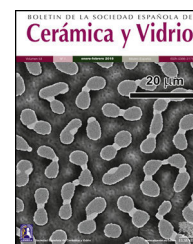




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Oxynitride glasses: a review



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ABSTRACT

Oxynitride glasses are special types of silicates or silicoaluminates which have been the object of many studies over the last forty years. They can be prepared by means of various complex methods, leading to variable levels of nitrogen incorporation, though in all cases giving limited transparency in the visible range. More recently, a new family of oxynitride glasses incorporating fluorine has been investigated. This paper outlines the effect of composition, in particular nitrogen and fluorine content, on properties such as glass transition temperature, hardness, Young's modulus, compactness and molar volume.

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Vidrios de oxinitruro: revisión

RESUMEN

Los vidrios de oxinitruro son vidrios de silicato o aluminosilicato especiales que han sido objeto de numerosos estudios durante los últimos cuarenta años. Pueden ser obtenidos mediante diferentes métodos, más o menos complejos, que permiten la incorporación de un porcentaje variable de nitrógeno pero, en cualquier caso, con una transparencia limitada en la región del espectro visible. En los últimos años las investigaciones en este campo se han ampliado con una nueva familia de vidrios de oxinitruros en los cuales se incorpora flúor en su composición. En este artículo se hace una revisión del efecto de la composición, especialmente del contenido en nitrógeno y flúor, sobre algunas de las propiedades de estos tipos de vidrios, como son la temperatura de transición vítrea, la dureza, el módulo de Young, la compactidad y el volumen molar.

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Palabras clave:

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Vidrios de oxifluoronitruros

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Introduction

Oxynitride glasses are special types of silicates or aluminosilicates formed in two systems, $M-Si-O-N$ and $M-Si-Al-O-N$ respectively, where M represents one or several modifier cations of elements such as Ca, Mg, Y or rare-earths. The aluminium expands the compositional range for glass formation, lowers the melting temperature and, in low amounts (1–2 at%), eliminates the phase separation observed in its absence [1–3]. Meanwhile, the incorporation of metal oxides lowers the melting temperature enough to allow the dissolution of silicon nitride or any other nitrogen source without decomposition [3,4].

When one begins to study these glasses, it is likely one will wonder why they have received so much attention for so many years. Initially the interest was down to the fact that they appeared as intergranular phases in silicon nitride ceramics (Fig. 1) [5]. A better understanding of oxynitride glasses would therefore help to improve the way in which silicon nitride ceramics were processed, given they affected the performance of the ceramics at high temperatures. From this moment onwards, oxynitride glasses became objects of interest in their own right.

Numerous studies have been carried out on oxynitride glasses. It has been observed that nitrogen incorporation leads to significant increases in resistance, tenacity, elastic modulus and hardness [1,6–10]. The main pioneer for their study was Mulfingher [11], who was the first to incorporate a small amount of nitrogen into silicate glasses (<1 wt%) after first bubbling ammonia gas through a sodium silicate system melt. He suggested that nitrogen might substitute the oxygen atoms in the tetrahedra of the glass network. In a subsequent study [12] it was shown to be possible to incorporate up to 3 wt% nitrogen after melting borosilicate glass in an ammonia atmosphere. The results showed that nitrogen-infused glasses had higher viscosities and electrical resistivities. However, this method was not further explored given the limited levels of nitrogen incorporation achieved (maximum 3 wt%). Davies and Meherali [13] confirmed that the solubility of nitrogen in the glass is chemical rather than physical and pointed out

that, to be able to incorporate more significant amounts of nitrogen, the glass should be melted under a reducing atmosphere. Dancy and Janseen [14] investigated nitrogen solubility in the $CaO-SiO_2-Al_2O_3$ system, comparing different chemical methods for incorporating this anion into the melt. They discovered that, when silicon nitride is added in a nitrogen atmosphere, its incorporation is quick and good levels were achieved (4 wt%).

Jack [7] pointed out the close similarity shared by the structural units in silicate glasses (SiO_4 tetrahedra) and silicon nitride (SiN_4 tetrahedra), as well as the similarities between the $Si-O$, $Al-O$ and $Si-N$ length bonds. He suggested that nitrogen could be incorporated into silicate and aluminosilicate glass networks. In fact, this author was the first to achieve 10 at% nitrogen incorporation in glasses of the $SiO_2-Al_2O_3-Si_3N_4$, $SiO_2-MgO-Si_3N_4$ and $SiO_2-Y_2O_3-Si_3N_4$ systems. However, he did not investigate the effects of this nitrogen incorporation on the properties of these glasses. It was Loehman [15] who looked into this, studying glasses in the $Y-Si-Al-O-N$ system with up to 7 at% nitrogen. He suggested that properties such as glass transition temperature (T_g), hardness and fracture toughness increased along with the nitrogen content.

However, none of the studies described above were carried out while maintaining a constant cationic ratio. Drew and his co-workers [16,17] carried out systematic studies in the $M-Si-O-N$ and $M-Si-Al-O-N$ ($M=Mg, Ca, Y$ and Nd) systems. The team prepared compositions with a constant cationic ratio, and modified oxygen and nitrogen contents. They were therefore able to determine the effect of substituting oxygen by nitrogen in the different systems. This work showed that incorporating nitrogen in a given composition, while maintaining a constant cationic ratio, resulted in increased viscosity, glass transition temperature, devitrification resistance, refractive index, dielectric constant and electrical conductivity across all of the systems studied. Moreover, it was observed that the glass forming region in $M-Si-O-N$ systems was significantly smaller than in $M-Si-Al-O-N$ systems, revealing the ability of aluminium to expand the compositional range for oxynitride glass formation.

