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Review: Elaboration, structure and mechanical properties of oxynitride glasses

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ABSTRACT

Oxynitride glasses are glasses where three-fold coordinated nitrogen atoms substitute for 2-fold oxygen ones, hence resulting in a larger interatomic cross-linking degree. Such glasses were first observed at the grain boundary in silicon nitride ceramics, where they govern the high temperature behavior. Later, they were prepared as bulk materials and motivated numerous researches thanks to their large viscosity, glass transition range, elastic moduli, hardness and fracture toughness among inorganic and non-metallic glasses. The different chemical systems that were investigated, the synthesis routes and the sources for these exceptional mechanical properties are reviewed. Oxynitride glasses are not easy to process and suffer from the loss of transparency as nitrogen is incorporated over some critical content. Nevertheless, they are attractive “specialty” glasses in various niche areas thanks to their large refractive index and dielectric constant, improved chemical durability, high softening point, ... and in the first place to their exceptional mechanical properties.

1. INTRODUCTION

Nitrogen is a common element in the universe with the $1s^2 2s^2 2p^3$ electron configuration. It is found in gases like N_2 or NH_3 , in organic compounds where it forms a wide variety of bonds

and functional groups with various elements, as well as in ceramics. In the case of silicon nitride (Si_3N_4), nitrogen is three-fold coordinated to silicon (sp^2 hybridization). This results in an increase of the cross-linking degree in comparison with oxygen, which is two-fold coordinated (like in SiO_2). Besides, metal-nitrogen bonds are more covalent than metal-oxygen bonds because of the lower electronegativity of nitrogen ($\chi_{\text{N}} = 3.04$ and $\chi_{\text{O}} = 3.44$). Nitride ceramics, and especially those based on silicon nitride (such as the “sialons”), are advantaged by excellent mechanical properties (hardness, stiffness, toughness and strength) at room temperature, and remain strong ($\sigma_r \approx 1$ GPa) and creep-resistant up to 1300 °C in air¹. Nitrides may also exhibit interesting functional properties such as thermal and electrical conductivities (AlN) and semiconductor (GaN)².

In the 1960’ Mulfing^{3 4} introduced a low amount of nitrogen in oxide melts by using various gases, such as ammonia. In the 1970’ oxynitride glasses were discovered at grain-boundaries in silicon nitride ceramics by K. H. Jack, when compounds such as Y_2O_3 were used as sintering additives for Si_3N_4 ^{1 4}. In order to better understand the role of this secondary intergranular phase on the mechanical properties of silicon nitride ceramics, and in particular on their creep behavior, oxynitride glasses were synthesized as bulk materials, by adding silicon nitride as a nitrogen source in oxide powder mixtures. Worldwide investigations (Fig. 1) on oxynitride glasses from various chemical systems (silicon-based, phosphate-based, etc) revealed remarkable mechanical properties, both at room and at elevated temperature, with fracture toughness being typically twice larger for nitrogen glasses than for the parent oxide composition, and a viscosity coefficient increasing by about three orders of magnitude as one out of five oxygen atom is substituted by a nitrogen one. About 15 papers in international scientific journals have been published yearly since 1980. Nevertheless, the loss of transparency at nitrogen contents larger than 15 eq. % led to broaden the scope of applications beyond optics. Emerging fields include hardening and functionalization of surfaces by means of amorphous

oxynitride thin film deposition, and biocompatible and bioactive materials for implantology. Besides, present investigations focus on improving the atmosphere control and the purity of the starting powders, and explore new synthesis routes to achieve a better transparency at large nitrogen content.

2. GLASS CHEMICAL SYSTEMS

2.1 Silicate-based

Several oxynitride glasses systems were explored over the past decades ⁴, among which silicate-based oxynitride glasses were probably the most studied. Cations were usually added to reduce the melting temperatures of the starting mixtures, which would otherwise require melting temperatures high enough to cause the decomposition of the melt (formation of Si and N₂ from Si₃N₄) ⁵, and to ease the glass formation, resulting in M-Si-O-N systems where M can be a combination of secondary cations and represents alkalines ⁶, alkaline-earths ^{7 8 9 10 11}, or rare-earths (*RE*) ^{12 13 14}. The addition of aluminum to form M-Si-Al-O-N glasses was also often reported ^{15 16 17 18 19 20 21 22}. Aluminum was found to increase nitrogen solubility, to widen the range of glass formation (Fig. 2), and to prevent demixing. Y-Si-Al-O-N glasses were found very successful in this regard ^{23 24 25}. Other sub-system includes M-Si-Mg-O-N glasses, as Mg also widen the compositional range, while resulting in close mechanical properties ^{26 27 28 29 30}. The nitrogen content of oxynitride glasses is usually expressed either in at %, wt % or eq % (equivalent percent). The eq. % in nitrogen (also noted e/o) is expressed as: $\text{eq. \% N} = \frac{3N \cdot 100}{3N + 2O}$, where N and O are the molar concentrations of nitrogen and oxygen respectively. It is calculated separately for anions and cations, and accounts both for the chemical composition and for the valence of the ions. In the presence of aluminum and/or magnesium, homogeneous glass batches, few cm³ large, with up to 30 e/o N can be obtained ^{31 32}, while transparency is retained for nitrogen contents below 15 e/o N (Fig. 3).

Mixed glasses families were explored, as in the M-Si-P-O-N system^{33 34 35 36}, of which the Na-Ca-Si-P-O-N (with nitrogen content up to 28.5 e/o) was investigated recently because of its interesting bioactive properties, that could be interesting for medical use. Indeed, a major issue with bioactive glasses is their low compressive strength, and oxynitride glasses are promising in this regard.

Few glasses in the M-Si-B-O-N system were reported, because the melts experienced large weight losses in boron as it is prone to volatilization at high temperatures^{37 38}. However, the sol-gel route in a Na-Ba-Si-B-Al-O-N glass led to more satisfying glasses with higher nitrogen content, up to a few wt.% (about 6 e/o^{39 40}). They present an increase in Young's modulus (E) with increasing nitrogen, as in silicate-based oxynitride glasses.

2.2 Phosphate-based

M-P-O-N glasses are usually synthesized either via the ammonolysis route for large batches (to be discussed later on)^{41 42 43 44 45 46 47} or via sputtering for thin films⁴⁸, with nitrogen content up to 33.5 e/o or even slightly higher, although it is unsure if glasses richer in nitrogen are of the same nature^{46 49}. They are promising materials as solid-state electrolytes due to their strong ionic conductivity and chemical durability, especially the Li-P-O-N system^{50 51 52}. Moreover, their tendency to devitrify is smaller than for their oxide counterparts, they are less hygroscopic and exhibit larger elastic moduli^{49 53}.

2.3 Borate-based

M-B-O-N oxynitride glasses were not studied much. Amorphous thin films were obtained in the Li-B-O-N system by magnetron sputtering under nitrogen^{54 55}. In this latter system, the formation of B-N-B bonds was found to enhance the diffusion of Li ions, likely via some charge delocalization (within these bonds) and thus thanks to the reduction of the electrostatic

interaction with the Li ions. Besides, the nature of the B-N bonds was found to depend on the composition of the sputtering target.

The solubility of nitrogen in borate-based glasses is quite low no matter the synthesis route, being only a few tenths of wt% (about 1 e/o)^{56 57 58 59 60}. On a side note, one paper claimed to have synthesized an oxynitride glass free from Si, P and B in the Ca-Ba-Mg-Al-O-N system, showing a similar increase in T_g and a decrease of the thermal expansion coefficient with increasing nitrogen content as in other oxynitride glasses, but no further report dealt with this system since then⁶¹.

3 SYNTHESIS

3.1 Synthesis routes

a) Melting

The first synthesis route consists in melting the various oxides (SiO_2 , Al_2O_3 , MgO , Y_2O_3 , etc.) and nitrides (mostly Si_3N_4 and AlN) precursors at temperatures ranging from 1300 to 1850 °C depending on the melt composition^{62 63 64}, so that every reactant is melted and that the mixture viscosity is low enough to quench it. This step usually lasts for an hour in order to obtain a homogeneous melt. The nitrides may be mixed with the already synthesized oxide glass to prevent compounds decomposition due to side reactions, which will be further detailed in § 3.5 a)⁵. Both melting and annealing stages must be conducted in oxygen free environment to limit the loss of substituted nitrogen atoms in the liquid. Nitrogen atmosphere has been mostly used so far, although argon or argon- N_2 or argon- H_2 mixtures were sometimes used⁶⁵, mostly in gas flow protecting devices (Fig. 4). In addition, large cooling rates (typically from 600 to 1000 °C.min⁻¹) are required as soon as the liquid composition lies close to the border of the glass forming region⁶⁶. Glasses cooled with slow cooling rates turn out to be more transparent^{10 62}.

