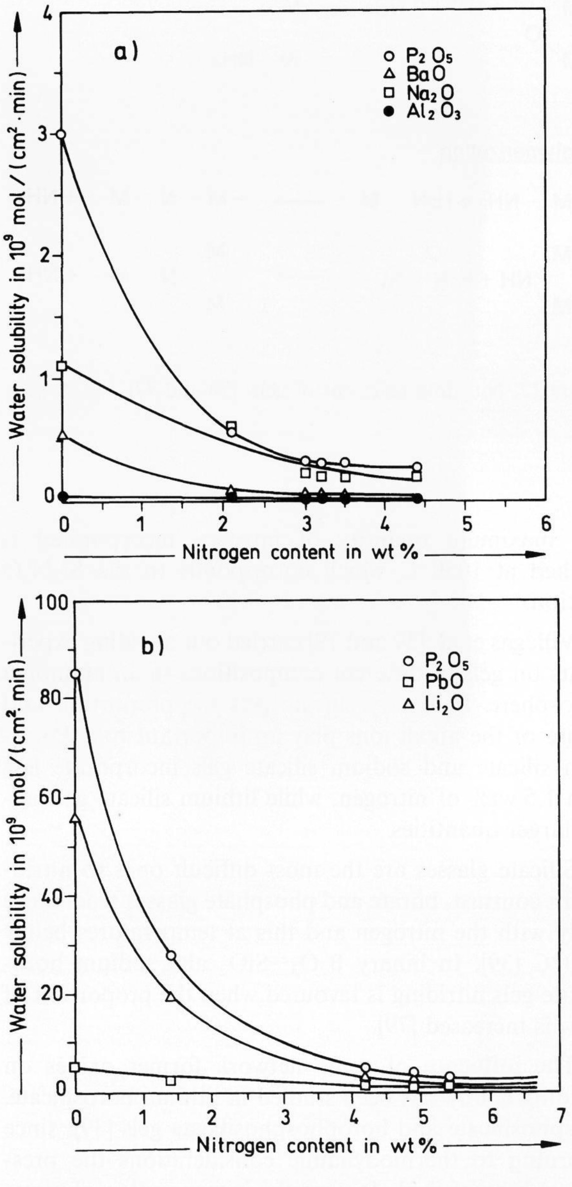
The preparation of oxynitride glasses by the conventional melting procedure requires very high temperatures, generally above 1700 °C, to obtain homogeneous glasses. This disadvantage can be avoided by using the sol-gel process as an alternative; the possibilities of this process have been investigated by many authors [39, 63, 76 to 79]. The large specific surface area which the gels offer before being densified due to their porosity is the origin of their reactivity with ammonia and its compounds. For this reason, the higher the degree of sintering the lower is the quantity of nitrogen that can be incorporated into their structure.

The first experiments on nitriding gels were effected by Brinker [80], who treated borosilicate gels with dry ammonia at 460 °C. In this way, he succeeded in incorporating around 3 wt% nitrogen in the form of $-NH_2$ groups, which favour the elimination of −OH groups and of organic rests and increase the transition temperature. When porous gels are heated in a current of ammonia, first physical adsorption of the ammonia on the −OH groups takes place, followed by water condensation and the formation of amino groups (figure 12) [76 to 77]. At temperatures between 400 and 600 °C B−N bonds start to be formed (as is indicated by the shoulder at 1510 cm^{-1} observed in the infrared absorption spectra) at the expense of B−O−Si groups. Above 750 °C the incorporation of nitrogen into the gel increases, and is directly bonded to the network former ions M (Si, Al) due to the diminution of the oxygen ions. At this temperature $-NH_2$ and =NH groups can still be identified. The formation of M−N bonds increases with temperature and concentration of the network-forming ions. The establishment of =N− linkages is optimum near the transition temperature.

The nitriding conditions of a finely dispersed xerogel of SiO_2 in an ammonia atmosphere were studied by Sjöberg [81]. The nitrogen starts to be incorporated at around 800 °C, which approximately coincides with the temperature of the decomposition of the ammonia.



Figures 10a and b. Model of dissolution kinetics of phosphate glasses in two successive stages: a) the rate of dissolution adjusts to the square root of time (determined by the diffusion of water into the glass), b) the rate of dissolution evolves proportional to time.



Figures 11a and b. Water solubility of the components of two nitrided phosphate glasses after Pascual [73]; a) $25\,Na_2O \cdot 20\,BaO \cdot 3\,Al_2O_3 \cdot 52\,P_2O_5$, b) $25\,Li_2O \cdot 20\,PbO \cdot 55\,P_2O_5$.