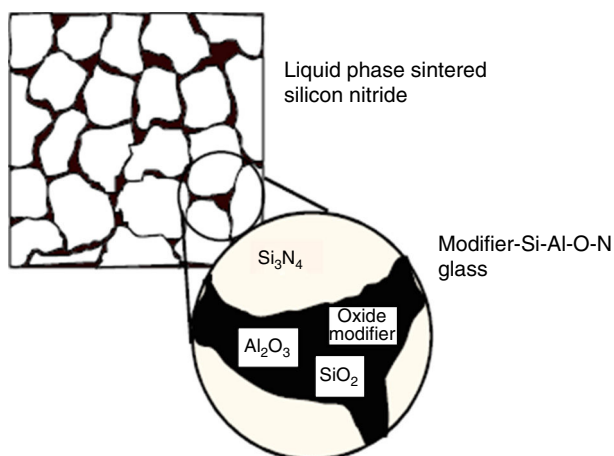


Fig. 1 – Schematic representation of liquid-phase sintered silicon nitride and the intergranular oxynitride phase [5].

Synthesis

The preparation of oxynitride glasses is much more complex than for the equivalent non-nitrogen glasses [18]. The main difficulties encountered include high melting temperatures, the need for a reducing atmosphere to prevent the oxidation of the melt, the limited amount of crucibles available for this process and the limited number of nitrogen sources.

Oxynitride glasses can be synthesised using different methods. Traditionally they are prepared by melting the correct mixture of the corresponding oxides and nitrides in crucibles under an argon or nitrogen atmosphere. The melting temperatures oscillate between 1550 °C and 1850 °C. The upper limit is determined by the decomposition of the silicon nitride, while the lower limit is determined by the high viscosity of the melt at that temperature.

Most of these glasses are obtained using silicon nitride or aluminium nitride as the nitrogen source. Messier and Deguire [19] concluded that using aluminium nitride instead of silicon nitride reduces the number of spherical elemental silicon precipitates that end up dispersed in the glass. It has been experimentally demonstrated that the incorporation of nitrogen is higher when the nitrides are melted than by reaction of the melt with gaseous nitrogen or ammonia. Other nitrogen sources such as Ca_3N_2 [20], Mg_3N_2 , Si_2ON_2 and Li_3N [18] have also been used. In order to avoid oxidation, melting should be carried out in a reducing atmosphere. Under these conditions, metallic crucibles (Mo, Nb, Ta and W), boron nitride crucibles and graphite crucibles lined with boron nitride can be used.

Meanwhile, as stated above, oxynitride glasses have also been obtained by ammonolysis of melts. In this method, the melt is treated with gaseous nitrogen and/or ammonia at high temperatures and for long periods of time. However, the amount of nitrogen ultimately incorporated in this case is limited [11,12].

Oxynitride glasses have also been prepared at low temperatures by means of sol-gel methods [21,22]. Oxide gels can be transformed into oxynitride gels by treating anhydrous ammonia at temperatures of between 400 and 1100 °C. The oxynitride gel is converted into glass by vacuum heating at just above the glass transition temperature, generally around 900 °C, causing some of the nitrogen is lost in the gel-glass transition. Brinker and Haaland [23] used this method to synthesise colourless, dense and homogeneous glasses with up to 2 eq% nitrogen in the Na–Al–Ba–Si–O–N system. Similarly, Rajaram and Day [24] were able to incorporate up to 25 eq% nitrogen in the M–Na–P–O–N system (M = alkaline-earth metals).

The most recent method of synthesis allows the preparation of oxynitride glasses with higher nitrogen contents than those obtained by any of the methods described above [25–30]. In this method, the modifier is introduced as a metal or metal hydride, and reacts with the gaseous nitrogen at relatively low temperatures to form nitrides. These nitrides react with the SiO_2 (oxygen source) and with the Si_3N_4 (usually inert at these temperatures). A melt containing Si, O, N and the metallic cation is formed, which dissolves the remaining SiO_2 and Si_3N_4 , and is finally cooled at below the glass transition temperature. Glasses in the M–Si–O–N and M–Si–Al–O–N (M = Ln, Ca, Mg, Sr or Ba) systems have been prepared using this method.

Properties

Optical properties

Oxynitride glasses have traditionally been considered as candidates for optical applications, because of their high refractive index values, hardnesses and softening temperatures. However, the main obstacle is their low transparency in the visible spectrum. As a general rule, oxynitride glasses are less transparent than the equivalent oxide glasses. They generally present a greyish-black colour and are only translucent in thin sections, with their transparency being a function of the level of impurities generated during their synthesis.

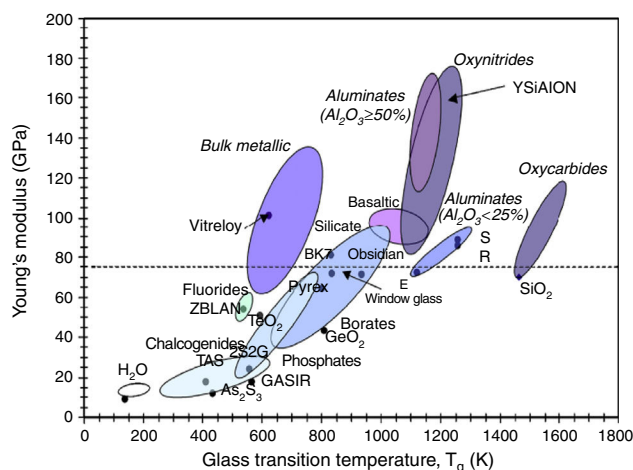
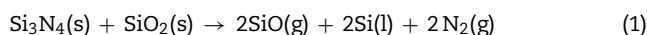


Fig. 2 – Young's modulus at 293 K (except for amorphous ice, 77 K) and glass transition temperature for several glass systems [35].

