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MECHANICAL PROPERTIES OF OXYNITRIDE GLASSES

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Abstract

Oxynitride glasses combine a high refractoriness, with T_g typically $>850^\circ\text{C}$, and remarkable mechanical properties in comparison with their parent oxide glasses. Their Young's modulus and fracture toughness reach 170 GPa and $1.4 \text{ MPa}\cdot\text{m}^{0.5}$, respectively. Most reports show

good linear relationships between glass property values and nitrogen content. There is a clear linear dependence of Young's modulus and microhardness on fractional glass compactness (atomic packing density). They also have a better resistance to surface damage induced by indentation or scratch loading. The improvements stem from the increase of the atomic network cross-linking - thanks to 3-fold coordinated nitrogen - and of the atomic packing density, despite nitrogen being lighter than oxygen and the Si-N bond being weaker than the Si-O bond.

For constant cation composition, viscosity increases by ~ 3 orders of magnitude as ~ 17 eq.% oxygen is replaced by nitrogen. For rare earth oxynitride glasses with constant N content, viscosity, Young's modulus, T_g and other properties increase with increasing cation field strength (decreasing ionic radius).

Research continues to find lighter, stiffer materials, including glasses, with superior mechanical properties. With higher elastic moduli, hardness, fracture toughness, strength, surface damage resistance, increased high temperature properties, oxynitride glasses offer advantages over their oxide counterparts.

1 | INTRODUCTION

Researchers are investigating new types of glasses which possess enhanced mechanical properties such as higher elastic moduli, hardness, strength and fracture toughness. Oxynitride glasses, in which nitrogen atoms substitute for oxygen in silicate or aluminosilicate glass networks, are examples of these new glasses which exhibit higher elastic modulus and hardness, greater slow crack growth resistance, improvements in fracture resistance and increased glass transition and softening temperatures and viscosities compared

with their oxide counterparts.¹⁻³ These changes in properties are known to be due to the increased cross-linking within the glass structure as 2-coordinated bridging oxygen atoms are replaced by 3-coordinated nitrogen atoms.⁴⁻⁷

Many of the studies of oxynitride glasses have been on glasses in the Y-Si-Al-O-N system.^{5,7-9} Loehman⁸ suggested correlations between the nitrogen content of Y-Si-Al-O-N glasses and properties. Glass transition temperature (T_g), microhardness and fracture toughness were seen to increase while thermal expansion coefficient decreased with increasing amounts of silicon nitride added to a yttrium alumino-silicate glass. IR spectroscopy confirmed the formation of Si-N bonds in the glass network. However, increasing the silicon nitride content results in increases in the Si:(Y+Al) ratio and therefore the observed changes in properties are attributable to both the increased glass-network connectivity resulting from replacement of O-Si-O bridges by O-Si-N< linkages and the replacement of the other cations (Al and Y) by silicon, also leading to greater cross-linking.

Further systematic investigations^{10,11} on glasses with fixed cation ratios and varying N:O ratio showed, unambiguously, that incorporation of nitrogen results in increases in microhardness, glass transition temperature (T_g), viscosity, resistance to devitrification, refractive index, dielectric constant and a.c. conductivity. In a more extensive study of the Y-Si-Al-O-N system⁵, it was confirmed that microhardness, elastic moduli, glass transition temperature, viscosity, all increase systematically with nitrogen content while the coefficient of thermal expansion (CTE) decreases with increasing N:O ratio for different series of glasses. These trends were also confirmed by other authors.⁷

At first sight, the enhancement of the mechanical properties stemming from the partial substitution of oxygen by nitrogen can be attributed to the increased cross-linking within the glass atomic network. Nevertheless there still remain some striking and poorly understood features regarding the incidence of nitrogen on fracture toughness, on the elastic moduli or on the viscosity. Some of these are discussed in the present paper.

2 | REPRESENTATION OF OXYNITRIDE GLASS SYSTEMS AND PREPARATION OF GLASSES

The concept of reciprocal salt pairs is a convenient approach for representation of both Si-Al-O-N and M-Si-Al-O-N systems,^{1-3,5,10,11} where M = Mg, Ca, Sr, Y and the rare earth lanthanides (RE). The four-component Si-Al-O-N system is a square plane which has, as components, the oxides and nitrides of silicon and aluminium (the salt pairs). The introduction of a further cation gives a five-component system represented by Jänecke's triangular prism.^{5,10,11} The concentrations of all components are expressed in equivalents instead of atoms or gram-atoms, in fact, as equivalent percentages (eq.%) of either cations or anions as follows:

$$\text{equivalent \% (eq.\%) of Si} = (4[\text{Si}] \times 100) / (4[\text{Si}] + 3[\text{Al}] + v_{\text{M}}[\text{M}]) \quad (1)$$

where [Si], [Al] and [M] are, respectively, the atomic concentrations of Si, Al and the modifying cation M and 4, 3 and v_{M} are their respective normal valencies.

$$\text{equivalent \% (eq.\%) of N} = (3[\text{N}] \times 100) / (2[\text{O}] + 3[\text{N}]) \quad (2)$$

where [O] and [N] are, respectively, the atomic concentrations of oxygen and nitrogen within any composition and 2 and 3 are their respective valencies.

$$\text{equivalent \% (eq.\%) oxygen} = 100 - \text{eq.\% N} \quad (3)$$

2.1 | Glass Preparation

Oxynitride glasses⁴⁻⁵ are prepared by mixing the appropriate powders – silica, alumina, the modifying oxide(s) plus silicon nitride or aluminium nitride (accounting for the oxide impurities in the nitrides) – in isopropyl alcohol in a ball mill with sialon milling media, followed by evaporation of the alcohol. Glasses (50-60g) are melted in boron nitride lined graphite crucibles under 0.1MPa nitrogen pressure at 1600-1750°C for 1h. Following melting, the glass is quickly removed from the furnace and poured into a preheated graphite mould at a temperature close to T_g (~850-900°C). The glass is annealed at this temperature for one hour to reduce thermally induced stresses and then slowly cooled.

3 | MECHANICAL PROPERTIES AT ROOM TEMPERATURE

3.1 | Elasticity and Hardness

Figure 1 shows the effect of nitrogen content on Young's modulus (E) of different Y-Si-Al-O-N glasses^{5,7,9,12} with fixed Y:Si:Al ratios and, as expected, E increases linearly with increasing nitrogen content. Figure 2 shows the effect of nitrogen content on microhardness (μH) of Y- and Er-Si-Al-O-N glasses^{5,7,9,12} with fixed M:Si:Al ratio and, as with E, μH increases linearly with increasing nitrogen content. Elastic modulus and hardness data for a range of oxynitride glasses have been analysed² and show also good linear relationships

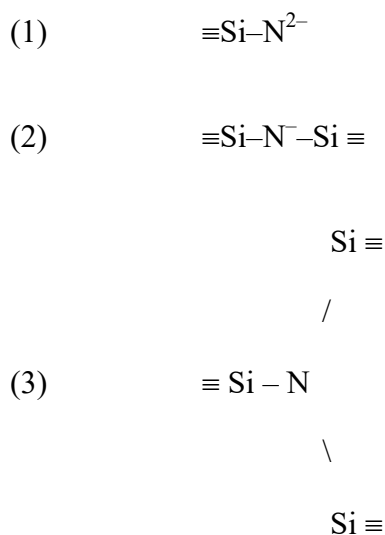
between glass property values and nitrogen content with correlation coefficients generally of the order of 0.99.