Other reactants were sometimes used, such as fluorides in the case of oxyfluoronitride glasses ⁶⁷ or hydroxides ⁵⁸. More recently, hydrides and metals were used as some are highly reacting with nitrogen when heated, and form glasses with much larger nitrogen content compared to those obtained by conventional melting (up to 68 e/o ^{12 68}). However, some metals can reduce several oxides like silica in the melts, leading to formation of metallic micro-particles including silicides ^{12 68 69}. Alternatively, oxynitride glasses were prepared with nitrogen overpressures up to 200 MPa successfully preventing nitrogen loss in the glass ^{65 70}, or by self-propagating high-temperature combustion synthesis (*SHS*) ⁵⁷.

b) Ammonolysis of melts

A second way to synthesize oxynitride glasses consists in realizing the ammonolysis of the glass melt *i.e.* the substitution of oxygen for nitrogen using N₂ and/or NH₃ flowing gas, at temperatures typically below 900 °C in the case of phosphate-based glasses ^{41 71}. For example, starting from a NaPO₃ glass, the reaction is:

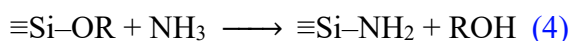
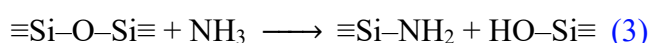
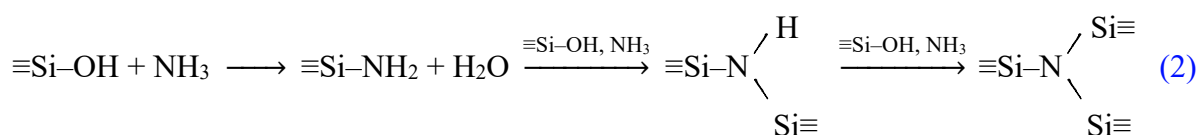


This reaction must take place at temperatures larger than 600 °C to allow for the decomposition of NH₃ but smaller than 800 °C to prevent from the reduction of phosphorous and the formation of a colored and heterogeneous glass. The benefit of this synthesis route is to add nitrogen to the medium but without its counterion, in opposition to the use of nitrides. Furthermore, it is more suitable to oxides such as P₂O₅ that suffer from volatilization at high temperatures, or because of their reactivity with nitrides ⁷², and is mostly used for phosphate-based oxynitrides ⁵. However, these exotic synthesis routes take longer time (>10 h) in order to incorporate large amounts of nitrogen, due to the slower liquid/gas reaction kinetics ^{3 73}. The resulting glasses

usually are transparent, and it should be noted that the nitrogen content increases with increasing temperature^{41 42 53 74 75 76}. Nevertheless, glasses turn black if the ammonolysis temperature is too high because of a reduction reaction of the phosphorus oxides^{71 73 77}.

c) Sol-gel

The third way is the sol-gel route, which consists firstly to synthesize a gel using reactants like alkoxides. Less common precursors composed of Si-CH₃ and/or Si-H groups may be used, as they are highly reactive to NH₃^{78 79}. The second step consists to realise the gel (or else the colloidal silica⁸⁰) ammonolysis according to various mechanisms such as reactions (2) to (4)^{39 79 81 82}. This step is carried out using an ammonia flow at temperatures ranging from 400 to 1300 °C for a few hours, the purpose of the gas flow being to remove the gaseous products formed (alcohols and water), therefore displacing the equilibrium and allowing more nitrogen to be substituted. In the case of a silica gel:



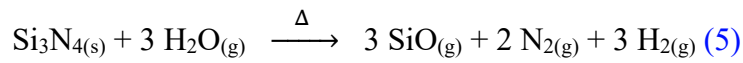
This synthesis route also presents the benefit to avoid the use nitrides, thus broadening the range of glass compositions. The glasses were described as optically transparent, in opposition to glasses obtained using the melting route with sometimes high nitrogen content (close to 38 e/o⁸² or even higher in the case of oxynitride glasses fibres⁸³).

An analogous route uses polymers like polysiloxanes which, once pyrolyzed under ammonia, give oxynitride glasses^{84 85}. The pyrolysis temperature and atmosphere are crucial, especially

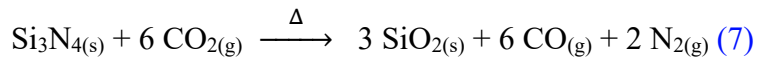
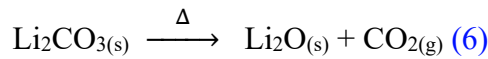
to prevent trapped free-carbon within the structure, of which a content even lower than 0.2 wt.% may colour the glass.

3.2 Starting materials

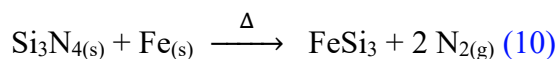
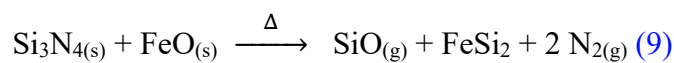
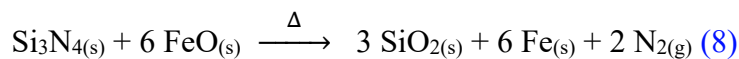
Various compounds, for instance SiO₂, exhibit a few amounts of adsorbed water even at temperatures as high as 1000 °C when the particles size is very fine⁸⁶. It can decompose nitrides during the synthesis according to⁸⁷:



Some oxides such as Li₂O are brought in the medium starting from carbonated precursors, because of their reactivity with the ambient atmosphere. It is thus important to realize their complete decarbonization to both free the melt from CO₂ bubbles and to prevent the oxidation of Si₃N₄ (and thus the loss of nitrogen in the glass) via various mechanisms^{87 88}. In the case of Li₂CO₃:

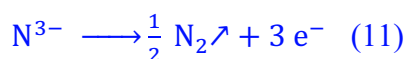


Impurities are other sources of side reactions and have to be considered even in weak quantities, especially iron (as metal or oxides), a common impurity in reactants used in oxynitride glasses synthesis⁸⁹. In the presence of Si₃N₄, the various iron containing impurity species may result in metallic micro/nano inclusions (such as iron silicides), even at temperatures as low as 1200 °C:



Consequently the glass becomes opaque, even for a content of inclusions as small as 0.05 vol.%^{62 90 91}.

In the case of phosphorous oxynitride glasses, which were first reported in the early 80s by Marchand⁷¹, phosphate salts such as NaPO₃ and LiPO₃^{34 42 92 47 93 94 71}, ammonium phosphates^{53 95}, phosphoric acid⁴⁵ as well as phosphate oxide glasses are used as starting materials. Under NH₃ flowing gas, the 3-fold coordinated N³⁻ anions may subsequently result in the following oxidation reaction,



which confers a reducing character to the oxynitride liquid that may promote the reduction of cations such as copper or silver to metals.

3.3 Crucibles

The materials for the crucibles in which the glasses are synthesized is of paramount importance, as it may interact in various ways with the melt. Some should be avoided, such as platinum crucibles as they form alloys with the reactants under reducing atmospheres^{26 96}, oxide-based crucibles dissolve in the melt, zirconium and tantalum crucibles are oxidized because of the reactants⁵, and graphite crucibles might pollute the melt or even reduce oxides such as P₂O₅⁹⁷⁹⁸. Graphite crucibles coated with boron nitride or pure BN crucibles allow to maintain a reducing atmosphere (local scale) and facilitate the demoulding of the glasses⁶³. However, the use of BN results in the presence of BN inclusions in the glasses^{16 26 63}. Crucibles made in transition metals such as Mo, W and Nb were mostly not found to react with the powder mixtures or with the nitrated melt, but the dissolution of Nb and the formation of molybdenum silicides were sometimes observed^{8 34 88 99}. Sometimes, the crucibles are covered so that the

gaseous SiO molecules produced by various reactions are trapped inside, thus maintaining a partial pressure in SiO large enough to prevent further decomposition of the compounds (see § 3.5)^{100 101}.

3.4 Atmosphere

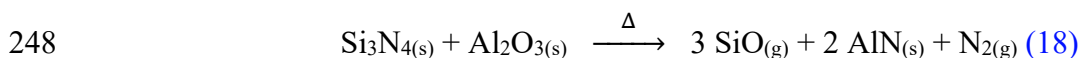
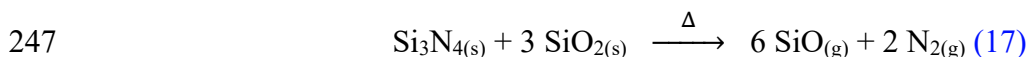
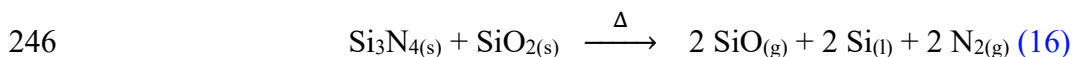
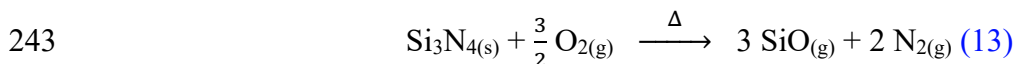
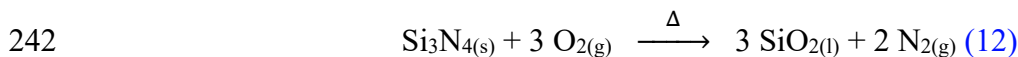
In comparison with N₂, NH₃ is more favorable to the nitridation process, both in terms of quantity and kinetics^{73 102}. However, the processing of oxynitride glasses under NH₃ flowing gas is limited to temperatures below 800 °C due to the loss of reactivity of NH₃ at higher temperature, which follows the decomposition of NH₃ into N₂ and H₂ gas. So far, the synthesis under ammonia chiefly concerned phosphate-based oxynitride compositions. As soon as temperatures higher than 1300 °C are required, as in the case of silicon oxynitrides, argon or N₂ gas atmosphere are used and nitrogen is further incorporated to the powder mixture by means of nitrated compounds (Si₃N₄, AlN). In this later case it is mandatory to keep the oxygen partial pressure as small as possible. Although argon gas can be used, a large partial pressure of N₂ helps preventing side reactions.

3.5 Choice of the chemical composition

The choice of the oxynitride glasses chemical composition depends much on the stability of the reactants in the melt considering the synthesis atmosphere. In fact, several side reactions may alter the chemical composition of the glass and thus its properties, in addition to heterogeneities like trapped gas bubbles due to the high viscosity of oxynitride glass melts, or metallic micro-particles (as discussed before).

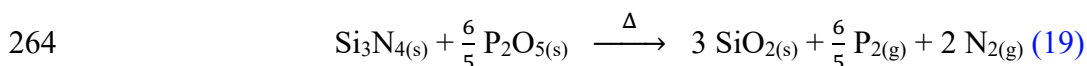
a) Side reactions

In the case of silicate glasses, several possible side reactions were reported^{5 26 103 104 105 106}.



249 Reactions (12), (13), (14) and (17) can be prevented by maintaining a large enough partial
 250 pressure in N₂, but this will not be sufficient if the temperature is too high ^{26 103 104}. However,
 251 it was shown based on a thermodynamic analysis that as soon as the temperature is high enough,
 252 the decomposition reactions (16) and (18) cannot be suppressed, even if a large partial pressure
 253 in N₂ is maintained ¹⁰³. Therefore, reactions (15) (16) and (18) can only be avoided by lowering
 254 the synthesis temperature ¹⁰⁵. The addition of metallic silicon to the melt effectively limits the
 255 formation of bubbles in the glass according to reactions (14) and (16), but metallic silicon or
 256 silicide domains remain in the glass ¹⁰⁷.