Despite this problem having been addressed in several studies [19,31–33], no progress has been made towards obtaining transparent glasses with high nitrogen contents. The main reason for this is the precipitation of silicon generated during the decomposition of silicon nitride at temperatures above 1650 °C, according to Greskovich and Prochazka [34]:



Two methods have been suggested to avoid this reaction: the synthesis under 1.6 MPa pressure of nitrogen [19] and the substitution of silicon nitride by aluminium nitride [19,32]. However, neither of these methods has been experimentally proven to be successful. Meanwhile, it has been observed that compositions melted at low temperatures (1400–1500 °C) present improved transparency. Furthermore, oxynitride glasses prepared using the sol-gel method are more transparent than the equivalent glasses prepared by traditional means.

Mechanical and thermal properties

In a previous work by Rouxel [35] Fig. 2 was presented, which shows Young's modulus as a function of glass transition temperature. As shown in this representation, oxynitride glasses present high values for both of these properties, higher than most other glass systems. Most significantly, the glass transition temperature of oxycarbide glasses is about 300 °C higher.

The relationship between Young's modulus and glass transition temperature is also reported by this author (Fig. 3), showing that changes in the modulus-temperature slope occurs at higher temperatures for oxynitride glasses than for any other system.

A considerable amount of research related to glass formation and properties has been published for a wide variety of M–Si–O–N and M–Si–Al–O–N systems, where M is a metal such as Ca, Mg, Y, Al or Nd. The effect of nitrogen incorporation on these properties has also been reported for these systems. A first group of studies [17,18,36,37] reported the

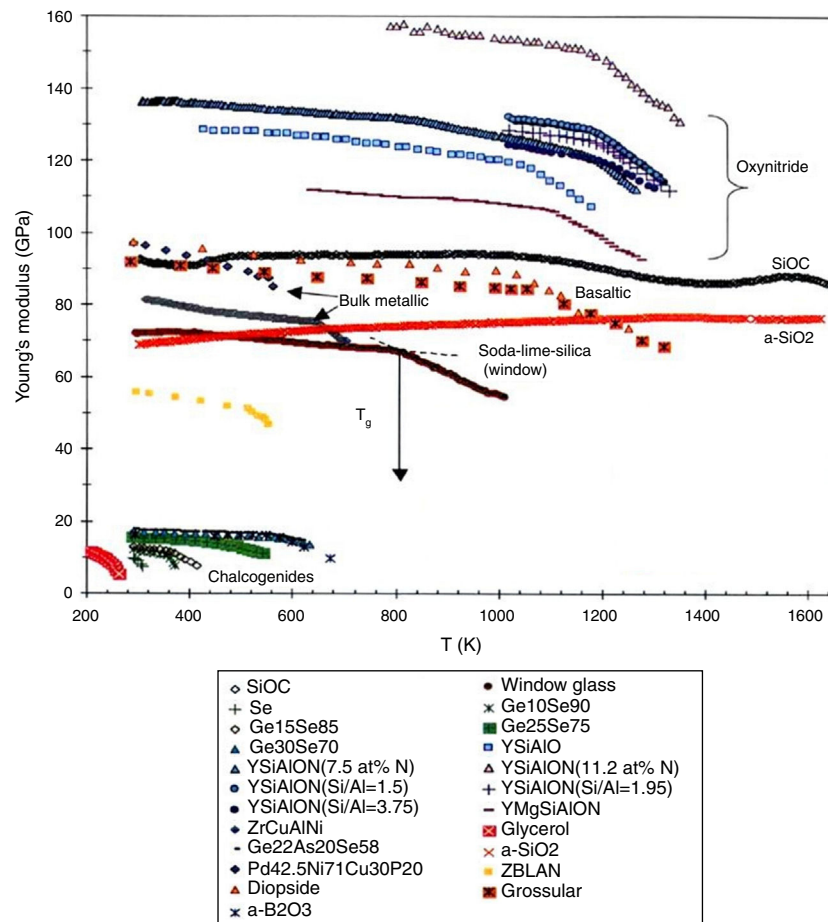


Fig. 3 – Variation of Young's modulus with temperature for several glass systems [35].

correlation between properties variation and the amount of silicon nitride dissolved. In all cases, glass transition temperature, hardness, toughness and fracture resistance increased with increased nitrogen content, while the thermal expansion coefficient decreased. Infrared spectroscopy showed that the nitrogen became chemically bonded to the silicon in the glass network and, substituting the oxygen, led to a stiffer, more cross-linked network [18]. However, the cationic ratios of these compositions varied throughout and it was not possible to unequivocally establish that the increases in the different properties were due solely to the increased levels of nitrogen in the glass.