Gradients of plots of elastic modulus versus nitrogen content are in the range 0.8 to 1.8 GPa.(eq.%N)⁻¹ with the majority of gradients close to 1.0 GPa.(eq.%N)⁻¹. Gradients of plots of microhardness versus nitrogen content lie in the range 0.07 to 0.13 GPa.(eq.%N)⁻¹ with the majority of the gradients close to 0.1 GPa.(eq.%N)⁻¹. Generally, the substitution of 20 eq.% N for oxygen in these glasses gives rise to an increase in Young's modulus of 25-45 GPa and an increase in hardness of ~1.5-2.5 GPa.

It is noteworthy that the Si-N binding energy (437 kJ.mol⁻¹) is smaller than that of the Si-O bond (800 kJ.mol⁻¹)¹³. Indeed, there is no straightforward relationship between elastic moduli and binding energies. It should be recalled, for instance, that pure amorphous silica and standard window glass (about 30% alkaline and alkaline-earth oxides) compositions lead to glasses with nearly identical Young's moduli (~ 70 GPa) in spite of much different average binding energies. There might be three sources for the increases of the elastic moduli with increase in nitrogen content:

- i) The increase of the atomic compactness (note that elastic moduli are expressed in Pa, i.e. in volume density of energy);
- ii) The greater resistance to bending of the Si-N-Si bond compared with the Si-O-Si bond,¹⁴ which results from the more covalent nature of the Si-N bond, and
- iii) The increased anion coordination with Si when N replaces O (likely to correlate with i).

The nitrogen atoms may be coordinated to 1 (non-bridging), 2 (partial bridging with bonding also to a modifying cation) or 3 (completely bridging) Si atoms, as in:



In the case of (1) and (2), the local charge on the non-bridging or partially bridging nitrogen ions is balanced by the presence of interstitial modifying cations in their local environment. Sakka⁶ has shown from MAS-NMR analysis that for a glass with composition (in eq.%) 21Y:48Si:31Al containing about 10 eq.% N, the average coordination number of N atoms is 2.86. If it is assumed that only type (2) and (3) coordinations are present, it was estimated that 86% of N atoms were 3-fold coordinated and 14% were 2-fold coordinated with Si.

Nitrogen substitution for oxygen in oxynitride glasses leads to a reduction in molar volume (MV) which may be calculated using the expression:

$$\text{MV} = \frac{\sum_1^i x_i m_i}{\rho} \quad (4)$$

where x_i is the atomic fraction of each element i in the glass, m_i is its atomic mass and ρ is the measured glass density. Conversely, the fractional glass compactness (C), i.e. the minimum theoretical volume occupied by the ions in the glass divided by the effective volume of the glass, increases with increasing nitrogen substitution. Glass compactness or atomic packing density may be calculated according to the expression:

$$C = \frac{\sum_1^i x_i v_i \cdot N}{\sum_1^i x_i m_i} \cdot \rho \quad (5)$$

where x_i is the fraction of ionic species i , v_i is the volume of ionic species i , m_i is the atomic mass of species i , N is Avogadro's number and ρ is glass density. In general, an average value is obtained, as the radii of each ion will depend upon their local coordination within the glass. Usually v_i is calculated using the ionic radii given by Shannon¹⁷. Rouxel¹⁸ has conclusively shown that, for a wide variety of different types of glasses, Young's modulus is very sensitive to the fractional compactness of the glass structure. Indeed, for oxynitride glasses at least, the increase in the atomic packing efficiency with the incorporation of nitrogen predominates over the decrease of the interatomic binding energy.

Figure 3 shows that changes in molar volume and fractional glass compactness as a function of nitrogen content for some Y-Si-Al-O-N glasses are linear.² Figure 4 shows that there is a monotonic correspondence between fractional glass compactness and both microhardness and Young's modulus for these same Y-Si-Al-O-N glasses.² These changes in molar volume and compactness indicate that the replacement of oxygen by nitrogen induces a

contraction of the glass structure, as already suggested.¹⁴ The reason for this contraction still remains to be elucidated.

When the Si and N contents are fixed, E increases when Al is replaced by Y, such that increases in the Y:Al ratio have the same effect on E as increasing the N content.^{5,9} In the case of silicate (oxide) glasses, non-bridging oxygen (NBOs) atoms replace bridging oxygen atoms as modifier contents increase. In the case of (2) above, while the N atom links two silicon atoms rather than three, it is still effectively a "bridging" ion. With fixed Y and N contents and Si:Al ratio decreasing, E once again increases which appears to result from an increase in the proportion of Al ions in 5- and 6-fold coordination with oxygen.⁹ A loss of 4-fold coordination of Al reduces the Al-O-Si linkages and increases the number of NBOs. Yttrium acts to compensate the charge difference between Al and Si as a "network dwelling" cation creating Al-O-Y linkages, which then results in higher coordination of O with Y.¹⁶ These effects also lead to an increase in glass network compactness or a contraction of the glass structure.

The effects of nitrogen substitution for oxygen and yttrium substitution for magnesium in a series of Mg-Y-Si-Al-O-N glasses on various properties has been investigated.¹⁹ The cation ratios used were 28M:56Si:16Al with M = Mg or Y with Mg:Y ratios of 28:0, 14:14 and 0:28. As expected from the previous results presented in Figure 1, nitrogen substitution for oxygen at a fixed cation ratio results in a linear increase in Young's modulus.

Figure 5 shows changes in Young's modulus as a function of Mg content for 0, 10 and 15 eq.% N glasses and confirms that oxygen replacement by nitrogen has a much more significant impact upon E than changes in Mg:Y ratio.¹⁹ The increase in Young's modulus for

each eq.% oxygen substituted by nitrogen is of the order of 1.4 GPa. Thus, increasing N content to 15 eq.% results in an increase in Young's modulus of these glasses by ~21 GPa, which contrasts with a decrease when Mg is substituted for Y of the order of 3 to 6 GPa which is within the limits of experimental error (± 3 GPa).

As might be expected, density decreases when magnesium substitutes for yttrium due to the lighter atomic weight of Mg. However, there is also a decrease in the molar volume with Mg as shown in Figure 6. Unlike the case when oxygen is replaced by nitrogen, there is no apparent linear correlation between molar volume and magnesium content. The decrease is to be expected since Mg has a smaller ionic volume than Y. The glass compactness data show¹⁹ that, while changes are small compared to those observed for increasing nitrogen content, there is a general trend towards a decrease in glass compactness as magnesium substitutes for yttrium. Data for Ca- and Ca-Y-Si-Al-O-N glasses²⁰ confirm the linear relationships between Young's modulus or hardness and fractional glass compactness²¹. Increases in Young's modulus when nitrogen substitutes for oxygen and yttrium substitutes for magnesium are mainly due to increases in glass compactness. The overall conclusion was that the effects of anion replacement (N for O) and modifier cation replacement (Mg for Y) on elastic modulus are independent of each other and additive, rather than synergistic.