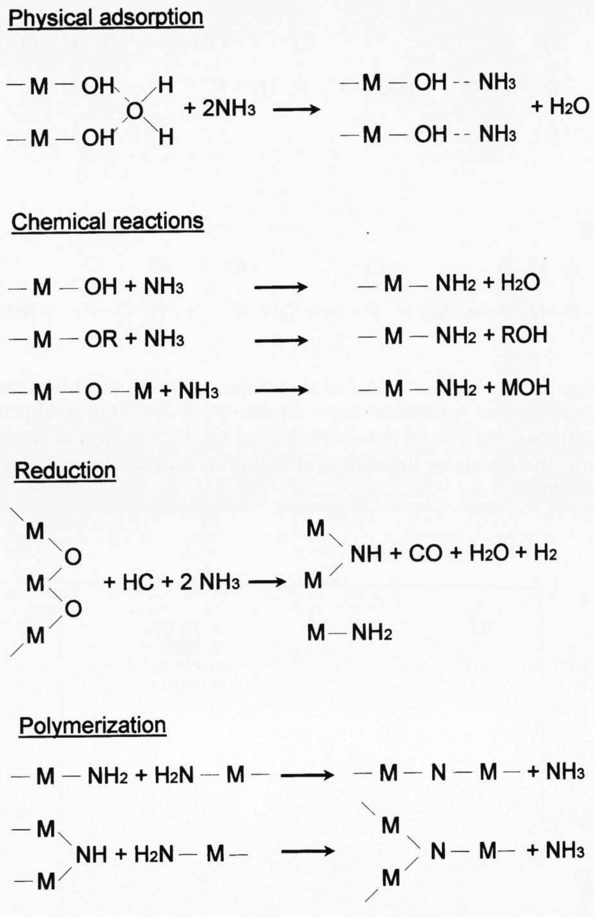


Figure 12. Nitriding reactions of gels [76 and 77].

The maximum quantity of nitrogen incorporated is reached at 1050 °C which corresponds to the Si_2N_2O relation.

Villegas et al. [39 and 79] carried out nitriding experiments on gels of different compositions in an ammonia atmosphere. In binary silicate gels the proportion and nature of the alkali ions play an important role. Potassium silicate and sodium silicate gels incorporate less than 1.5 wt% of nitrogen, while lithium silicate gels admit larger quantities.

Silicate glasses are the most difficult ones to nitridate. In contrast, borate and phosphate glasses react more easily with the nitrogen and this at temperatures below 1000 °C [39]. In binary $B_2O_3-SiO_2$ and sodium borosilicate gels nitriding is favoured when the proportion of B_2O_3 is increased [79].

The influence of some network former oxides on nitriding ability has been studied in lithium borosilicate, phosphosilicate and borophosphosilicate gels [39], since according to thermodynamic considerations the presence of lithium oxide favours the incorporation of nitrogen. In all cases, the nitriding of the gels is more intense than that of the corresponding glasses of the same composition. In borosilicate gels (figures 13a and b) the highest incorporation of nitrogen (12 wt%) was achieved at 1100 °C. The reactivity of the lithium phosphosilicate samples is lower than that of the lithium borosilicate samples. Figures 13c and d show that the highest nitrogen content (3.9 wt%) is obtained after a three-hour treatment in an ammonia atmosphere at 1100 °C. In these samples the formation of Si_2ON was identified. When the treatment time is prolonged, the nitrogen content will be reduced to below 0.4 wt%. This may be explained by the fact that the phosphorus nitride, which is formed at around 700 °C, induces the nitriding of the silicon at higher temperatures. Thus, it may be assumed that the larger portion of the incorporated nitrogen is found to be forming part of the oxynitride phase. In other words, the nitrogen content is higher at lower temperatures, where the nitrided phosphors are still stable. Glasses of the same composition obtained by melting behave in a similar fashion. However, in the melted glasses no crystalline oxynitride is formed.