In order to clarify this situation, Drew [37] carried out exhaustive studies of the glasses in the M–Si–O–N and M–Si–Al–O–N systems with variable O: N ratios and fixed cationic compositions. With this set-up, it was possible to directly compare systems with different modifiers but constant nitrogen contents, as well as systems with different nitrogen contents in a given glass system. These studies showed that in glasses in the Mg–, Ca–, Y– and Nd–Si–Al–O–N systems with a fixed cationic ratio, the incorporation of nitrogen caused glass transition temperature, viscosity, resistance to devitrification, refractive index and dielectric constant values to increase. Subsequent studies [8,16,17] confirmed that, when bridging and non-bridging

oxygens are replaced by nitrogen, glass transition temperature, viscosity, hardness, Young's modulus, fracture toughness and chemical durability all increased linearly with nitrogen content, while the thermal expansion coefficient decreased.

Several studies have also been conducted into systems with mixed modifiers. Rouxel and his co-workers [38] observed in several oxynitride glasses the same mixed-modifier effect that appears between calcium and magnesium in alkali silicate and aluminosilicate glasses. This effect is revealed as a non-monotonic trend in glass transition temperature when calcium is replaced by magnesium. Pomeroy et al. [39] studied several compositions of Si–Al–O–N glasses modified by trivalent mixed modifiers (La–Y, La–Er and Nd–Y) corresponding to rare-earths. The results showed that properties such as glass compactness, Young's modulus, microhardness, glass transition temperature and dilatometric softening temperature (T_{ds}) all increased linearly with the effective cationic field strength (ECFS) of the modifiers. In contrast, molar volume and the thermal expansion coefficient both decreased. These results were consistent with those obtained in previous studies [10,40,41] in glasses with fixed cationic ratios and only one modifier. It was then suggested that all these glasses present the same silicoaluminate glass network with oxygens and nitrogens. The only difference is the force with which the modifiers attract the adjacent

non-bridging oxygens. The magnitude of the attractive forces should increase as cation field strength (CFS) increases. This higher attractive force explains the decrease in molar volume, and the increase in glass compactness and Young's modulus. As these attractive forces on the non-bridging oxygens increase, the motion resistance of the $-\text{Si}-\text{O}-\text{Si}-\text{N}-$ chains should also increase, as well as the motion resistance of the structural units. These two effects can be ascribed to the increase in glass transition temperature and dilatometric softening temperature, respectively. By way of conclusion, it was suggested that, all other factors being equal, the effective cationic field strength controls the properties of $\text{Si}-\text{Al}-\text{O}-\text{N}$ glasses with one or two rare-earth modifiers.

However, in other studies [42,43] it has been shown that this conclusion was only valid for mixed modifiers of the same valence. In fact, in systems with several modifiers whose valences are not equal, such as those in the $\text{Mg}-\text{Y}-\text{Si}-\text{Al}-\text{O}-\text{N}$ system, other correlations are needed to explain the variations in properties when one cation replaces another. In these works, only linear correlations were obtained, representing glass transition or dilatometric softening temperatures as a function of the number of tetrahedra per effective modifier. This parameter is defined as the difference between the number of modifier cations and the cations needed to charge balance the tetrahedral AlO_4^- . The presence of these structural units means that there are fewer proper modifier cations. As a consequence, a linear relationship between thermal properties and the number of structural $(\text{Si}, \text{Al})(\text{O}, \text{N})_4$ units is to be expected, since it reflects a higher density of linkages within the glass network. In other words, a higher proportion of structural units coordinated with the same modifier cation should be reflected in a higher linking intensity with this modifier.

A special case: oxyfluoronitride glasses

Painter and his co-workers [44] studied the variation in properties and thickness of the glass layer formed in the grain boundaries during the sintering of silicon nitride doped with F and Cl. The results showed that the addition of these two highly-electronegative anions strongly influences the mechanical properties of these ceramics at high temperatures. Significant decreases in softening temperature and viscosity were also reported. These oxynitride glasses, formed at the triple points and grain boundaries of the silicon nitride-based ceramics, are known as oxyfluoronitride glasses.

There is very little information available on oxyfluoronitride glasses and their properties. Vaughn and Risbud [45] incorporated nitrogen into glasses in the $\text{Zr}-\text{Ba}-\text{Al}-\text{Y}-\text{O}-\text{F}$ system with the intention of increasing their thermal stability and improving their mechanical properties. What they actually observed was an increase in the glass transition temperature and crystallisation temperatures, as well as hardness. Fletcher and Risbud [46] used nitrogen to increase the stability and chemical durability of some fluorophosphate glasses in the $\text{M}-\text{Al}-\text{P}-\text{O}-\text{F}-\text{N}$ system (where $\text{M} = \text{Ba}, \text{Na}$).

However, it was not until 20 years later that the first systematic studies were carried out in order to determine the combined effect of adding nitrogen and fluorine to aluminosilicate glasses. Hanifi and his co-workers [47] explored the

glass-forming region in the $\text{Ca}-\text{Si}-\text{Al}-\text{O}-\text{N}-\text{F}$ system and compared it with that obtained previously by Hampshire et al. [1] in the $\text{Ca}-\text{Si}-\text{Al}-\text{O}-\text{N}$ system (Fig. 9). The results showed that the glass-forming region at 1700°C in the oxynitride system is smaller than that obtained at a lower temperature (1650°C) with added fluorine (oxyfluoronitride system). The glass-forming region is seen to expand in compositions that are richer in calcium (up to 49 eq%). The addition of fluorine, even in low quantities (1 eq%), expands the glass-forming region and facilitates the dissolution of the modifier cations and nitrogen in the melt.