For rare earth-Si-Al-O-N glasses with constant nitrogen content, Young's modulus and hardness increase linearly with increasing cation field strength ($CFS = v/r^2$, v is valency and r is ionic radius).²²

Poisson's ratio (ν) data indicate that ν increases with increasing N content. Poisson's ratio is defined as the negative of the ratio of transverse contraction strain to longitudinal extension

strain in the direction of elastic loading in pure tension ($\nu = -\epsilon_t/\epsilon_l$) and is a measure of the resistance of a material to volume change upon change of shape. It is small for shear-resistant materials, such as covalently bonded solids, and tends towards 0.5 for incompressible bodies. For glasses in general, ν lies between 0.1 and 0.4 and decreases as the cross-linking of the glass network increases¹⁸. A high degree of cross-linking usually results in a low atomic packing density and, hence, in a relatively open structure as exemplified by the cases of amorphous silica and amorphous germania. Silicate glasses have typically ν values around 0.2–0.25, while oxynitride silicate glasses exhibit higher values, up to 0.36^{18,20,23}. In this regard the observed increase of ν with increasing N content is surprising; but it corroborates the fact that nitrogen increases both the cross-linking and the atomic compactness.

3.2 | Fracture Behavior of Oxynitride Glasses

The fracture behavior of Y-Si-Al-O-N glasses (35Y:45Si:20Al) has been assessed by means of flexural strength measurements on an oxide glass and one containing 17 eq.% N.²⁴ 3-point bending test bars were prepared with different polished surfaces down to 1 μm and 1/4 μm . Two “flame polishing” heat treatments, at $T_g-20^\circ\text{C}$ or $T_g+20^\circ\text{C}$, were carried out under nitrogen atmosphere on the polished flexural specimens in order to round out the crack tips produced during the surface-finishing step. Fracture analysis was used in order to determine the origin of the fracture and the fracture mirror radius. Without any heat treatment (just after polishing), the mean flexural strengths of the oxide and oxynitride glasses are similar with similar deviations in strength values. Indeed, fracture occurs from defects present on both the plane surface and the chamfer so that the contribution of the intrinsic (bulk) materials

properties remains minor. A heat treatment at $T_g - 20^\circ\text{C}$ for 30 minutes results in an increase in strength to 295 MPa for the oxide glass and to 344 MPa for the oxynitride glass which is twice the strength measured on the non-treated glasses. Fracture occurs mainly from defects on the plane surface. After heat treatment at $T_g + 20^\circ\text{C}$, the strength of the oxynitride glass is three times higher (479 MPa) than without treatment whereas there is no significant increase for the oxide glass so that there is a significant difference in strength between the two glasses. Following this treatment, samples fractured from within the bulk of the material and it is clear that nitrogen is effective in enhancing the strength. However, with the strength value obtained after heat treatment, and further considering a fracture toughness of about $1 \text{ MPa}\cdot\text{m}^{0.5}$ the critical flaw size is expected to be of the order of ~ 1 micron, i.e. one thousand times larger than the typical scale of the glass network structure. Therefore, the reason for the strengthening effect is likely to be in the global stiffening and tightening of the glass network and a possible reduction of the sensitivity to the presence of existing flaws due to nitrogen.

The general trend with fracture toughness (K_{Ic}) of materials is that as refractoriness increases, brittleness also increases. Polymers are less brittle than metals and, in general, metals are less brittle than glasses and ceramics. This tendency also holds within a given class of materials: low melting point metals such as lead or tin are much more ductile than refractory metals such as tungsten or molybdenum. However, in the case of silicon oxynitride glasses T_g increases with increasing nitrogen content^{20,22} and preliminary experiments, by means of the indentation cracking method²⁵, suggest that fracture toughness is increased as nitrogen is incorporated into the glass. The so-called parent oxide glasses (nitrogen free compositions) exhibit toughness values of about $0.7\text{-}0.9 \text{ MPa}\cdot\text{m}^{0.5}$, whereas the substitution

of 15 eq.% nitrogen for oxygen results in values 40 % higher^{20,23} ranging from 1 to 1.4 MPa.m^{0.5}.

The subcritical crack growth (SCG) resistance of Y-Si-Al-O-N glasses in an aqueous environment has been studied^{26,27} in order to determine the power-law exponent, n , in the crack velocity (v) – applied stress intensity (K_I) relationship:

$$v = A(K_I)^n \quad (6)$$

where A is a constant. For a Y-Si-Al-O-N glass containing ~7 at.% N, $n = 63$ which was a factor of three higher than for the oxide glass with the same cation ratios²⁶. For a glass containing 18 at.% N, an even higher value of $n = 142$ was reported²⁷. Clearly, nitrogen additions increase the resistance to slow crack growth of these glasses with shifts to significantly higher applied stress intensity ranges as compared with oxide glasses. This can be attributed²⁸ to the susceptibility of three-membered $(-\text{SiO}_3)^{2-}$ ring structures to attack by water in aluminosilicate glasses whereas when nitrogen is added, the fraction of these structural units is reduced and the extra cross-linking Si–N bonds are more resistant to attack. The benefits are that the glasses containing nitrogen exhibit longer lifetimes under fixed applied stress conditions. Since nitrogen improves both fracture toughness and fatigue resistance, the scratch pattern of an oxynitride glass also significantly differs from that of the parent oxide glass as shown in Figure 7. Nitrogen improves the resistance to crack initiation and propagation and also to chipping during a scratch experiment, while the abrasive mode begins at lower normal loads. The radial cracks are less significant because of a better stress-corrosion resistance for the oxynitride glass. Subsurface lateral cracking is also less pronounced and the damage along the groove is more regular.

4 | MECHANICAL BEHAVIOR AT HIGH TEMPERATURE

4.1 | Temperature dependence of the elastic moduli

The temperature dependence of Young's modulus for glasses exhibits a transition range between a slow softening rate and a faster rate, corresponding to the glass transition as shown in Figure 8. In the case of oxynitride glasses the softening rate immediately above T_g ($dE/dT(Tg^+)$), i.e., in the supercooled liquid range, is relatively large ($\sim -100 \text{ MPa}\cdot\text{C}^{-1}$) compared with that for parent oxide glasses and for standard silicate glasses ($\sim -50 \text{ MPa}\cdot\text{C}^{-1}$). The difference is even more pronounced for the shear modulus ($d\mu/dT(Tg^+) \sim -245$ and $\sim -30 \text{ MPa}\cdot\text{C}^{-1}$ for oxynitride and for oxide glasses, respectively),²⁹ so that silicon oxynitride glasses exhibit a dramatic increase of Poisson's ratio (ν) above T_g as shown in Figure 9. Recalling that ν is a reflection of the overall network connectivity¹⁸, then the larger decrease of $\mu(T)$ (larger than for glycerol!) with respect to $E(T)$, and the corresponding rapid increase in $\nu(T)$ – comparing with those of organic liquids such as bitumen or glycerol – is an indication of the dramatic softening and destructuring of the glass network above T_g . For relatively stiff glasses¹⁸ such as oxynitride glasses, with $E > 10 \text{ GPa}$, then in the range $T_g < T < 1.1T_g$:

$$E = E(T_g)T_g/T \quad (7)$$

And for all glasses:²⁹

$$\mu = \mu(T_g)(T_g/T)^\alpha \quad (8)$$

In the case of oxynitride glasses, α is about 9-10, i.e. as high as for a-Se, whereas for a-SiO₂ $\alpha = 0.07$ and is 0.98 for a soda-lime-silica glass.