257 The use of Ellingham diagrams quickly tells whether the reduction of an oxide by a nitride
 258 is thermodynamically favorable ($\Delta G < 0$). For example, the reduction of oxides such as Li₂O,
 259 Al₂O₃, MgO, CaO and BaO by Si₃N₄ is not thermodynamically feasible in the usual temperature
 260 range of syntheses, in opposition to Na₂O P₂O₅ K₂O Cs₂O and ZnO ^{5 88 72 108 109}. Nevertheless,
 261 this reduction is sometimes observed via an exothermic reaction in the form of vapours ³⁷.
 262 However, let us recall that such a tool brings no information about the kinetics. In the case of
 263 P₂O₅, the reduction reaction is written:



Note that weight losses in P in the M-Si-P-O-N system can partly be avoided using a 3-step synthesis ³⁶: The oxide-based glass is first synthesized, then the N-containing glass is obtained via the melting route by crushing beforehand the previous glass with Si₃N₄, and finally the N-P-containing glass is synthesized in the same way by crushing beforehand the N-containing glass with P₂O₅.

Since reactions (5) to (10) and (12) to (19) are thermally activated, the lowest synthesis temperature needed to obtain a homogeneous melt should be chosen when transparent glasses are sought ¹⁰³.

Note that the presented reactions in this paper also occur when using AlN, which is the other commonly used nitride for oxynitride glasses synthesis. When the system is at equilibrium, the nitrogen pressure resulting from AlN decomposition into aluminum and molecular nitrogen is lower than the one resulting from Si₃N₄ decomposition into silicon and molecular nitrogen, whatever the temperature ¹⁰⁷. Therefore, there should be less metallic micro-particles in the glasses when using AlN, meaning they should be more transparent. However, the consequences of using AlN over Si₃N₄ changes with the synthesis conditions of the glass: it may provide a clearer glass ¹⁰³, have no effect on the transparency ⁹⁰, or oppositely remain undissolved in the glass ^{72 110} as its melting temperature is higher, making the choice of the nitride more complicated than expected.

Beside Si₃N₄ and AlN, the use other nitrides was reported such as Li₃N, Ca₃N₂, TiN, YN, NbN, Ba₃N₂ or the Si₂N₂O oxynitride alternatively ^{22 111 112 113}, but they may present various drawbacks: Mg₃N₂, Ca₃N₂, Ba₃N₂, LaN and Li₃N are hygroscopic, while some are difficult to prepare ^{114 115}.

To summarize, the most suitable nitride must fulfil several requirements: i) reduce as few oxides as possible, *i.e.* the Gibbs free energy of the oxidation reaction of a nitride AN_x into its oxide AO_y ($\frac{2}{y} \text{AN}_x + \text{O}_2 \longrightarrow \frac{2}{y} \text{AO}_y + \frac{x}{y} \text{N}_2$) must be higher than the Gibbs free energies of the

290 $\frac{2}{y} M + O_2 = \frac{2}{y} MO_y$ reactions of the oxides composing the glass (where M is a metal). Note that
 291 in a few cases, an oxide can be nitrated rather than reduced by Si_3N_4 , which in a Ti-oxynitride
 292 glass led to the crystallization of TiN ²¹. ii) It must melt in the usual temperature range of the
 293 syntheses when mixed with the other precursors, and be soluble in the glass to obtain a glass-
 294 matrix free from heterogeneities iii) but not decompose according to previously presented side
 295 reactions, and specifically the Gibbs free energy of the $\frac{2}{x} AN_x \longrightarrow \frac{2}{x} A + N_2$ reaction must be
 296 positive over the temperature range of the syntheses in order to prevent the formation of metallic
 297 micro-particles and the loss of N_2 . These conditions must also be considered when using metals
 298 or hydrides as reactants, as they will form nitrides upon heating in a N_2 atmosphere.

299 It should be noted that the loss of transparency that is often observed in oxynitride glasses
 300 containing more than 15 eq. % N, is more likely to result from impurities and side reactions
 301 occurring in the melt, such as the reduction of silicon to form transition metal silicide
 302 nanoparticles, rather than from the incorporation of nitrogen in the glass network itself ⁶².

303

304 b) Chemical composition

305 Oxides

306 There are sometimes weight losses that are not anticipated by the Ellingham diagrams. For
 307 example, weight losses of MgO ^{62 116}, SrO ⁹, CaO ⁶⁸, BaO ⁷, Y_2O_3 and Al_2O_3 ¹¹⁷ were reported
 308 and were found to increase with the temperature, the nitrogen content and the holding time.

309 Weight losses in Na and B were also reported, as their corresponding oxides, Na_2O and B_2O_3 ,
 310 are prone to volatilization at high temperatures ^{37 38 40 108}, and because Na_2O is reduced by Si_3N_4
 311 at temperatures above 850 K (Fig 5). However, several authors reported no significant loss of
 312 Na despite close experimental conditions ^{6 8}.

313 Fluorine

Fluorine is found to decrease the viscosity of the oxynitride melt, thus easing homogenization, to decrease both T_g and T_c temperatures, and to increase the solubility of nitrogen. In addition, the incorporation of fluorine widens the chemical range of glass formation, decreases the melting point of the reactants mixture, with a negligible incidence on hardness and elastic moduli^{118 119 120}. However, the use of fluorides may lead to the crystallization of NaF and CaF₂, to demixing and to loss of Si in the form of SiF₄ gas, which is detrimental to the environment^{121 122}. The latter can be prevented by choosing a glass composition where Al-F bonds are favored over Si-F bonds¹²³.

Rare-earths

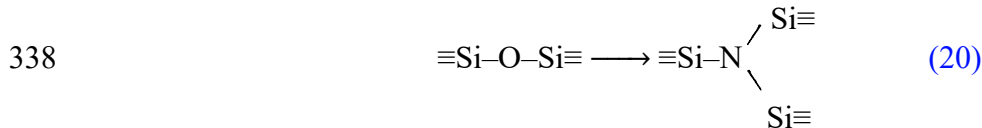
The use of rare-earths in oxynitride glasses leads to an increase in T_c , T_g , and in an increase in hardness and Young's modulus^{18 28 124 125}, which are found to increase with the cationic field strength (CFS) of the rare-earths, itself depending on their coordination number¹²⁶: $CFS = \frac{z}{r^2}$, where z is the ion charge and r the ionic radii. Indeed, rare-earths show a strong CFS , thus enhancing the stacking density and leading to a more rigid system. The change of the thermal expansion coefficient with the CFS is not linear¹⁸. In the search for stiff and hard glasses, yttrium has been the most widely investigated rare-earth.

4 STRUCTURE AND PHYSICAL PROPERTIES

4.1 Incorporating nitrogen into the atomic network of glasses

a) Silicates

The atomic structure of glasses is of paramount importance to understand the macroscopic properties. Early studies show that nitrogen is incorporated into the atomic network by substituting oxygen, thus increasing the crosslinking because of its larger coordination number¹²⁷ according to:



In fact, nitrogen-containing gaseous species such as NH_3 or molecular N_2 that are present in the synthesis environment were not detected in oxynitride glasses^{46 49 128}. It was proposed that the substitution of oxygen by nitrogen benefits from the fact that Si-N and Si-O bond lengths are very close²⁶. For example, the average values of the Si-N and Si-O bond lengths were estimated in a Y-Ba-Si-O-N glass by neutron diffraction experiments, and are centered on 1.72 and 1.61 Å respectively¹²⁹. Slightly different values, but close to each other, were reported for a Na-Si-O-N glass¹³⁰. Although nitrogen atoms are mainly bridging, non-bridging nitrogen ($\equiv\text{Si}-\text{N}^--\text{Si}\equiv$) and possibly double non-bridging nitrogen ($\equiv\text{Si}-\text{N}^{2-}$) exist as well^{127 129 131 132}, thus forming bonds with other cations such as rare-earths^{126 133 134}. The average coordination number of nitrogen ranges between 2 and 3, with three-fold coordinated nitrogen atoms being predominant over two-fold coordinated ones^{127 129}. In oxynitride glasses obtained via the ammonolysis route, NH and NH_2 groups exist in the glass when the ammonolysis is incomplete^{39 135 136}.

Silicon in oxynitride glasses is 4-fold coordinated to both oxygen and nitrogen, hence leading to structural units such as SiO_4 , SiO_3N , SiO_2N_2 , and SiON_3 ^{137 138}. Although the presence of SiN_4 structural units could not be evidenced by means of Magic-Angle Spinning solid-state Nuclear Magnetic Resonance spectroscopy (*MAS-NMR*)¹³⁷, such units may survive due to the incomplete dissolution of the Si_3N_4 nitrogen precursors. The connected Q^n units (where n is the number of bridging anions coordinated to a cation tetrahedron Q) form sheet, chain and cycle structures in the glass network¹²⁶. Their relative populations vary with the chemical composition of the glasses. The incorporation of nitrogen induces the formation of $\text{Si}(\text{O}, \text{N})_4$ mixed tetrahedra^{120 126 137 139 140}. At low nitrogen content, SiO_3N units are the most

frequently encountered whereas SiO_2N_2 tetrahedra become predominant at large nitrogen content. The SiON_3 population is usually small. Therefore, a typical silicon oxynitride glass network consists of Si-O-Si and Si-N-Si linkages^{126 137}. It is not excluded that the structure of nitrogen-rich oxynitride glasses obtained using metals or hydrides as reactants differs from the one of glasses obtained by conventional melting of oxides and nitrides and quenching, but further studies are required to clarify this point¹².