The fluorine solubility threshold was established as 7 eq% for glass compositions of 20 eq% nitrogen (keeping the $\text{Al}:\text{F}$ ratio constant). However, for lower nitrogen contents, this threshold was found to be higher: 8 eq% F for compositions with 10 eq% N, and 10 eq% F for compositions with 5 eq% N. Similarly, it was found that the solubility threshold of nitrogen increased from 26 eq% to 40 eq% in a fluorine-free composition with 1 eq% F. However, for 5 eq% F, the solubility threshold decreased again to 25 eq% N. The authors concluded that fluorine affects nitrogen dissolution in the melt, lowering the melting temperature and preventing the formation of crystalline phases. This study opened up the possibility of obtaining glasses with even higher nitrogen contents by using fluorine as a melting agent, harnessing the well-known beneficial effects of nitrogen incorporation on the glasses' physical and mechanical properties.

In another study [48], the systematic replacement of oxygen by nitrogen and fluorine was investigated in a composition with a fixed cationic ratio $\text{Ca}:\text{Si}:\text{Al}$ (28:57:15). The results showed that the introduction of fluorine had no effect on molar volume, glass compactness, Young modulus or hardness. However, the thermal properties were greatly affected: the glass transition temperature decreased by 21°C for each equivalent of fluorine introduced. This effect was attributed to the substitution of bridging oxygens with terminating fluorines and the consequent reduction in connectivity of the glass network. Meanwhile, the results observed for the introduction of nitrogen were consistent with those obtained previously for oxynitride glasses: increased glass compactness, Young modulus, microhardness, glass transition temperature and softening temperature. The gradients obtained for T_g and T_{ds} were between 2.5 and 3°C per equivalent of nitrogen introduced. The authors highlighted the independence of Young modulus and microhardness from the glass transition temperature in these oxyfluoronitride glasses (as shown in Fig. 10), in contrast to earlier results [35].

In a later study, these same authors [49] analysed more exhaustively the physical, thermal and mechanical properties, confirming these results. Likewise, they sought to explain the changes in properties in relation to glass structure. To do so, the glass transition temperature values for different glasses (with fixed nitrogen and variable fluorine contents, or vice versa) were represented as a function of the cross-link density (CLD) (Fig. 11). As would be expected, a linear dependence was revealed. However, rather than the data all appearing on a single line, they are grouped in different lines depending on their nitrogen and/or fluorine content. Parallel lines are observed for different fluorine contents with a fixed nitrogen content. The authors explained this effect based on the assumption,

possibly wrong, that all the aluminium is in four-fold coordination. However, it is highly probable that, when the fluorine is introduced into the compositions, some of the aluminium atoms would change their coordination state to V or VI. In this instance, the values for CLD would be different, likely adjusting to a single adjustment line.

This study confirmed the almost nonexistent effect of fluorine on mechanical properties. These properties (Young modulus and glass microhardness) were shown to be dependent on glass compactness (Fig. 12). The higher the packing of the glass network, the higher the values achieved for these two mechanical properties.

These authors also studied how the introduction of nitrogen and fluorine affected the compactness of the network. To do so, the free volume of the network was determined as the difference between the molar volume and the volume occupied by a mole of ions. Meanwhile, glass compactness was calculated as the relationship between the volume occupied by a mole of ions and molar volume. Results (Fig. 13) indicated that, while nitrogen considerably lowers the free volume, fluorine introduction increases it only slightly. The lower the free volume, the greater the glass compactness and, therefore, the better the mechanical properties. The fact that fluorine barely affects either the free volume or glass compactness explains how the mechanical properties remain constant with the introduction of fluorine into oxynitride glass compositions.

These compositions were analysed by studying their crystallisation [50]. The results obtained showed that, while oxyfluoronitride glasses are inert when immersed in simulated body fluid, the glass-ceramics are favourable to the deposition of hydroxyapatite and also release calcium. Therefore, the authors suggest the potential of these glass-ceramics for use as biomaterials, provided their composition is adjusted to obtain the most suitable crystalline phases.

A similar study [51], performed in a system with mixed modifiers and a fixed cationic ratio of C:Si:Al (20:50:30), confirmed these results. These authors completed this study by analysing the effect of replacing calcium by other modifiers, such as Y, Er and Nd [52], for fixed nitrogen and fluorine contents. The results obtained clearly showed that the glass properties are either solely dependent on the effective cation field strength, if modifier cation valency is the same (e.g. substituting Mg for Ca), or on the effective cation field strength and the number of (Si, Al) (O, N, F) tetrahedra associated with each modifier when Ca is replaced by the trivalent modifiers. Combining these correlations with those observed in previous studies linking glass properties to N and F substitution for O, the authors remarked that the properties of Ca–M–Si–Al–O–N–F glasses can be described by correlations involving independent, but additive contributions by N and F substitution, effective cation field strength and the number of tetrahedra associated with each modifier ion.