4.2 | Viscosity

As with elastic modulus and hardness, glass transition temperature and viscosity of oxynitride glasses increase linearly with increasing nitrogen substitution for oxygen.^{3,5,7,9,12,30-}

³³ Figure 10 shows the viscosity-temperature relationships for a series of glasses^{3,5,9,12,24,30,31} with composition (in eq.%) of 28Y:56Si:16Al:(100-x)O:xN (x=0, 5, 10, 18) and these are compared with glasses^{3,31,32} of composition (in eq.%) of 30La:45Si:25Al:(100-y)O:yN (y=0 and 30). It can be seen that viscosity increases by about 0.10 to 0.13 orders of magnitude per eq.% N for the Y-Si-Al-O-N glasses and by 0.10 orders of magnitude per eq.% N for the La series of glasses. As with other properties, these effects are due to the increased cross-linking within the glass structure as 2-coordinated bridging oxygen atoms are replaced by 3-coordinated nitrogen atoms. More extensive measurements and data collection and analysis is required before a general rule for viscosity increase with nitrogen content can be developed.

The effect of fixed Si:Al and Y:Al ratios on viscosity of oxynitride glasses with constant O:N ratio have also been investigated and, in general, non-linear variations are observed.^{3,5,7,28,30,31} With fixed N and Y contents and decreasing Al:Si ratio from 12 to 16 eq.%, there is a reduction in viscosity but any further changes with further increase in Al are slight. It appears that the change in Al:Si ratio does not change the degree of cross linking of the network significantly but simply leads to the replacement of Si-O-Si bridges by Al-O-Si

linkages as shown by Raman spectroscopy analyses³³ with Al in 4-fold coordination and as an integral part of the glass network.

With fixed N and Si contents, as Y:Al ratio decreases, there is a reduction in viscosity of greater than 1 order of magnitude as Al content increases from 4 to 16 eq.% Al and then, with further increase in Al content, viscosity increases once more. At these higher Al:Y ratios (> 16 eq.%), 4-fold coordinated Al is prevalent and enhancement of the cross-linking of the glass network occurs, caused by the formation of more Al-O-Si linkages and Y acting as a network dwelling cation providing charge balance for the AlO_4 tetrahedra.^{5,7,31,33}

Figure 11 shows the viscosity-temperature relationships for glasses^{31,34} with composition (in eq.%) of 28RE:56Si:16Al:83O:17N where RE is Eu, Ce, Sm, Dy, Y, Ho, Er. Viscosity is seen to increase by about 3 orders of magnitude in the order: $\text{Eu} < \text{Ce} < \text{Sm} < \text{Dy} < \text{Y} < \text{Ho} < \text{Er}$, that is, increasing with the introduction of smaller rare earth cations into the glass structure and, hence, increasing CFS. The activation energy for viscous flow was observed^{31,32,34} to increase as cation field strength increases so, at any temperature, not only do glasses with smaller cations have higher viscosities but also the activation energies for viscous flow are higher, reaching values of >1200 kJ/mol for the Er-Si-Al-O-N glasses.

The coordination of the RE^{3+} with oxygen depends on the ratio of the RE ionic radius to that of the oxygen ion, where larger rare earth ions have coordinations of 7-9 and smaller REs have 6-fold coordination³⁴ which has been attributed to the strong ionicity of the RE-O bond which does not change appreciably with the size or field strength of the rare earth cation. The spacing of the RE ions within the network also becomes more regular as ion size decreases and the resulting increase in CFS allows the RE ion to compete more strongly for NBOs as

the attractive forces between the RE ion and the surrounding network structural units increase. However, as a linear trend in properties is observed, it may be concluded that the overall structures of these RE-Si-Al-O-N glasses remain similar and the property changes solely depend on the modifier cation field strength.

It is noteworthy that despite relatively high glass transition temperatures (typically above 850°C), oxynitride liquids are characterized by remarkably large activation energies for viscous flow (typically above 1000 kJ.mol⁻¹). Indeed, the fragility index (m) of the liquid as defined by Angell:³⁵

$$m = d \log_{10} \eta / d(T(\eta = 10^{12} \text{ Pa.s})/T) \quad (9)$$

is large enough ($m \sim 50$) for oxynitride glasses to be considered as relatively fragile liquids.

The seemingly atypical behavior of oxynitride glasses regarding their viscosity-temperature dependence and the influence of nitrogen upon the atomic packing density can be tentatively explained on the basis of an heterogeneous atomic network, with segregation of nitrogen into highly polymerized and relatively rigid regions that are surrounded by “softer” and less refractory regions, i.e. clusters embedded in a less viscous matrix. On the one hand, the matrix would favor a high packing density by allowing for atomic or molecular displacement. On the other hand, it would be responsible for the strong temperature sensitivity of the viscosity – or fragility.

5 | SUMMARY

As nitrogen substitutes for oxygen in alumino-silicate glasses with Y and other rare earth modifiers, elastic modulus, hardness, fracture toughness, strength, slow crack growth resistance and viscosity increase as a result of both increased cross-linking and higher atomic compactness due to the presence of three-fold coordinated nitrogen in the glass network. For a constant cation ratio, elastic modulus, hardness and viscosity increase monotonically with nitrogen substitution for oxygen. For rare earth oxynitride glasses with constant nitrogen content, these properties increase with increasing cation field strength (decreasing ionic radius). For oxynitride glasses, molar volume decreases and the fractional glass compactness increases with increase in nitrogen content and this is presumably the major reason for the increase of the elastic moduli.

Nitrogen increases fracture toughness (by up to 40% as >15 eq.% N is substituted for oxygen) and also the resistance to scratch damage. For Y- and rare earth (RE-) Si-Al-O-N glasses, viscosity increases by about three orders of magnitude as 17 eq.% N is substituted for oxygen. Viscosity generally increases as more Si or Y is substituted for Al but this is not a linear relationship and is a smaller effect than with nitrogen. Interestingly, despite their high refractoriness, oxynitride glasses appear to be relatively fragile liquids above T_g , with a fragility index as high as 50.

With higher elastic moduli, hardness, fracture toughness, strength, greater surface damage resistance, increased properties at high temperatures, oxynitride glasses offer advantages over their oxide counterparts in applications such as glass fibres, damage resistant glass layers,

structural parts and for other potential uses requiring better mechanical performance and thermal stability.