b) Phosphates

Phosphate-based oxynitride glasses are composed of various species including orthophosphate $[\text{PO}_4]^{3-}$ ³⁵, pyrophosphate $[\text{P}_2\text{O}_7]^{4-}$ ^{35 49 141}, oligophosphate $[\text{P}_n\text{O}_{3n+1}]^{n-2}$ ¹⁴² and metaphosphate $[\text{P}_n\text{O}_{3n}]^{-n}$, where n is the number of PO_4 tetrahedra in the chain^{35 143}. The Q^n units in phosphate glasses show linkages such as Q^3-Q^3 , Q^2-Q^2 , and Q^2-Q^1 indicating a glass network consisting of reticulated parts, chains and/or rings¹⁴² where two different kinds of nitrogen atoms are encountered, namely two-fold nitrogen N_d ($-\text{N}=\text{O}$) and three-fold nitrogen N_t ($-\text{N}\langle\text{O}$). The way nitrogen substitutes for oxygen is presented in Fig. 6^{46 49 144}. In the first case (Fig. 6a), the substitution of $\frac{2}{3}N_d$ requires 1 NBO ($=\text{O}$) double-bonded to a phosphorus atom, while in the second one (Fig. 6b) the substitution of $\frac{1}{3}N_d$ requires $\frac{1}{2}$ bridging-oxygen (BO) ($-\text{O}-$). Terminating OH groups are not considered due to their low concentration¹⁴⁵. Two rules can then be deduced from these schemes: i) $N_d = 1NBO + \frac{1}{2}BO$, and ii) $N_t = \frac{3}{2}BO$. The N_t and N_d populations follow the same trend no matter the system. There is slightly more N_t than N_d with increasing nitrogen content, up to the point where the N_t population seems to reach a limit corresponding to one N_t per tetrahedron¹⁴⁶, while the N_d population becomes predominant and increases even more^{43 46 95}. The N_t/N_d ratio was found close to 3 no matter the N/P ratio in ref.¹⁴⁵. It is suggested that nitrogen substitutes randomly for oxygen in the glass to form PO_3N units

¹⁴⁶. Then, the observed fraction of $P(O, N)_4$ mixed tetrahedra suggests that nitrogen preferentially substitutes for oxygen atoms bridging PO_4 and PO_3N units ^{146 147}, which are hence changed to PO_3N and PO_2N_2 units as illustrated in Fig. 7. As nitrogen enters the network, the PO_4 population drastically decreases, while the PO_2N_2 population and mostly the PO_3N population increase with increasing nitrogen content ^{43 45 145 146 95 148}. The PO_3N population increases up to some equilibrium fraction, while the PO_2N_2 population keeps increasing. This matches the proposed mechanism, where firstly PO_3N tetrahedra are formed at the expense of PO_4 tetrahedra, and then connected PO_4 - PO_3N tetrahedra are converted to PO_3N - PO_2N_2 tetrahedra ¹⁴⁸, finally resulting in homogeneously distributed oxynitride micro-domains. A different mechanism is proposed in lead-containing glasses, where PO_4 tetrahedra close to lead atoms are preferentially nitrated into PO_3N tetrahedra ^{43 148}. Phosphorus oxynitride glasses are thus based on PO_4 , PO_3N and PO_2N_2 units. The PO_3N and PO_2N_2 units can be sub-divided into various sub-units, that are distinguishable by means of *NMR* ¹⁴²: $PO_3N(a)$: P connected to 2 *BO*, 1 *NBO* and 1 N (N_t or N_d); $PO_3N(b)$: P connected to 1 *BO*, 2 *NBO* and 1 N (N_t or N_d); $PO_3N(c)$: P connected to 0 *BO*, 3 *NBO* and 1 N (N_t or N_d); $PO_2N_2(a)$: P connected to 1 *BO*, 1 *NBO* and 2 N (N_t or N_d); and $PO_2N_2(b)$: P connected to 0 *BO*, 2 *NBO* and 2 N (N_t or N_d). Although PON_3 and PN_4 tetrahedra are found in compounds such as P_4ON_6 ¹⁴⁹, such units were not reported in oxynitride glasses so far. This is because at large N/P ratio, crystallization occurs and prevents the formation of such units. Some papers focused on mixed M-Si-P-O-N oxynitride glasses ^{33 35}, which present P-O-Si linkages as well as traces of 6-fold coordinated silicon atoms. It was suggested that the content in SiO_6 octahedra decreases with increasing nitrogen content. Moreover, it appears that P-N bonds form preferentially with respect to Si-N bonds.

c) Borates

Investigations into boron-containing oxynitride glasses are very limited and therefore little is known about such materials. When boron is incorporated by means of a sol-gel route, B-N bonds form at the expense of Si-O-B linkages^{39 40}. Such bond formation was not confirmed in glasses made by the conventional melting route. Whether $B(O, N)_x$ units exist, with x being equal to 3 and/or 4 depending on the boron atoms coordination number (3 or 4), or whether isolated BN units form still remain to be elucidated^{38 40}. In view of the low solubility of BN in oxide melts the latter hypothesis is more likely⁵⁹.

d) Aluminosilicates

Aluminum is mostly 4-fold coordinated in oxynitride aluminosilicate glasses. However, a fraction of the Al atoms (about one third in *RE*-Mg-Si-Al-O-N glasses) is present in higher coordination states (up to 5-6)^{137 140}. The larger the nitrogen content is, and the larger the 6-fold aluminum content becomes¹⁵⁰. Although aluminum can form bonds with nitrogen, Si-N bonds form preferentially over Al-N bonds¹³⁷. Nevertheless, solid-state *NMR* investigations brought to light the existence of AlO_3N structural units in addition to the AlO_4 tetrahedra¹³⁷. Besides, the formation of AlO_2N_2 and $AlON_3$ was evidenced in oxynitride glass-ceramics¹⁵¹, but not in oxynitride glasses though. Nevertheless, it is noteworthy that these latter structural units are hardly detectable because of the quadrupolar broadening of the peaks in solid-state *NMR*^{150 152}. Therefore, aluminosilicate oxynitride glasses are composed of Al-O-Al and Si-O-Al linkages, while Al-N-Al and/or Si-N-Al linkages are expected as a result of mixed $Al(O, N)_4$ tetrahedra^{126 137}. In phosphate-based glasses, aluminum is also present in AlO_4 AlO_5 and AlO_6 polyhedra¹⁵³, forming Al-O-P linkages^{33 72}, but there is no certainty regarding the existence of Al-N bonds in such glasses.

e) Fluorine

Few studies dealing with oxyfluoronitride glasses were reported^{24 31 67}. In phosphate-based oxynitride glasses, fluorine can form P-F bonds, thus acting as a depolymerization agent leading to $P(O, F)_4$ and $P(O, N, F)_4$ units. The formation of PO_2FN units was suggested¹⁵⁴. Fluorine can also be linked to *M* cations such as Na or Ca, thus forming compounds such as CaF_2 ^{155 156}. In the case of aluminosilicates glasses, an increase in fluorine leads to an increase in Al(V) and Al(VI) at the expense of Al(IV)^{31 157}. A few possible reasons could be that a fraction of the aluminum forms $Al[O_xF_y]^{n-}$ oxyfluorides complexes. The presence of nitrogen does not seem to change the fluorine environment. In fact, the effects of nitrogen and fluorine on the properties of such glasses seem additive and independent^{67 120}.

f) Sulfur

New mixed oxy-sulfide nitride glasses (MOSN), obtained from the ammonolysis of oxy-sulfide phosphate melts, where nitrogen substitutes for both oxygen and sulfur, were investigated in the past few years^{158 159 160}. These glasses, which combine high ionic conductivities, suitability for thin film processing, resistance toward devitrification and chemical durability, are promising materials as solid state electrolytes in all solid state batteries. Their structure is chiefly based on mixed $P(O, S, N)_4$ tetrahedra.

g) Rare-earths

Rare-earths (*RE*) in glasses are characterized by their high coordination states^{18 126 161}. In the case of oxynitride glasses, the impacts of nitrogen and rare-earths on their properties are additive and independent¹²⁵. *RE* cations are mainly bonded to oxygen and found in a +3 oxidation state, with the exception of europium, which also occurs in a +2 oxidation state.

h) Miscellaneous: Be, Mg, Ge

A recent study in Be-containing oxynitride glasses showed that beryllium is present as BeO_4 structural units, having a similar role to that of aluminum⁸. This results in Si-O-Be linkages. There is no evidence for a bonding between Be and N. The coordination number of magnesium is usually high in oxynitride glasses (>4)¹⁶². However, depending on the chemical composition, a fraction of the magnesium atoms exists as MgO_4 structural units, thus forming Mg-O-Si linkages^{126 140 162 163}. The addition of more nitrogen into the glasses leads to an increase of the amount of 4-fold magnesium¹⁶². However, Mg-N bonds were not reported so far in oxynitride glasses. The structure of germanophosphate oxynitride glasses was recently investigated⁷⁷. Germanium is present in GeO_4 , GeO_5 and GeO_6 polyhedra that mostly forming Ge-O-P linkages (rather than Ge-O-Ge linkages). Nitrogen substitution has various effects on their structures: It preferentially substitutes Ge-O-P linkages to form Ge-O-Ge linkages and mixed $\text{P}(\text{O}, \text{N})_4$ tetrahedra, and depolymerizes both the phosphate and the germanate network, as GeO_4 tetrahedra becomes the most predominant germanium-based polyhedra. Whether germanium form Ge-N bonds, or solely bonds to oxygen to form GeO_x units (x equal to 4, 5 and/or 6) remains to be elucidated.

4.2 Physical properties

Oxynitride glasses exhibit higher T_g and T_c , and a lower thermal expansion coefficient than their oxide counterparts^{22 26}. They further show up with a larger refractive index^{10 22}, ionic conductivity (in particular in the Na-Si-O-N¹⁰¹, Li-Si-O-N⁶⁴ and Li-P-O-N⁵¹ systems), dielectric constant^{164 165 166}, and density²⁶. Some minor change of the heat capacity were also reported^{167 168}. Nitrogen also improves the corrosion resistance in water^{169 94} as well as in acidic or alkali media^{127 170}. It seems that the incorporation of nitrogen has little effect on the cytotoxicity of the glasses³⁶, but slightly reduces the bioactivity^{120 171}. Moreover, oxynitride

glasses present a reducing character because of the N^{3-}/N^0 redox couple, that causes either the nitridation of various oxides or their reduction into metallic or inter-metallic particles (such as iron-silicides), which is a likely source for the loss of transparency^{172 173 174}. The reducing character of the nitrated melt was studied both in phosphorous and in silicon oxynitride glasses¹¹⁵, and explains the reduction of Eu^{3+} to Eu^{2+} in an europium-doped Y-Si-Al-O-N oxynitride glass¹⁷⁵. Furthermore, rare-earth containing oxynitride glasses exhibit luminescent properties^{76 175 176}. The concept of optical basicity was extended to oxynitride glasses and a linear relationship was found between the anionic polarizability (O^{2-} and N^{3-} anions) and the composition¹⁷⁷. The introduction of nitrogen into the melt results in increases of the shear viscosity¹⁶⁹ and of the surface tension¹⁷⁸. The viscosity of oxynitride liquids is mostly very sensitive to temperature^{77 147}. For examples, Y-Si-Al-O-N and Ca-Si-Al-O-N glass forming liquids can be considered as relatively “fragile” per the C.A. Angell classification¹⁷⁹, as will be discussed in § 5.4. However, this trend does not apply to all systems and the fragility index is found to decrease with the N/P ratio in LiPON and NaPON glasses¹⁴⁷, while it increases with the N/P ratio in LiNaGePON glasses⁷⁷.