Structural considerations

The changes in properties observed with the progressive incorporation of nitrogen in the glass network are explained by Mulfenger's theory [11]. This author suggests that the

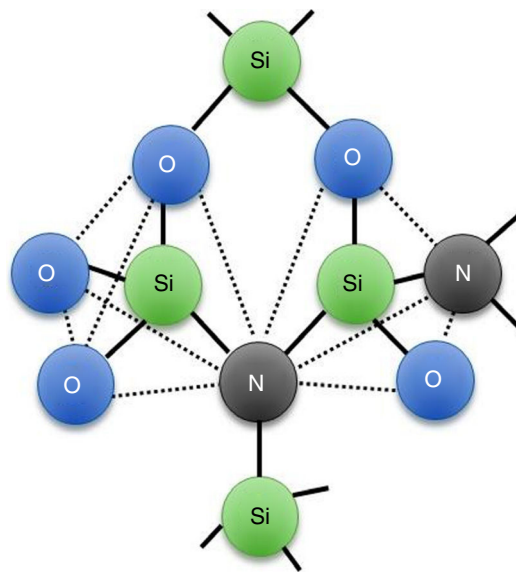


Fig. 4 – Oxygen substitution by nitrogen and increase in the cross-link density.

oxygens in the SiO_4 tetrahedral are partly replaced by nitrogen atoms, leading to an increase in the coordination index of the non-metallic atoms, as shown in Fig. 4.

This increase in the coordination index of the non-metallic cations results in a stiffer glass network due to a higher bond density. In fact, the improvement in the different properties in line with the increase in nitrogen content is a consequence of a more compact glass network, since nitrogen can bond to three tetrahedra, while oxygen can only link to two. However, initially there was no evidence of this, since the data published on infrared spectroscopy [15] suggested only the presence of Si–N bonds. Later, studies were published on the coordination of nitrogen in oxynitride glasses using FTIR and XPS [21], suggesting that nitrogen was present not only in tricoordinated form, but also in different environments as a non-bridging anion:



Nitrogen atoms can therefore take the form of either $\text{N}^{[3]}$, $\text{N}^{[2]}$ or $\text{N}^{[1]}$, as represented in Fig. 5 [29]. Meanwhile, oxygen atoms can appear as either $\text{O}^{[2]}$, $\text{O}^{[1]}$ or $\text{O}^{[0]}$, although $\text{O}^{[0]}$ is highly improbable.

Modifier cations balance the charge of both the non-bridging nitrogens and the oxygens. Since $\text{N}^{[3]}$ is such a powerful network “former”, it is accepted that even $\text{N}^{[2]}$ plays a role in network formation [53].



Fig. 5 – Possible links of the nitrogen atoms in a silicon oxynitride network [29].

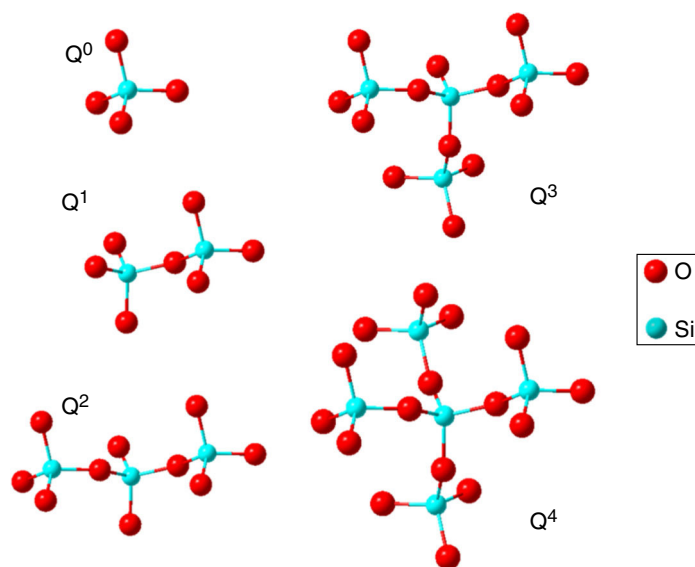


Fig. 6 – Possible structural units Q in silicate oxynitride glasses [29].

The glass structure is formed with different Q^n structural units made up of SiX_4 tetrahedra with n bridging anions ($X = O$ or N), depending on the cross-link level of the glass network. The possible values for n range from 0 to 4, leading to the 5 possible structural units which are represented in Fig. 6 [29].

Fig. 7 shows a schematic representation of an oxynitride glass network in a $M-Si-Al-O-N$ system [54]. The network-forming cations Si^{4+} and Al^{3+} , occupy the centre of the tetrahedral positions and are linked by bridging oxygens and nitrogens. The modifier cation is trivalent (M^{3+}) and balances the excess charge of the tetrahedral $[AlO_4]^-$. However, it also acts as a network modifier, creating non-bridging nitrogens and oxygens since the $M:Al$ ratio is higher than 1:3.

Dolekcecic and his co-workers [56,57] used Raman spectroscopy to study glass structure in $Er-Si-Al-O-N$ glasses

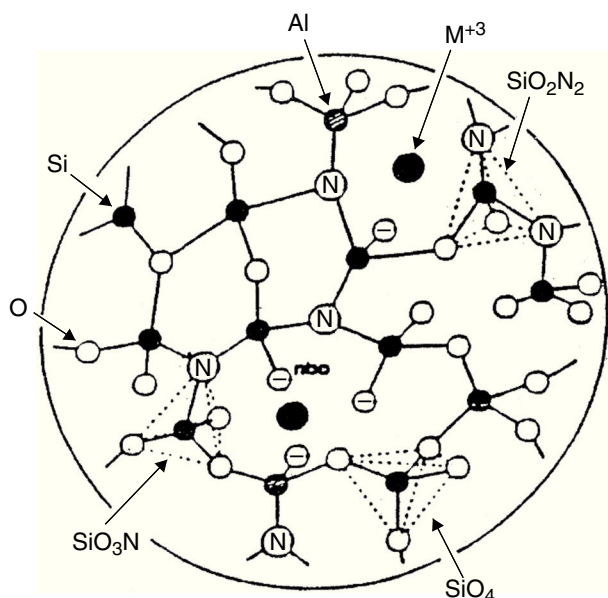


Fig. 7 – Schematic representation of an oxynitride glass network [55].

with nitrogen contents of between 0 and 22 eq%. They confirmed the preference of nitrogen to bond to silicon rather than aluminium. The study showed that nitrogen incorporation leads to a series of structural changes in the glass. While the number of Q^2 units remains unaltered when nitrogen is incorporated, the number of Q^3 units diminishes as the number of Q^4 units rises. The authors suggested that the conversion follows a particular model (Fig. 8) [47].