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Figure Captions

Figure 1. Effect of nitrogen content on elastic modulus of Y-Si-Al-O-N glasses with different cation compositions (in eq.%).^{5,7,9,12}

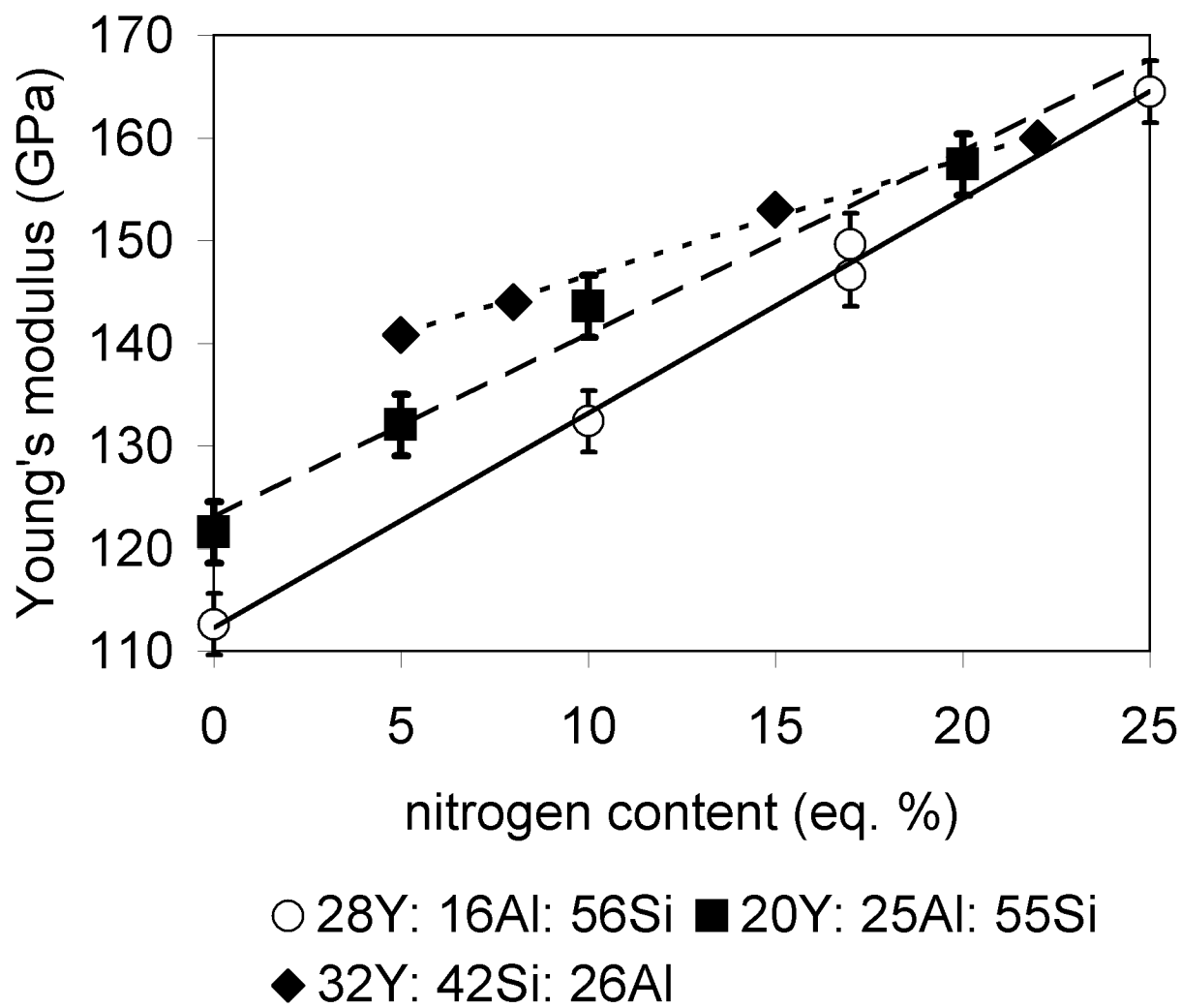


Figure 2. Effect of nitrogen content on microhardness of Y- and Er-Si-Al-O-N glasses with cation composition (in eq.%).

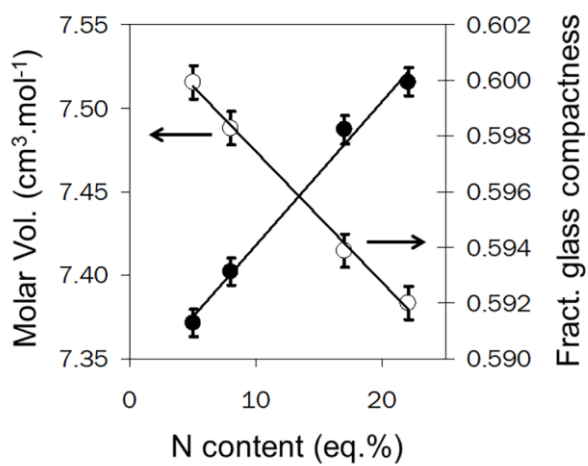


Figure 3. Effect of nitrogen content on molar volume and fractional glass compactness for a glass with cation composition (in eq.%): 36.5Y:42.3Si:21.2Al.²