The biocompatibility and enhanced durability of silicon oxynitride glass systems is of paramount interest for biomedical applications as bioactive oxide glasses suffer from relatively small strength, hardness and stiffness, which prevent applications in major load-bearing applications. In such a field of applications, the improvement of the mechanical performance induced by the substitution of oxygen by nitrogen is decisive.

5 MECHANICAL PROPERTIES

The mechanical properties of oxynitride glasses are mostly directly correlated to their nitrogen content. Hardness, elastic moduli, fracture toughness and viscosity increase with the nitrogen content, no matter the system^{22 26 44 53 58 105 180}. Since the Si-N bond is weaker than the Si-O

bond, the atomic packing density and the fine details of the atomic arrangement, including the increase of the cross-linking, come into play. In contrast with the case of silicon oxynitride glasses (SiON), the mechanical properties of phosphorus oxynitride glasses (PON) were scarcely reported and are thus discarded in the following paragraphs. Nevertheless, PON follow the same general trends as SiON: the introduction of nitrogen increases hardness, stiffness, chemical durability, resistance to stress corrosion, toughness and strength. In the case of PON glasses, which exhibit relatively low T_g and mechanical performance and are particularly sensitive to humidity, the substitution of oxygen by nitrogen results in a dramatic and often critical improvement of the mechanical properties and durability, hence enlarging the field of applications for human bone replacements, metal sealing (thanks to relatively large expansion coefficients) or solid electrolytes for rechargeable batteries. For PON, K is typically between 30 and 35 GPa, E is between 35 and 45 GPa, and H is between 1.5 and 2.5 GPa.

5.1 Elastic moduli and Poisson's ratio

Oxynitride glasses possess the largest elastic moduli among non-metallic glasses, with E reaching about 190 GPa (SiYAlON system). The bulk modulus of a material can be seen as reflecting a volume density of energy. This is expressed by what is known as the 1st Grüneisen rule: $K = \frac{mnU_o}{9V_o}$, where U_o is the atomic bonding energy, V_o the atomic volume at equilibrium, and m and n are the power law exponents of the pair potential,

$$U(r) = \frac{nU_o}{(m-n)} \left[\left(\frac{r_o}{r} \right)^m - \frac{m}{n} \left(\frac{r_o}{r} \right)^n \right] \quad (21)$$

This expression can be extended to a multicomponent glass composition using the average dissociation enthalpy $\langle U_o \rangle$ and the volume $\langle V_o \rangle$ of an equivalent mole of glass (also referred to as an *atom gram*) (see ref. ²³ for details). The dissociation enthalpy was calculated for many glasses from different chemical systems, including metallic ones, and is shown in Fig. 8 as a

function of the glass transition temperature. In the same way that the shear modulus of crystalline materials is found to scale with the melting point, $\langle U_0 \rangle$ is found to increase with T_g . However, the energy range for silicon oxynitride glasses (from 550 to 700 kJ·mol⁻¹) is quite close to the one for silicate glasses, and there is no one to one relationship between elastic moduli and T_g for glasses, as shown in Fig. 9. In fact, the Si-N bond is weaker than the Si-O one, and much larger than metallic bonds, but metallic glasses appear to compete well with oxynitride ones, whereas silicate glasses are usually less rigid. For example, K reaches values as large as 139 and 159 GPa for Y_{0.146}Si_{0.232}Al_{0.034}O_{0.31}N_{0.29} and Pd_{0.4}Cu_{0.3}Ni_{0.1}P_{0.2} glasses respectively. For vitreous silica, $K \approx 33$ GPa. The reason for this counter-intuitive observation lies in the fact that the atomic packing efficiency (C_g) is much larger ($\langle V_0 \rangle$ is smaller) in metallic glasses than in non-metallic ones, and furthermore that it is larger in silicon oxynitride glasses than in oxide silicates. In the case of a disordered arrangement of atoms, C_g can be determined from the ratio of the effective volume occupied by a mole of atoms (V_0), as estimated from the atomic radii ($V_0 = \mathcal{N} \sum_i \frac{4}{3} \pi x_i r_i^3$, where \mathcal{N} is Avogadro number and x_i and r_i are the atomic fraction and ionic radius of the i^{th} element), to the corresponding volume of glass, calculated from the specific mass of the glass (ρ) and the molar mass of the constituents (m_i):

$$C_g = \frac{\mathcal{N} \sum_i (4/3) \pi x_i r_i^3}{(\sum_i x_i m_i) / \rho} \quad (22)$$

The atomic packing density typically ranges between 0.45 and 0.55 for silicate glasses, between 0.57 and 0.65 for silicon oxynitride ones and reaches values as large as 0.8 in precious metal based metallic glasses. Therefore, an efficient atomic packing is found to compensate easily for a relatively small energy content. Consistently with a large packing density, oxynitride glasses show up with relatively large values for ν , typically around 0.26-0.32, whereas for oxide silicates ν is between 0.15 (a-SiO₂) and 0.25 (Fig. 10). The increase in

Young's modulus is roughly linear with the nitrogen content and given by: $E(\text{GPa}) = E_0 + 4xN$ (at.%), where E_0 is Young's modulus of the parent oxide glass (Fig. 11).

Makishima and Mackenzie (*M-M*)¹⁸¹ proposed a model to estimate the elastic moduli from the packing density, C_g , the molar fraction, f_i , and the volume density of energy, ΔH_{ai}^V ($\text{J}\cdot\text{m}^{-3}$), of the i^{th} oxide entering the glass composition. For instance, in the case of Young's modulus, these authors arrived at the following expression: $E = 2C_g \sum f_i \Delta H_{ai}^V$, where ΔH_{ai} is calculated from the molar dissociation energy ($\text{J}\cdot\text{mol}^{-1}$), the specific mass, ρ_i , and the molar mass, M_i , according to $\Delta H_{ai}^V = \frac{\rho_i}{M_i} \Delta H_{ai}$ ²³. Values for C_g obtained this way are mostly close to experimental data in the case of silicate glasses, but are greatly underestimated in the case of oxynitride glasses. An extension of this theory was proposed, using the ratio of formation free energies of monoatomic nitrogen on oxygen in their gaseous state at 298.15 K $\frac{\Delta G_f^\circ(\text{Ng})}{\Delta G_f^\circ(\text{Og})} = \frac{108.99}{54.99} = 1.98$, in order to take into account the energetic stabilization excess induced by the substitution of nitrogen in the glass network¹⁸². Thus, when the i^{th} compound of the glass is a nitride, the volume density of energy is calculated such as $\Delta H_{ai}^V = 1.98 \frac{\rho_i}{M_i} \Delta H_{ai}$, leading to better agreements with measured Young's moduli of oxynitride glasses. Nevertheless, these models are chiefly empirical and hardly help understand what is going on when compositional changes occur. Furthermore, such theoretical calculations require the knowledge of the actual value for the glass density (C_g determination), so that the ab initio character is somewhat lost. As was underlined by Daucé et al.¹⁸³ a reliable quantitative estimation based on the *M-M*-type approach is only possible for glasses with compositions close to those of crystallized compounds for which the actual ionic radii are accurately known. Furthermore, the dissociation energy is not a reticular energy and it is not obvious that C_g can be used as an ersatz of the Madelung constant. Back to the simple extension of the Grüneisen model, it turns out that for silicon oxynitride glasses, K increases rather exponentially with the volume density of energy (Fig. 12). As far as the change in the

ionic radii and interatomic bonding energy with composition can be neglected, this suggests a monotonic increase of the mn product with the nitrogen content. This is likely due to the marked increase of C_g with the nitrogen content, which would result in a steeper repulsive branch for the pair potential, that is in an increase of m . Interestingly, a large slope for the K versus $\langle U_0 \rangle / \langle V_0 \rangle$ correlation was also noticed for germanate and silico-aluminate glasses, where Ge and Al are known to experience 4, 5 and 6-fold coordination, which is a favorable situation toward an efficient packing. The mn product is close to 9 for phosphate and alkali-alkaline-earth silicate glasses, but is larger for metallic glasses¹⁸⁴ and for germanates and aluminates²³.

5.2 Hardness, indentation deformation and indentation cracking

The hardness (H) of silicon oxynitride glasses ranges between 6 and 13 GPa (Vickers indentation tests) and make these glasses the hardest of all glasses (Fig. 13). The largest values were reported for Rare-earth-Si-Al-O-N glasses (especially with yttrium). For a given system, H is found to increase almost linearly with the nitrogen content, with $H \approx H_0 + \alpha[N]$ (e/o) where α ranges from 0.07 to 0.12¹⁸⁵ (Fig. 14), where H_0 is the hardness of the parent oxide glass. The reason for oxynitride glasses being so hard is two-fold: i) the atomic network cross-linking degree is large thanks to 3-fold coordinated nitrogen, and ii) atoms are more efficiently packed in average in the presence of nitrogen. The combination of these two factors compensates for the Si-N bond being weaker than the Si-O bond. The effect of the average crosslinking degree on hardness was addressed by means of the topological constraints theory¹⁸⁵ and it was found that hardness increases linearly with the number of additional constraints Δn induced by the substitution of nitrogen. Since Δn increases linearly with the nitrogen content in e/o, this provides an explanation for the linear relationship between H and N e/o. Furthermore, according to this model the slope depends little on the composition of the parent nitrogen free glass. For

oxynitride glasses, the E/H ratio is typically in the 11-13 range, and ν is between 0.26 and 0.32. This makes these glasses sensitive to lateral (subsurface) and to radial cracking under a sharp indenter, as opposed to cone and median cracking (see Fig. 9 in ref. ¹⁸⁶) (Fig 15). Besides, because C_g is relatively large in such glasses, there is little room for stress accommodation through densification (as in the case of silica-rich glasses for example). Hence, in spite of the fact that silicon oxynitride glasses are stiff, hard, strong, and relatively tough (see next paragraph), they experience a well-developed radial crack system (Fig. 16).