These results were consistent with those obtained by Sakka [58], who claimed that 80% of the nitrogen atoms were present in SiO_3N structural units (Q^4). It must be noted that these structural units have a negative charge, similar to that found in the tetrahedral $[AlO_4]^-$, and that they therefore require a modifier cation to compensate. This leads to a greater cohesion of the glass network. This effect is contrary to what happens in the case of the equivalent oxide glasses, where the modifier cations only cause the glass network to rupture because of the formation of non-bridging oxygens.

In contrast to the above, the atomic structure of the new series of nitrogen-high oxynitride glasses (with up to 68 eq% nitrogen) synthesised by Hakeem et al. [25] is much more diverse. These authors claim that the higher the nitrogen

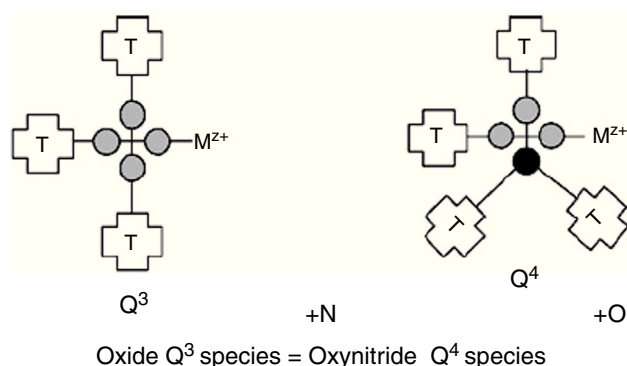


Fig. 8 – Q^3 to Q^4 conversion with nitrogen incorporation [56].

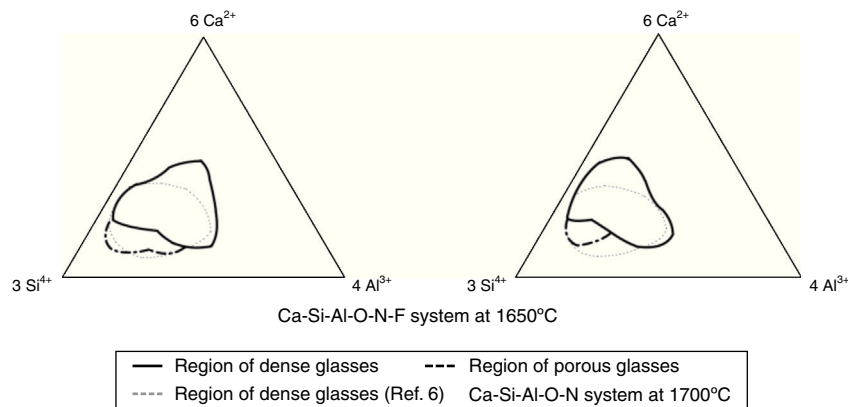


Fig. 9 – Comparison of the glass-forming region in the system Ca–Si–Al–O–N–F (20 eq% N) and the system Ca–Si–Al–O–N (20 eq% N) (Left: 1 eq% F; Right: 5 eq% F) [47]. (Ref. [6] in the original figure is Ref. [1] in this paper).

content, the higher the number of Si–N bonds, making the formation of species such as SiO_2N_2 , SiON_3 or even, SiN_4 is more favourable. For nitrogen contents lower than 20 at%, the main structural group is SiO_3N . However, for nitrogen contents higher than 35 at%, the main structural unit is SiO_2N_2 . Furthermore, the formation of Al–N bonds was detected when nitrogen levels are high, together with a greater probability of the presence of the $\text{N}^{[2]}$ and $\text{N}^{[1]}$ species. This study led to the conclusion that the atomic structure of oxynitride glasses strongly depends on their nitrogen content, as well as on their cationic composition.

Applications

Oxynitride glasses can be framed in a specialised group of “new” glasses with novel functions with high possibilities of being used in modern, highly specialised, industrial sectors such as optoelectronics, microelectronics, communications

technologies, biomedical devices, and niche areas of the automotive and architectural sectors [53].

The unique properties of oxynitride glasses have led to a search for possible areas of application. Commercial applications are limited by high economic costs, the relatively complex synthesis processes and their lack of transparency in the visible spectrum. However, their low chemical reactivity with the introduction of nitrogen is exploited in the manufacture of ordinary glass for windows in the form of cooling the glass sheets under a nitrogen flow [59].

Other potential areas for application include high-elastic modulus glasses for hard disks, ceramic seals, coatings on metals, encapsulation of radioactive waste storage, joints in structural ceramics, ceramic coatings for use at high temperatures and glass fibres. Likewise, other applications are possible in the area of safety, such as bullet-proof glasses and high resistance windows [58].