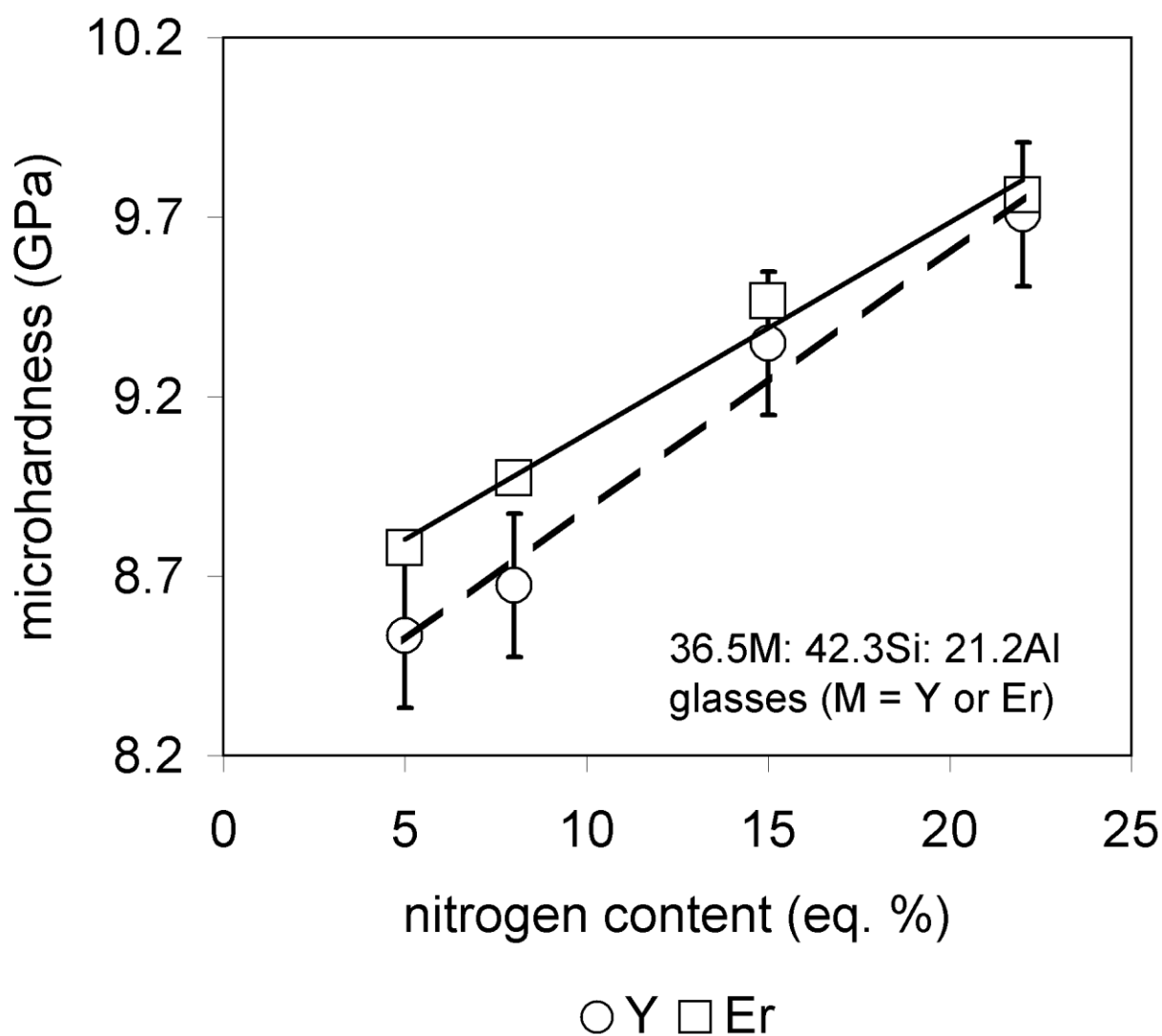


Figure 4. Effect of fractional glass compactness on microhardness and Young's modulus of a glass with cation composition (in eq.%) of $36.5\text{Y}:42.3\text{Si}:21.2\text{Al}^2$ (5N, 8N, 17N, 22N are nitrogen contents in eq.%).

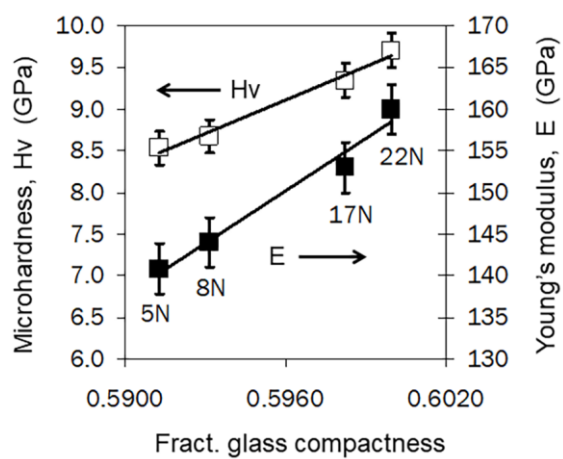


Figure 5. Changes in Young's modulus as a function of Mg content for glasses with cation compositions (in eq.%) of $x\text{Mg}:(28-x)\text{Y}:56\text{Si}:16\text{Al}$ ($x = 0, 7, 14, 21$ and 28) containing 0, 10 and 15 eq.% N, data from [17].

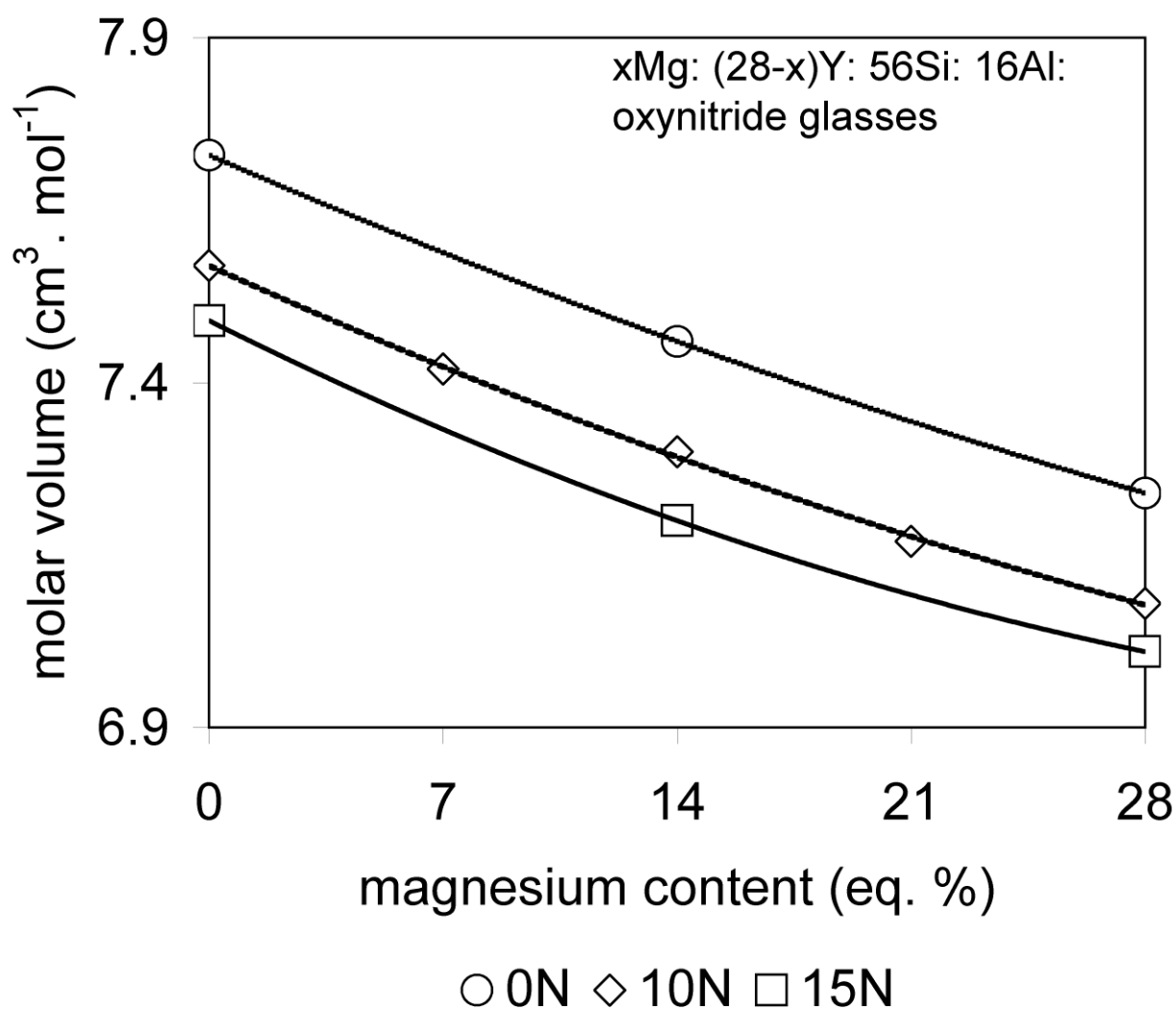


Figure 6. Molar volume as a function of Mg content for glasses with cation compositions (in eq.%) of $x\text{Mg}:(28-x)\text{Y}:56\text{Si}:16\text{Al}$ ($x = 0, 7, 14, 21$ and 28) containing 0, 10 and 15 eq.% N, data from [17].