5.3 Fracture toughness and slow crack growth

The fracture toughness of silicon oxynitride glasses, as estimated by means of indentation-cracking techniques (mostly), is in between 0.6 and 2.7 MPa·√m^{187 188 65 189 190 191 192 193 194}, and increases with the nitrogen content (Fig. 16). The incorporation of 15 e/o N in an oxide silicate glass typically results to a 10-15 % increase of K_{Ic} . Nevertheless, the actual increase, as measured by means of a self-consistent method, such as the Single Edge Precracked Beam (SEPB) or the Chevron-Notch (CN), is usually smaller¹⁹⁵. A relatively simple approach to predicting the fracture surface energy, γ , in a quantitative manner from the stoichiometric composition consists in assuming a propagating crack extends following a path disrupting the weakest links of the energy landscape and to estimate the surface energy from the bond strength and the bond concentration along this fracture surface¹⁹⁴. The fracture toughness, K_{Ic} , is then deduced by means of the classical expression from linear fracture mechanics: $K_{Ic} = \sqrt{\frac{2\gamma E}{1-\nu^2}}$. Let x_i be the stoichiometric fraction of the species involved in the i^{th} diatomic bonding energy U_{oi} (in J·mol⁻¹), between the i^{th} cation and a first neighbor oxygen anion in the case of an oxide glass, and let n_i be the number of such bonds supposed to be broken as the crack front propagates to the next unit, then γ is expressed as

$$\gamma = \frac{1}{2} (\sum_i 4/3\pi x_i r_i^3)^{-2/3} \mathcal{N}^{-1} C_g^{2/3} < U_o > \quad (23)$$

where ρ and M_o are the glass density (specific mass) and the molar mass of a representative unit (gram-atom of glass), \mathcal{N} is Avogadro number, and the $\frac{1}{2}$ prefactor on the right hand side member accounts for the fact that the bond disruption process leads to the formation of two complementary surfaces (a crack has two walls) (see ref. ¹⁹⁴ for details).

For example, Young's modulus as high as 150 GPa is typically measured for glasses from the RE-Si-Al-O-N system (RE: Y, Nd, Lu etc.). In such glasses, the mean energy ($< U_o >$ $< U_o > = \sum_i x_i n_i U_{oi}$), is calculated considering the number of Si-N bonds, taken as $\frac{3}{4} x_N$, and the remaining Si-O bonds equal to $x_{Si} - \frac{3}{4} x_N$. For example, for the $Y_{0.123}Si_{0.185}Al_{0.07}O_{0.547}N_{0.075}$ glass composition, taking U_{oSi-N} , U_{oAl-O} , U_{oY-O} equal to 437, 502 and 698 kJ·mol⁻¹ respectively, a fracture energy of 4.0 J·m⁻² and a theoretical toughness of 1.2 MPa·√m are calculated, quite close to the experimental value of 1.05 MPa·√m¹⁰³. The theoretical values are in the range 0.8-1.1 MPa·√m for oxynitride glasses (Fig. 16) and are close to the experimental values as obtained by the *SEPB* or by the *CN* method, but about twice smaller than the ones obtained by the indentation cracking method at large nitrogen content. It is thus concluded that the toughness of silicon oxynitride glasses with 5 to 20 at.% nitrogen is near 1 MPa·√m. In oxynitride glasses, calculations were performed considering nitrogen is three-fold coordinated and solely bonded to silicon, even though a non-negligible amount of Al-N bonds exists in such glasses ¹³⁷. When Poisson's ratio ν was not specified, a value of 0.28 was arbitrarily chosen as Poisson's ratio often ranges from 0.26 to 0.32 in silicon oxynitride glasses ^{65 189 188} (Fig. 10).

Silicon oxynitride glass is also present at the grain-boundaries in Si₃N₄-based ceramics, due to the liquid phase that forms in the high temperature sintering conditions thanks to the sintering additives (Al₂O₃, Y₂O₃ etc.). In these ceramics, a fracture toughness as large as 4-5 MPa·√m is obtained by controlling i) the size and the morphology of the elongated grains and

ii) the composition and crystallinity of the secondary grain boundary phase ¹⁹⁶. The theoretical approach introduced above results in a K_{Ic} value of about $1.44 \text{ MPa}\cdot\sqrt{\text{m}}$ for Si_3N_4 ($\nu = 0.28$ and $E = 300 \text{ GPa}$). This value is in agreement with the experimental one obtained for Si_3N_4 single crystal, that is regardless of any additional toughening phenomena such as crack deflection and crack front bowing due to the acicular shape of the $\beta\text{-Si}_3\text{N}_4$ grains, which lies between 1.5 and $2.0 \text{ MPa}\cdot\sqrt{\text{m}}$ ¹⁹⁷. This value can thus be seen as an optimum value for a straight through crack in a silicon nitride material.

The introduction of nitrogen in a silicate or a phosphate glass was found to increase the chemical durability and the resistance to environmentally assisted slow crack growth (known as the stress corrosion phenomenon). The study by Bhatnagar et al ¹⁸⁹ reveals a decrease of the crack growth velocity for a given stress intensity factor by over an order of magnitude in an Y-Si-Al-O-N glass in comparison to soda-lime-silica and borosilicate glasses in air, and an improvement of several orders of magnitude in water. Coon ¹⁹⁸ studied the slow crack growth resistance of a Y-Si-Al-O-N glass by means of the double cantilever beam technique, and concluded to a several orders of magnitude smaller crack velocity at a given stress intensity factor for the oxynitride glass in comparison to a standard glass slide (likely a soda-lime-silica glass). Besides, the stress corrosion exponent (Paris law exponent) is typically above 150 for the oxynitride glass and below 150 for the oxide silicate glass.

5.4 High temperature behaviour

a) Elasticity

In all cases but a- SiO_2 (and to a minor extent SiOC glass), the temperature dependence of the elastic moduli of glass exhibits a transition range between a slow softening rate and a faster one, corresponding to the glass transition (Fig. 17). The glass transition temperatures as well as the room temperature values of E and μ , and the softening rate immediately above T_g

($dE/dT(T_g^+)$ and $d\mu/dT(T_g^+)$, i.e., in the supercooled liquid range, are reported in Table I. Glass transition temperatures as measured from $E(T)$ curves are usually smaller by 10 to 20 K than the ones obtained by dilatometry with the same heating rate. There seems to be two kinds of behavior. For relatively stiff glasses such as oxynitride ones, and for $T_g < T < 1.1T_g$ ²³:

$$E / E(T_g) = T_g / T \quad (24)$$

In most cases, the shear modulus, which depends more on T than E , changes with T above T_g according to a power law expression¹⁹⁹ (Fig. 18):

$$\mu / \mu(T_g) = (T_g / T)^\alpha \quad (25)$$

where α ranges between 0.07 (a-SiO₂) and 9 (oxynitride glass) for the selected glass composition summarized in Table I. A value of 10 was reported for a-Se¹⁹⁹.

The temperature dependence of the elastic moduli reflects the degree of ‘‘fragility’’ (as defined by Angell²⁰⁰) of the liquid. Therefore, with α equal to 9 (and a fragility index, m , equal to 48), silicon oxynitride liquids show up as particularly fragile. In polycrystalline ceramics with glassy grain-boundary phases obtained by liquid-phase sintering, the fast softening observed beyond T_g is solely due to the effect of the liquid grain boundary films and pockets (see ref.²⁰¹ for a review on this problem). Amorphous silica exhibits an anomalous behavior characterized by a rising shear modulus in the [0.5-0.95] range for T/T_g ($d\mu/dT(T_g^-) = 3.1 \text{ MPa} \cdot \text{K}^{-1}$) and a strong resistance to de-structuration above T_g as evidenced by a remarkably slow softening ($d\mu/dT(T_g^+) = -5.3 \text{ MPa} \cdot \text{K}^{-1}$) and by the fact that ν remains almost constant from 0.5 to 1.2 T_g , suggesting that the liquid keeps a strong memory of the atomic structure of the glassy solid, with little changes of the average coordination and dimensionality throughout the glass transition range. On the contrary to a-SiO₂, oxynitride glasses soften rapidly with rising temperature in spite of a relatively high degree of interatomic connectivity, high T_g and large elastic moduli. This suggests that the oxynitride glass network consists of stiff (likely nitrogen-

rich) structural units embedded in a weaker phase (likely concentrating impurities, and alkaline and alkaline-earth species). Recalling that ν shows up as a mirror of the overall network connectivity, then the dramatic decrease of $\mu(T)$ (faster 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 network de-structuration above T_g .

b) Viscosity

The glass transition range is associated with a shear viscosity coefficient of 10^{12} - $10^{12.6}$ Pa·s. In the case of silicon oxynitride glasses, and in particular those containing rare earth, T_g is in between 1123 and 1273 K (Fig. 19), which makes these glasses more refractory than silicate and aluminosilicate glasses in the transition range, approaching the viscosity of a-SiO₂ for the largest nitrogen content. The viscosity increases typically by three orders of magnitude as the nitrogen content is raised by about 25 e/o N (about 11 at.% N). Nevertheless, the apparent activation (Q) energy for viscous flow, which can be obtained straightforwardly from an Arrhenius modelling of the temperature dependence of the viscosity ($\eta = \eta_0 \exp[Q/(RT)]$), is exceptionally large, typically between 800 and 1200 kJ·mol⁻¹ in the transition range. A striking value of 2100 kJ·mol⁻¹ was once reported for a Ca_{11.04}Si₁₀O_{13.21}N_{11.8} glass ($T_g \approx 1010$ °C, 58 e/o N)²⁰². In view of the great sensitivity to temperature change of the mechanical properties of oxynitride glass forming liquids, such as the elastic moduli and the viscosity coefficient, these liquids can be considered as particularly fragile ones. Indeed, the fragility index of oxynitride glasses, as defined by $m = d\log_{10}\eta/d(T(\eta=10^{12} \text{ Pa}\cdot\text{s})/T) \approx Q/(2.303RT_g)$, ranges typically from 47 to 55 ($m \approx 18$ for a-SiO₂) (Fig. 20).