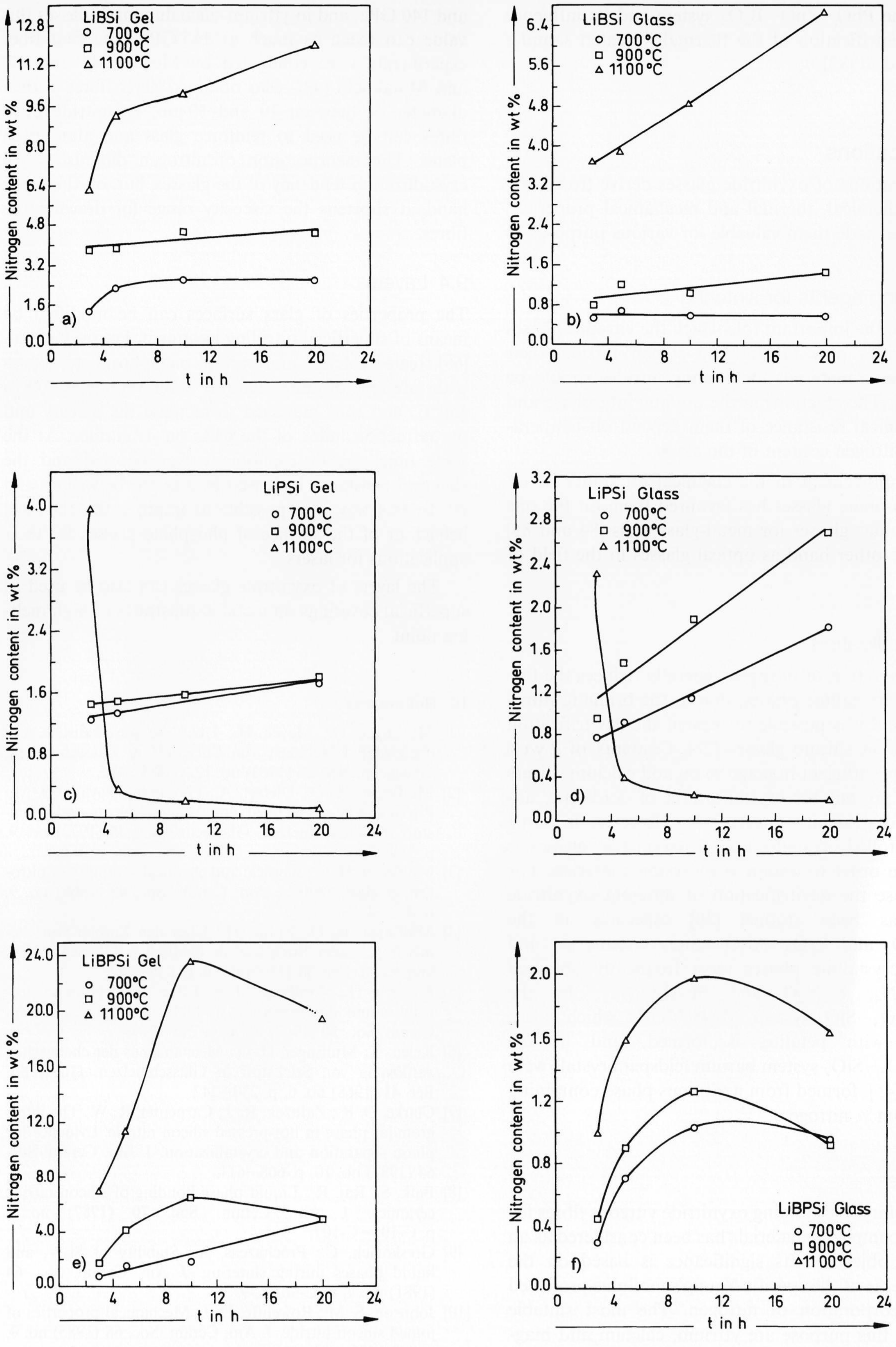
Lithium borophosphosilicate gels are those which incorporate the largest quantities of nitrogen (24 wt%) after 10 h of treatment with ammonia at 1100 °C (figures 13e and f). However, the nitrogen content decreases during long periods, which can be attributed to the instability of the phosphorus nitride.

The sol-gel procedure also offers the possibility of preparing very homogenous glasses for their subsequent nitriding. Starting from boron and lithium methoxide, and from boric acid and lithium hydroxide, Krüner and Frischat [63 and 78] prepared lithium borate gels, which they mixed, once powdered, with BN or with Li_3N and melted at 1350 °C in atmospheres of argon and ammonia. The incorporated quantity of nitrogen was only 0.2 to 0.3 wt%, similar to that obtained in glasses prepared by conventional melting and, in any event, less than that obtained in lithium silicate glasses. However, these small quantities of nitrogen were sufficient to provoke a notable increase of the transition temperature, microhardness and chemical durability.