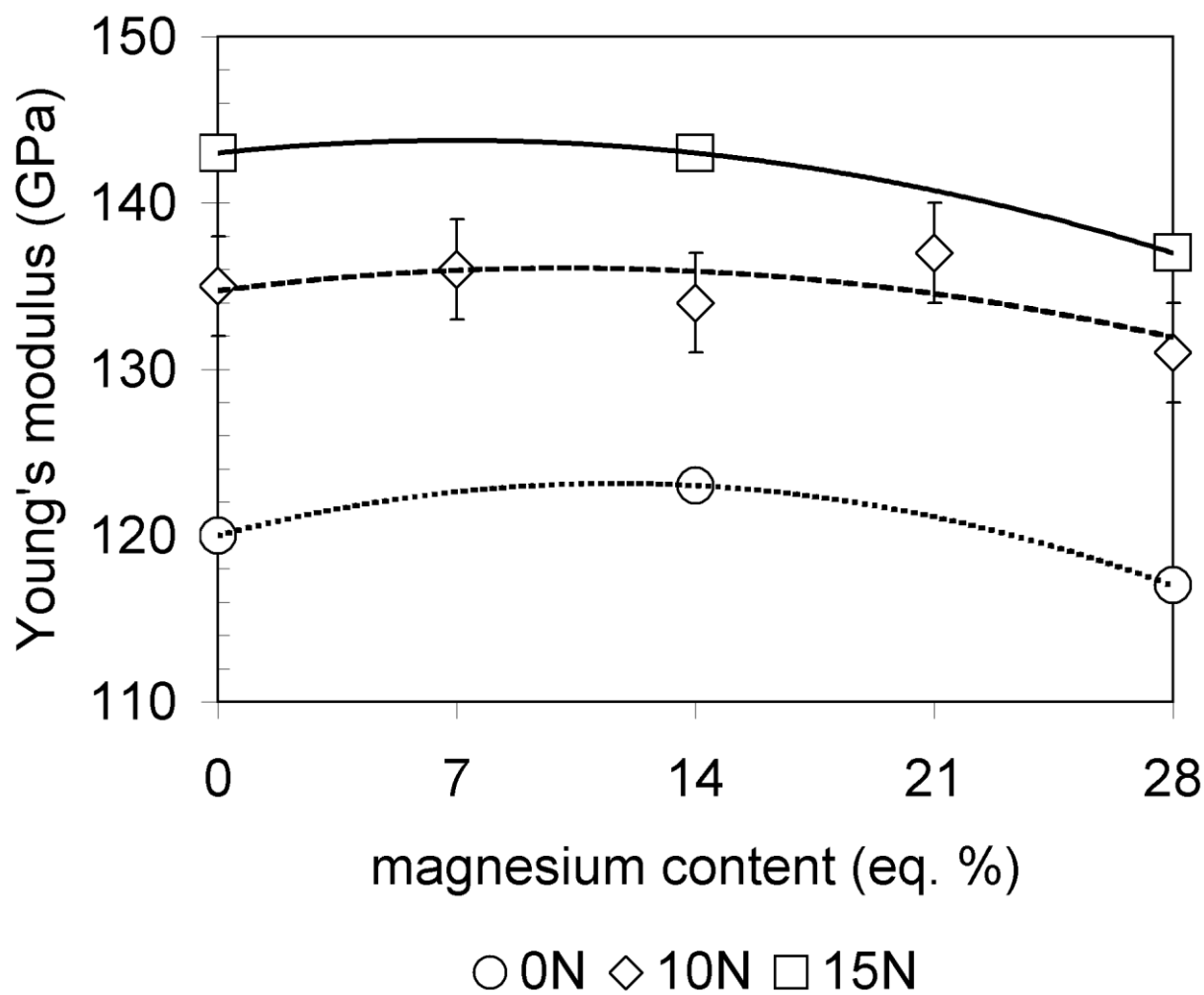


Figure 7. Images of the scratch grooves obtained in air at a constant normal loading rate of $0.1 \text{ N}\cdot\text{s}^{-1}$ on SiAlCaON glasses. The different scratch regimes are indicated in the case of the oxide glass.

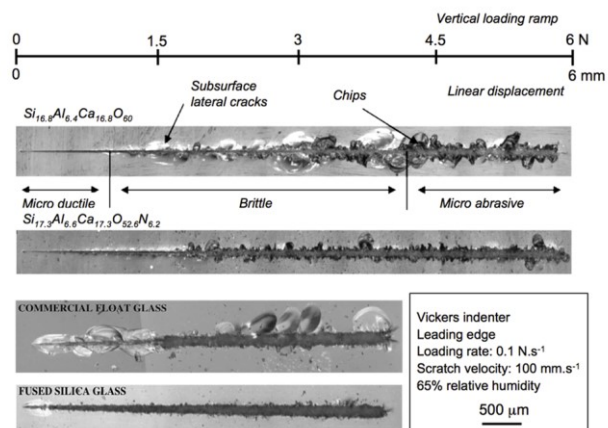


Figure 8. Young's modulus as a function of T_g/T (redrawn from [18]).

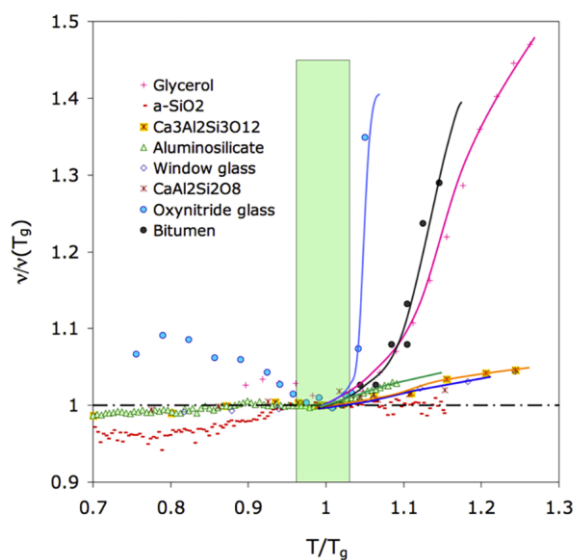


Figure 9. Relative Poisson's ratio, $v/v(T_g)$ as a function of T/T_g (redrawn from [29]).

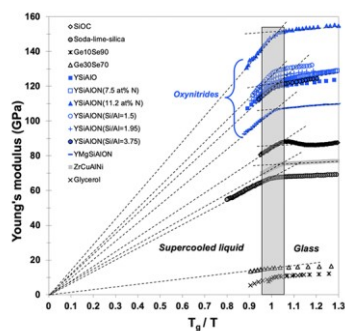


Figure 10. Log viscosity versus T (absolute) showing effects of N content for glasses with compositions (eq.%): 28Y:56Si:16Al (filled symbols), data from [24]; *30La:45Si:25Al (open symbols), data from [32].