The apparent activation energy for creep of silicon nitride-based ceramics reported by most of the authors roughly coincides with the activation energy for viscous flow (above T_g) of an oxynitride glass containing the same elements as the sintering aids used for the liquid phase

sintering. This result confirms the major importance of the glassy phase on the creep behavior of these ceramic materials.

6. GLASS-CERAMICS & COMPOSITES

The crystallization of oxynitride glasses was studied in various glass systems, and especially in *RE*-Si-Al-O-N ones. In most cases, devitrification occurs through a self-nucleation process, which was attributed to the presence of metallic nano/micro particles resulting from the decomposition of Si_3N_4 ^{4 203}. The crystal growth rate was observed to decrease with increasing nitrogen content in Li-Si-O-N glasses, likely because of the increase cross-linking and stability of the glass network in the presence of nitrogen^{204 205}.

A change in the nitrogen source (AlN or Si_3N_4) leads to different crystalline phases^{151 206}. Nitrogen is eventually found to have some incidence on both the relative fractions and the structures of the different phases^{206 207}. Depending on the composition, nitrogen may either not enter the crystallized phases^{100 205} or lead to the crystallization of oxynitrides^{151 187 208 209 118 210 211} or nitrides (such as ZrN)²¹². The elastic moduli, hardness and fracture toughness of the resulting oxynitride glass ceramics are typically improved by 25% in comparison to the oxynitride parent glass^{187 213}.

A few composites based on oxynitride glasses were reported. SiC/Y-Mg-Si-Al-O-N composites present increased Young's modulus, fracture toughness and hardness compared to the SiC-free glassy matrix^{214 215}. The higher the volume fraction of the SiC particles and the smaller their size, the stronger the increase. Alternatively, SiC fibres were incorporated in a Y-Si-Al-O-N glass, which was then crystallized²¹⁶. Si-Al-Ca-O-N oxynitride glass fibres were used as reinforcements in various oxide glasses²¹⁷ or in aluminum alloys²¹⁸. Si_3N_4 particles were dispersed or grown in various oxynitride glasses, such as *RE*-Mg-Si-O-N²¹⁹ and Y-Si-Al-O-N^{220 221}. TiN/Y-Mg-Si-Al-O-N composites were synthesized by nitriding in the melt a

TiO_xN_y oxynitride using AlN, and showed a great increase in Young's modulus, shear modulus, hardness and fracture toughness with increasing vol.% of TiN ¹¹⁵.

7. MOLECULAR SIMULATIONS AND *AB INITIO* MOLECULAR ORBITAL CALCULATIONS

Very few molecular simulations of oxynitride glasses were reported. One focused on the Na-Si-O-N system and showed similar trends in density and in mechanical properties with increasing nitrogen content as measured experimentally ¹³¹. It was also proposed here that *NBN* result from the substitution of *NBO* with nitrogen. Another paper focused on the (Sc)-(Y)-(La)-Mg-Si-O-N system, and observed close radial distribution function (*RDF*) with experimental data, but with some discrepancies especially on the glasses structure ²²².

Ab initio molecular orbital calculations were performed to determine the interatomic potential, the bending force constant and the stretching force constant of several glass model molecules for silicon oxynitride glasses ²²³. It would appear that while the stretching force constant (Si-N) of the model molecules decreases with increasing nitrogen content, the bending force constant (Si-N-Si) oppositely increases. A simple model to calculate the bulk modulus shows a stronger effect of the bending force constant over the stretching force constant, which could be a reason among others explaining why oxynitride glasses show stronger bulk modulus than their oxide counterparts.

8. CONCLUSIONS AND PERSPECTIVES

The unique mechanical properties of oxynitride glasses make them special glasses. Their Young's modulus is typically above 100 GPa, their hardness above 8 GPa and their toughness greater than 1 MPa·√m. By combining these properties with functional properties in the fields of optics, biomaterials, chemical reactivity or electricity, these specialty glasses appear suitable

for various applications in solid-state batteries, because of their strong ionic conductivity, as biomaterials for bone replacement, for special windows, coatings and reinforcement fibres thanks to their hardness, stiffness and chemical inertia, for innovative enamels¹³⁴ and for nuclear waste vitrification⁶³.

Nevertheless, oxynitride glasses are disadvantaged by their difficulty and their cost of production, inherent in the high temperatures required, typically above 1600° C for the melting step, in the use of nitrogen compounds and in the control of the atmosphere. Besides, in spite of notable progress in this area, the incorporation of nitrogen mostly results in the loss of transparency.

There remain several fundamental questions regarding the atomic arrangement in oxynitride glasses. In particular, the role of alkaline and alkaline-earth cations and the way nitrogen is connected to the structural units, such as (Si, Al)(O, N)₄ tetrahedra, remains to be elucidated. While nitrogen is lighter than oxygen and increases the cross-linking, oxynitride glasses are denser than their parent oxide glasses, exhibit a larger atomic packing density, a larger Poisson's ratio, and are stiffer and harder despite the Si-N bond being weaker than the Si-O one. Further structural investigations, in conjunction with molecular dynamic simulation, are required to get a better insight into the atomic scale structure of these glasses.

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TABLE I. High temperature elastic properties of a SiYAlON oxynitride glasses with 17 e/o N (adapted from ²³ and ¹⁹⁹). Typical glasses from other chemical systems are also reported for comparison. ¹)From Dilatometry or Differential Scanning Calorimetry; ²)Transition temperature observed in the $\mu(T)$ measurements by means of ultrasonic echography. ³)Softening rates measured in the glassy (-) and in the supercooled-liquid (+) range near T_g . ⁴) α as obtained by smoothly fitting the experimental data in the supercooled liquid range.

Glass	$T_g^{1)}$ (K)	$T_g^{2)}$ (K)	E_{RT} (GPa)	μ_{RT} (GPa)	$\mu(T_g)$ (GPa)	$E(T_g)$ (GPa)	$d\mu/dT$ (T_g^{-}) ³) (MPa·K ⁻¹)	dE/dT (T_g^{-}) ³) (MPa·K ⁻¹)	$d\mu/dT$ (T_g^{+}) ³) (MPa·K ⁻¹)	$\alpha^{4)}$
a-SiO ₂	1463	1370	70	30.4	31	76.8	3.14	2.95	-5.30	0.07
Y _{12.3} Si _{18.5} Al ₇ O _{54.7} N _{7.5}	1216	1236	142	55	45.2	122	-8.53	-103	-247	9.0
Zr ₅₅ Cu ₃₀ Al ₁₀ Ni ₅	683	651	81	29.5	27.4	72.9	-2.37	-108	-31.3	0.78
Soda-lime-silica	835	823	72	29.3	27.1	56	-4.74	-67	-30.9	0.98
Glycerol	193	193	1.03	0.35	4.8	9.5	-22.5	-190	-28.8	1.26

TABLE II. Viscous flow properties of an oxynitride glass with 17 e/o N in the transition range (reprinted from ¹⁹⁹). ¹)Glass transition temperature taken as the temperature at which $\eta=10^{12}$ Pa·s; ²)Viscosity at T_g as determined by DSC; ³)As defined by $m = d\log_{10}\eta/d(T(\eta = 10^{12} \text{ Pa·s})/T)$;

Glass	$T_g^{1)}$ (K)	$\eta(T_g)^{2)}$ $\times 10^{12} \text{ Pa·s}$	$\Delta H_a(T_g)$ (kJ·mol ⁻¹)	$\Delta S_a(T_g)$ (J·K ⁻¹ ·mol ⁻¹)	$m^{3)}$
a-SiO ₂	1463	0.8	510	66	18
Y _{12.3} Si _{18.5} Al ₇ O _{54.7} N _{7.5}	1216	1.9	1115	799	48
Zr ₅₅ Cu ₃₀ Al ₁₀ Ni ₅	683	8	428	267	33
Soda-lime-silica	835	3	571	331	36
Glycerol	193	3	253	704	68

1489 **FIGURE CAPTIONS**

1490 **FIGURE 1** Number of papers focusing on bulk oxynitride glasses per country before 2010
 1491 (red), and during the last 10 years (blue).

1492 **FIGURE 2** The glass forming region in the Y-Si-Al-O-N system at 1700 °C extending up to
 1493 about 7 at.% N, or 25 e/o N (reprinted from ²³¹).

1494 **FIGURE 3** Photographs of 4 mm thick glass specimens in the SiO₂-BaO-Al₂O₃-Si₃N₄ system
 1495 with 0 to 27 e/o N.

1496 **FIGURE 4** Schematic drawing and pictures of the atmosphere-controlled melting, quenching
 1497 and annealing facilities at the Glass Mechanics Lab. (Rennes, France).

1498 **FIGURE 5** Gibbs free energies of various $\frac{2}{y} M + O_2 = \frac{2}{y} MO_y$ and $\frac{2}{y} AN_x + O_2 = \frac{2}{y} AO_y + \frac{x}{y} N_2$
 1499 reactions with increasing temperature, normalized to 1 mole O₂ ^{224 225}. When a nitride can be
 1500 oxidized into various oxide species (like VO, V₂O₃, VO₂ or V₂O₅ in the case of vanadium),
 1501 only the reaction showing the lowest Gibbs free energies in the temperature range is shown
 1502 (as it is the one that will reduce the most oxides).

1503 **FIGURE 6** The substitution of oxygen by nitrogen with the formation of 2-fold and 3-fold
 1504 coordinated nitrogen atoms in phosphate oxynitride glasses ⁴⁶.

1505 **FIGURE 7** Preferential substitution of oxygen bridging PO₄-PO₃N tetrahedra ¹⁴⁶.

1506 **FIGURE 8** Dissociation energy $\langle U_0 \rangle$ as a function of the glass transition temperature (T_g) for
 1507 glasses from different chemical systems (elemental symbols represent host elements of metallic
 1508 glasses). Reprinted with some modification from ref. ¹⁸⁴.