More recently, a new family of materials based on oxynitrides with luminescent properties has gained special relevance due to its possible applications. Their high efficiency, broad emission band, high thermal resistance and

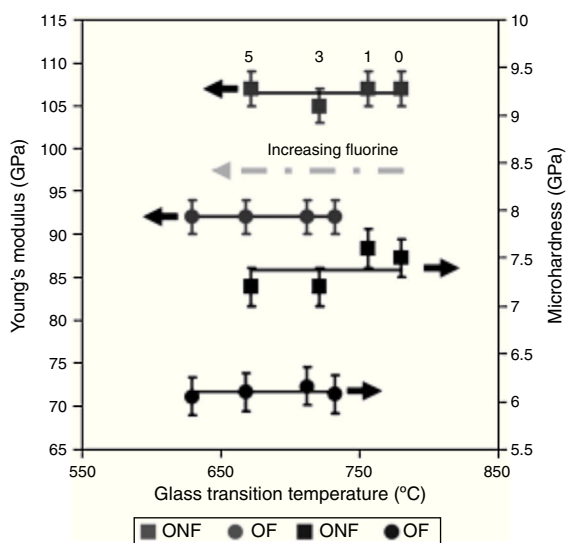


Fig. 10 – Independence of Young modulus and microhardness with regard to glass transition temperature for glasses with 20 eq% N (ONF) or 0 eq% N (OF) with different fluorine contents (0, 1, 3 and 5 eq%). [48].

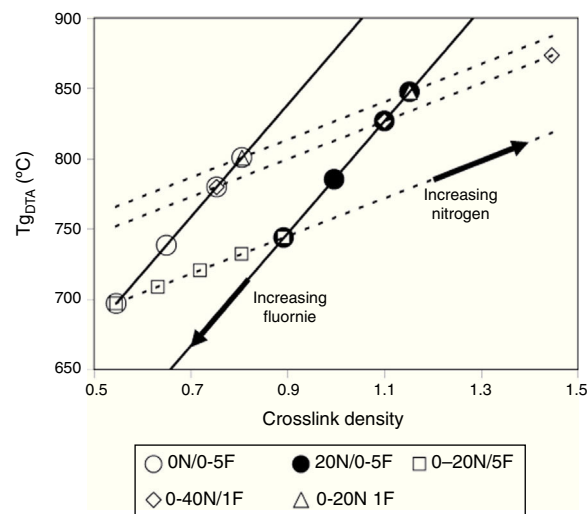


Fig. 11 – Effect of the crosslink density for different glasses (with fixed N contents and variable F contents or vice versa). [49].

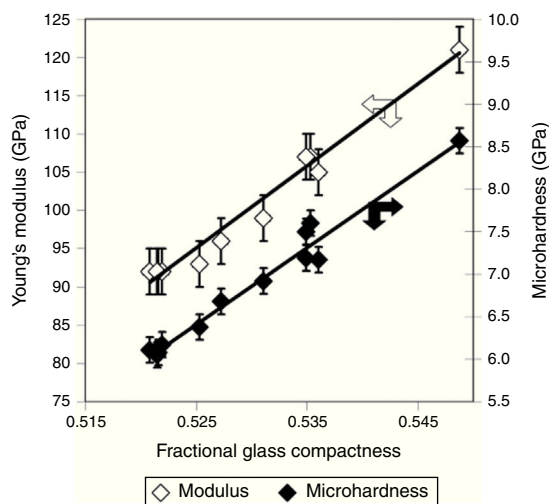


Fig. 12 – Effect of glass compactness on Young modulus and microhardness [49].

high chemical stability make luminescent oxynitride materials very interesting to work with, opening up a new field of research for oxynitride glasses [60–62].

The list of possible future developments include passive coatings on electronic substrates (due to their higher dielectric constants and elastic moduli); special stiff windows with thinner sections allowing weight and energy savings (due to their higher elastic moduli), hard disc drives with higher rotation speeds (due to their higher modulus and lower densities); new bioactive glasses and glass-ceramics (due to their better load-bearing properties); novel glass decoration enamels (due to the colour effects found in RE–Si–Al–O–N glasses); novel glaze systems for refractory protection (due to their higher viscosities); joints in silicon nitride based ceramics and in these ceramics-metals composites (due to the fact that the grain boundary glasses are similar in composition to the bulk glasses); higher temperature range glass-ceramics for structural applications (due to their higher refractoriness which would make them more stable at higher service temperatures) [63].

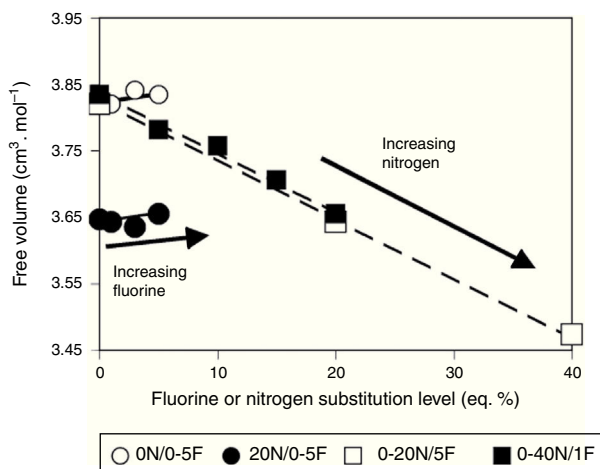


Fig. 13 – Free volume as a function of fluorine content for a fixed nitrogen content and vice versa [49].

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