Geyer and Rüssel [82] described an original procedure for nitriding magnesium silicoaluminate glasses. On the one hand, they prepared by the sol-gel method a magnesium silicate gel from magnesium acetate and tetraethoxisilane and on the other hand, they dissolved aluminium anodically in an electrolyte constituted by n-propylamine, acetonitrile and tetrabutylammonium bromide. This viscous solution is mixed with the magnesium silicate powder, dried at 700 to 1000 °C, treated in ammonia current and melted at 1500 to 1700 °C. In this manner they prepared homogenous oxynitride glasses with 7.95 wt% nitrogen.

8. Ionic implantation

The ionic implantation procedure can be considered as a very special case in the incorporation of nitrogen in glasses. Nitrogen ions have been incorporated into a



Figures 13a to f. Nitrogen content incorporated in gels and glasses of following compositions (in wt%) after Villegas et al. [39]: $10\,Li_2O \cdot 30\,B_2O_3 \cdot 60\,SiO_2$ (figure a: gel; figure b: glass); $10\,Li_2O \cdot 30\,P_2O_5 \cdot 60\,SiO_2$ (figure c: gel; figure d: glass); $10\,Li_2O \cdot 15\,B_2O_3 \cdot$ $\cdot\ 15\,P_2O_5 \cdot 60\,SiO_2$ (figure e: gel; figure f: glass).

glass of the $PbO-ZnO-B_2O_3$ system and its influence on the devitrification of the thermally treated samples was studied in [83].

9. Applications

The applications of oxynitride glasses derive from their excellent chemical, thermal and mechanical properties, which have made them valuable for various purposes.

9.1 Binding agents for sintering

Apart from the important role which the vitreous phases of oxynitrides play in sintering silicon nitride, their general use as materials for binding nitrides should be mentioned. The reactions in the binding interphase and the mechanical resistance of them depend on temperature and nitrogen content of the glass.

The improvement in the chemical durability of nitrided phosphate glasses has favoured them on the one hand as solder glasses for metal-glass seals [84 and 85] and on the other hand as optical glasses in the field of lasers.

9.2 Crystallization

The incorporation of nitrogen generally reduces the formation of crystalline phases, due to the bridging nitrogens. Thus, it was possible to prevent the devitrification of magnesium silicate glasses [28]. Contents of 2 wt% nitrogen are sufficient in magnesium and calcium silicate glasses to prevent the crystallization of cordierite, anorthite and gehlenite phases [51]. However, in some cases controlled crystallization of oxynitride glasses is desirable in order to obtain vitroceramic materials. For this purpose the devitrification of different oxynitride glasses has been studied [30] especially in the $Y_2O_3-SiO_2$ and $Y_2O_3-Al_2O_3-SiO_2$ systems [31 and 55]. The crystalline phases most frequently obtained are β-Si_3N_4, Si_2N_2O and $Si_4Al_4O_{11}N_2$. In the $MgO-Al_2O_3-SiO_2$ system, Mg_2SiAlO_4N, which is isostructural with petalite, is formed, and in the $BaO-Al_2O_3-SiO_2$ system barium feldspar crystals were identified [45], formed from a vitreous phase containing 8 to 10 atom % nitrogen.

9.3 Fibres

The possibility of obtaining oxynitride vitreous fibres for preparing composite materials has been considered as an important objective. Its significance is based on the sharp increase of the specific Young's modulus produced by the incorporation of nitrogen. The most suitable glasses for this purpose are yttrium, calcium and magnesium silicoaluminate glasses. While the highest tensile strength values of conventional glass fibres are between 440 and 490 MPa, nitrided calcium and magnesium silicoaluminate glasses reach levels of up to between 135 and 140 GPa, and in yttrium silicoaluminate glasses this value can reach as much as 165 GPa. The first fiber experiments were conducted by Messier [42 and 57] and Minakuchi [48], who obtained glass fibres with a diameter of between 10 and 30 μm. Oxynitride glass fibres can be used to reinforce glass and aluminium plates. The incorporation of nitrogen diminishes the crystallization tendency of the glasses, but, on the other hand, it shortens the viscosity range for drawing the fibres.

9.4 Layers

The properties of glass surfaces can be modified by means of superficial nitriding treatment. Petrovskii et al. [69] treated calcium and barium metaphosphate glasses with mixtures of ammonia and water vapour at 500 to 550 °C, and thus managed to increase the density and the refraction index of the glass on its surface. At the same time, the hydrophobicity was boosted and the chemical resistance increased by a factor between 8 and 10. In this way it is possible to improve the chemical behaviour of the surface of phosphate glasses for their applications for lasers.

The layers of oxynitride glasses can also be used as superficial coverings on metallic substrates of high melting point.

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