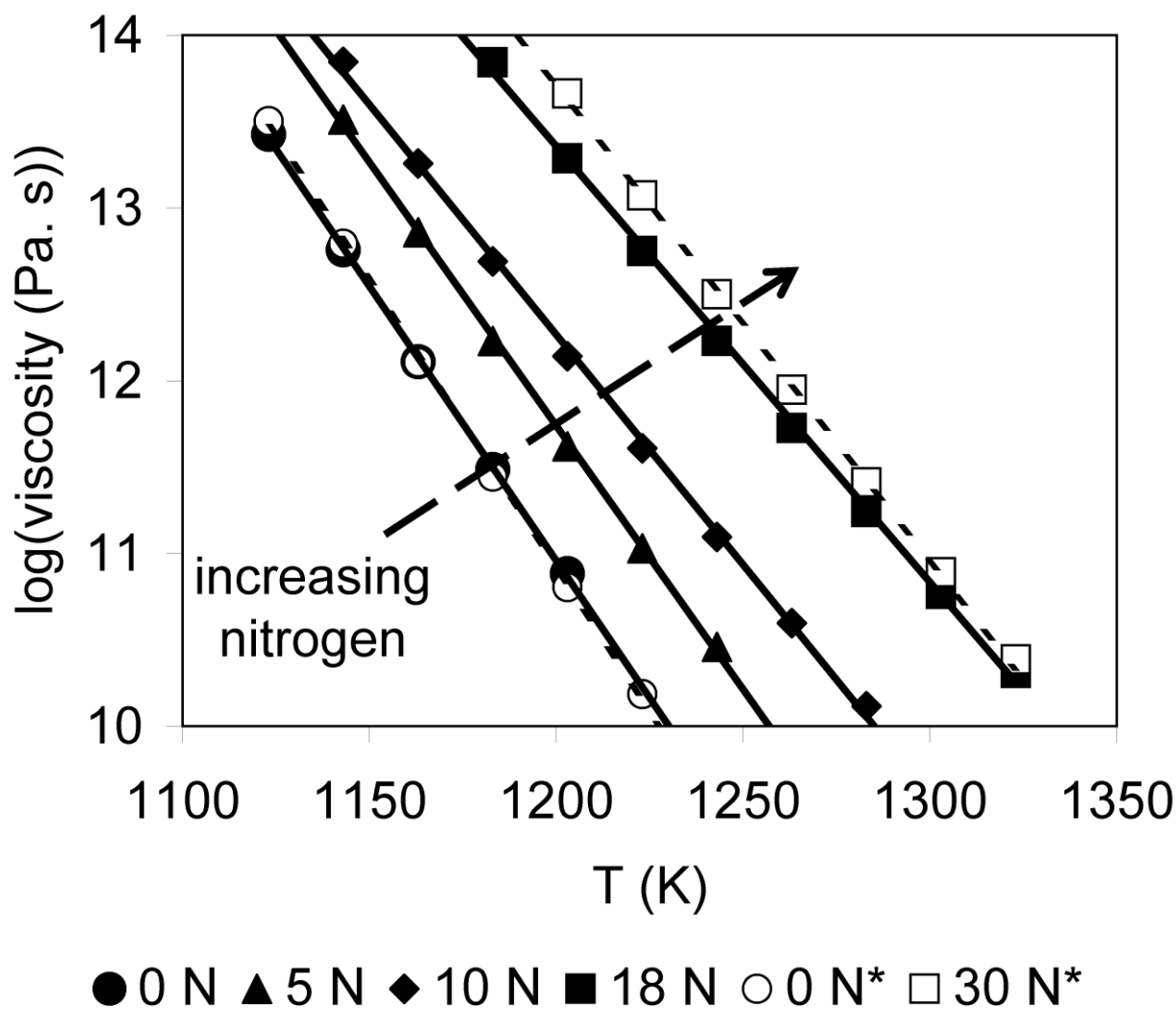


Figure 11. Log viscosity versus T (absolute) showing effects of cation field strength for glasses with compositions (in eq.%): 28RE:56Si:16Al:83O:17N (RE = Eu, Ce, Sm, Dy, Y, Ho, Er).

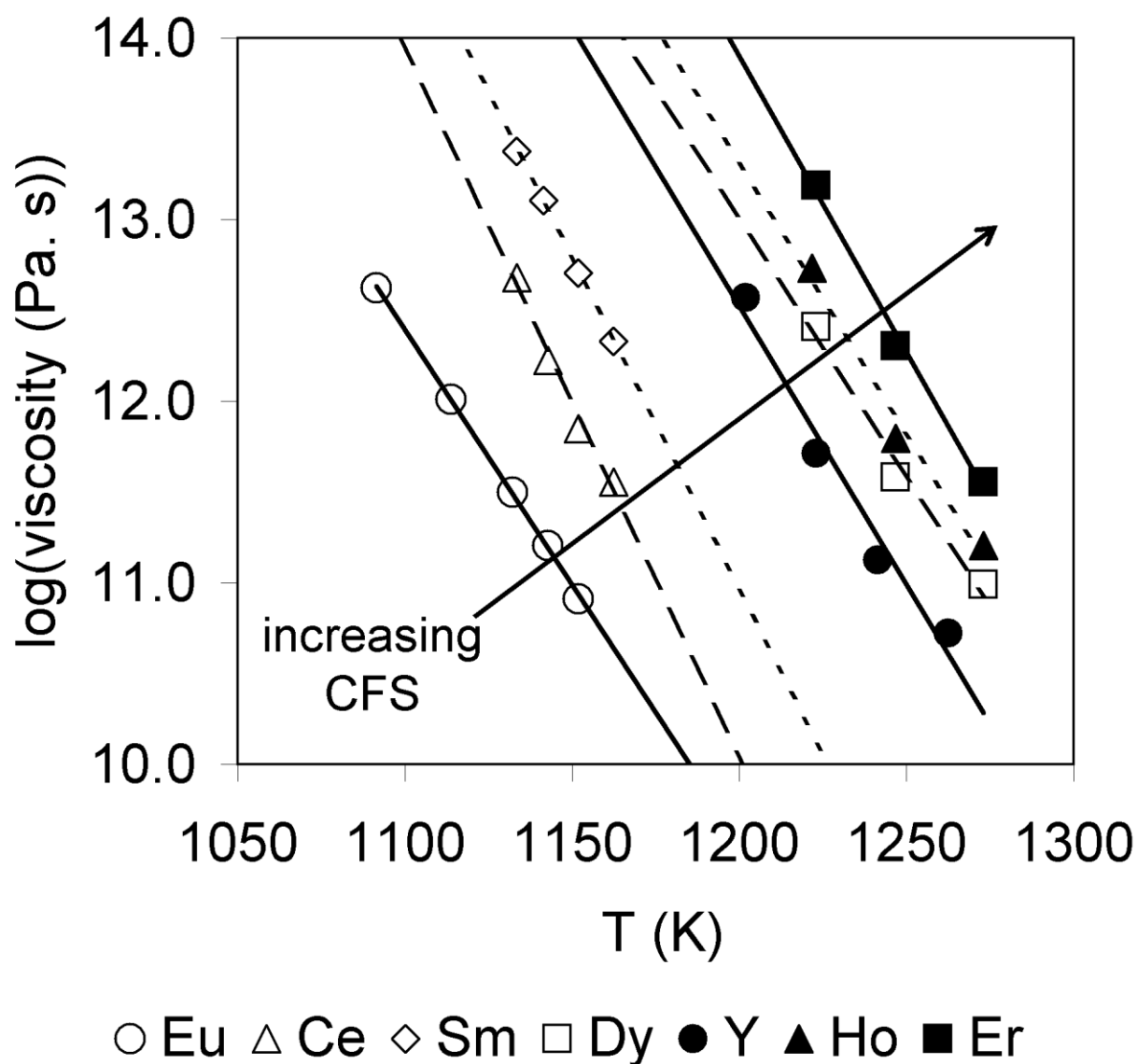


Figure 12. T_g -scaled logarithm of viscosity from which the fragility index is straightforwardly derived from the slope of the linear intercepts in the transition range. The scaling parameter used here is the viscosity corresponding to the glass transition temperature as obtained by classical means such as Dilatometry or mostly DSC. In most cases, this temperature corresponds to a viscosity close to 10^{12} Pa s. (redrawn from [29]).