1509 **FIGURE 9** Bulk modulus (experiments) as a function of the glass transition temperature
 1510 (reprinted and adapted from ref. ²³).

1511 **FIGURE 10** Poisson's ratio, ν , as a function of the atomic packing density, C_g (reprinted and
 1512 adapted from ref. ²³).

1513 **FIGURE 11** Young's modulus of oxynitride glasses with increasing nitrogen content ^{226 227 126}
 1514 ^{228 229}.

1515 **FIGURE 12** Bulk modulus, K , as a function of the volume density of energy $\langle U_0 \rangle / \langle V_0 \rangle$
 1516 ^{230 169 226 162 227 228 188}.

1517 **FIGURE 13** Hardness (mostly from Vickers indentation tests) as a function of the glass
 1518 transition temperature (reprinted and adapted from ref. ²³).

1519 **FIGURE 14** Hardness of silicon oxynitride glasses as a function of the nitrogen content in eq.
 1520 % N. Reprinted with permission from ¹⁸⁵.

1521 **FIGURE 15** Indentation cracking and driving-force map. Stress components are taken at the
 1522 border of the indentation imprint for sake of simplicity. Recall that $\sigma_{rr}(\theta=\pi/2)$, $\sigma_{\phi\phi}(\theta=\pi/2)$,
 1523 $\sigma_{rr}(\theta=0)$, $\sigma_{\theta\theta}(\theta=0)$ are the stress components governing the ring/cone-, the radial-, the
 1524 subsurface lateral-, and the median-cracks respectively (spherical coordinates with $\theta=0$ for the

vertical axis). (-) and (+) signs indicate the area where the stress component is compressive and tensile respectively. The red contour shows where the driving force is expected to vanish. Reprinted and adapted with permission from ref. ¹⁸⁶. The inset shows the radial cracks at a Vickers indentation site (4.9 N applied for 15 s) on a $\text{Sr}_{12.73}\text{Si}_{10}\text{O}_{20.08}\text{N}_{8.44}$ oxynitride glass (the bar is equal to 50 μm) ¹⁸⁸.

FIGURE 16 Measured and calculated fracture toughness of various oxynitride glasses ^{187 188 65 189 190 191 192 193}. Round dots indicate fracture toughness measured by chevron notched specimen technique, and squared dots indicate fracture toughness measured by indentation or other techniques.

FIGURE 17 Temperature dependence of Young's modulus of glasses from different chemical systems (reprinted and adapted with permission from ref. ²³).

FIGURE 18 Temperature dependence of shear modulus (μ). The curve fitting at $T > T_g$ corresponds to $\mu/\mu(T_g) = (T_g/T)^\alpha$ (reprinted and adapted from ref. ¹⁹⁹).

FIGURE 19 Shear viscosity coefficient, η , of glasses from different chemical system.

FIGURE 20 T_g -scaled logarithm of the shear viscosity coefficient (η) in the transition range from which the activation energy for flow as well as the fragility index are straightforwardly derived from the slope of the linear intercepts (reprinted and adapted from ref. ¹⁹⁹).

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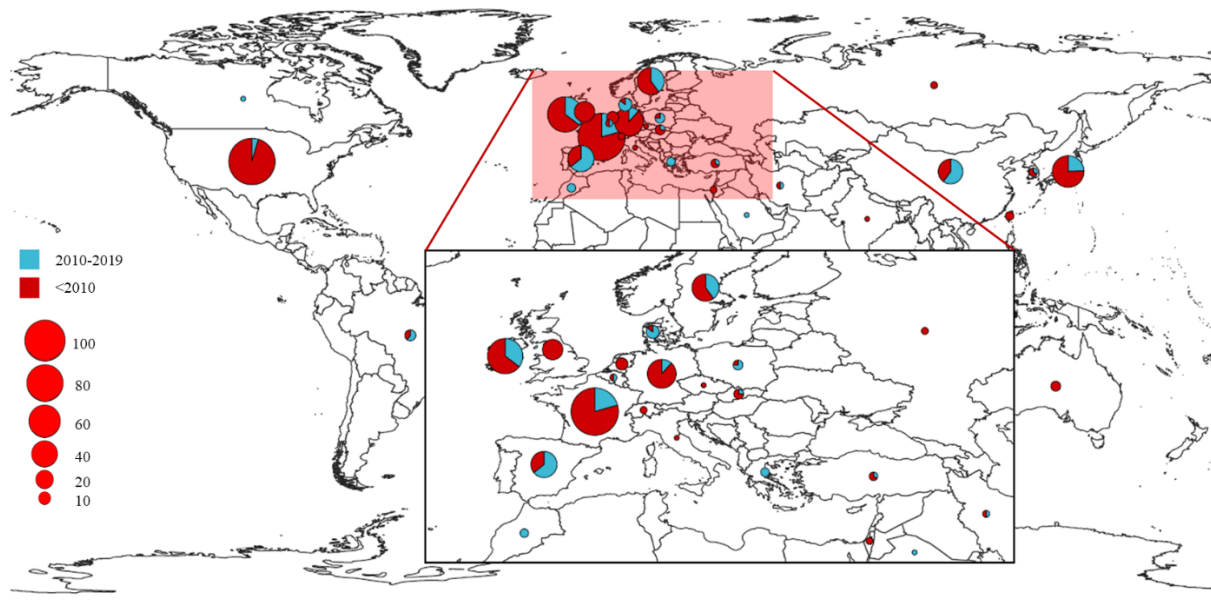


FIGURE 1 Number of papers focusing on bulk oxynitride glasses per country before 2010 (red), and during the last 10 years (blue).

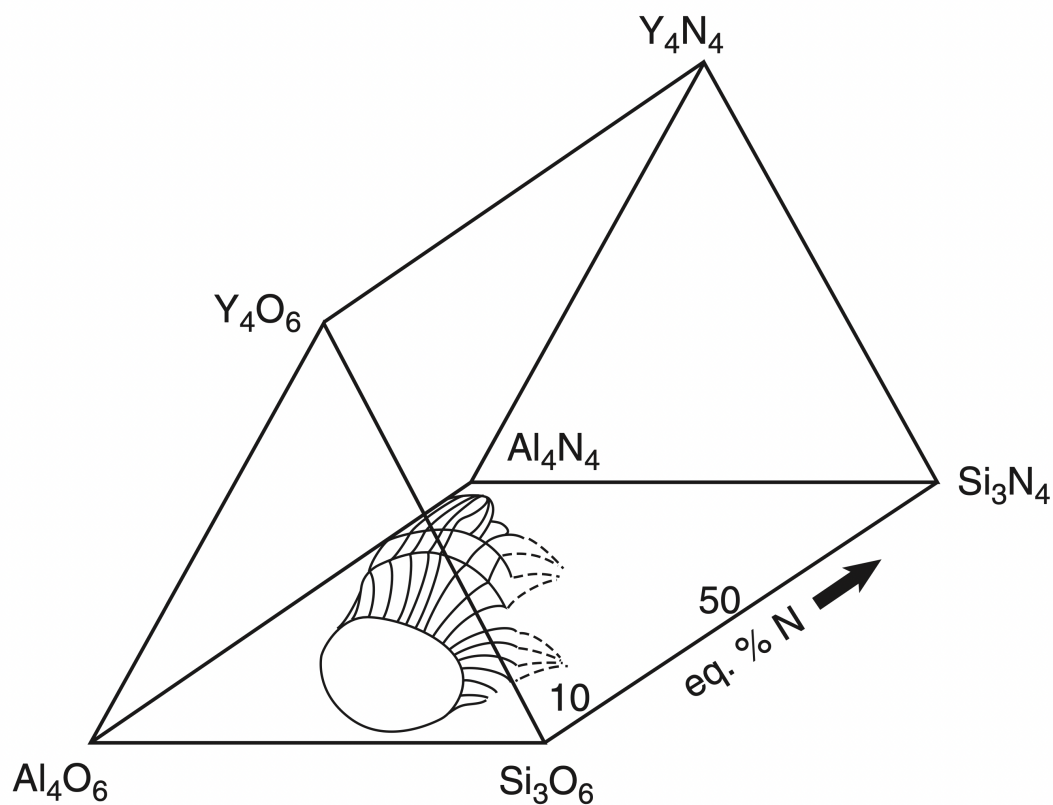


FIGURE 2 The glass forming region in the Y-Si-Al-O-N system at 1700 °C extending up to about 7 at.% N, or 25 e/o N (reprinted from ²³¹).



FIGURE 3 Photographs of 4 mm thick glass specimens in the $\text{SiO}_2\text{-BaO-Al}_2\text{O}_3\text{-Si}_3\text{N}_4$ system with 0 to 27 e/o N.

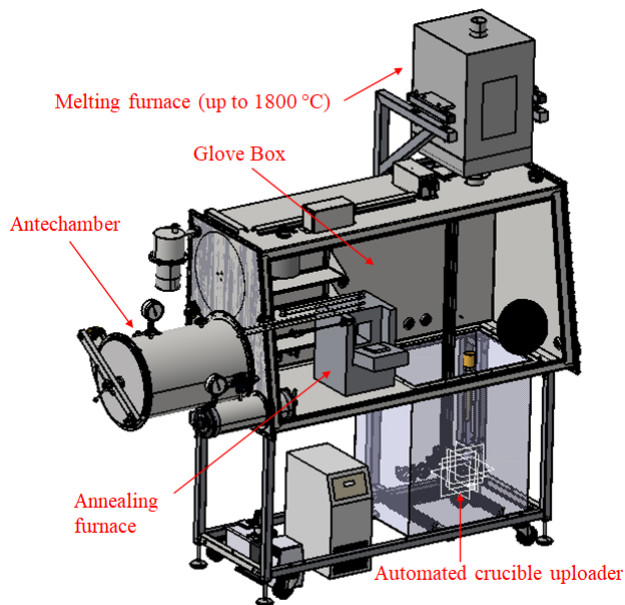


FIGURE 4 Schematic drawing and pictures of the atmosphere-controlled melting, quenching and annealing facilities at the Glass Mechanics Lab. (Rennes, France).

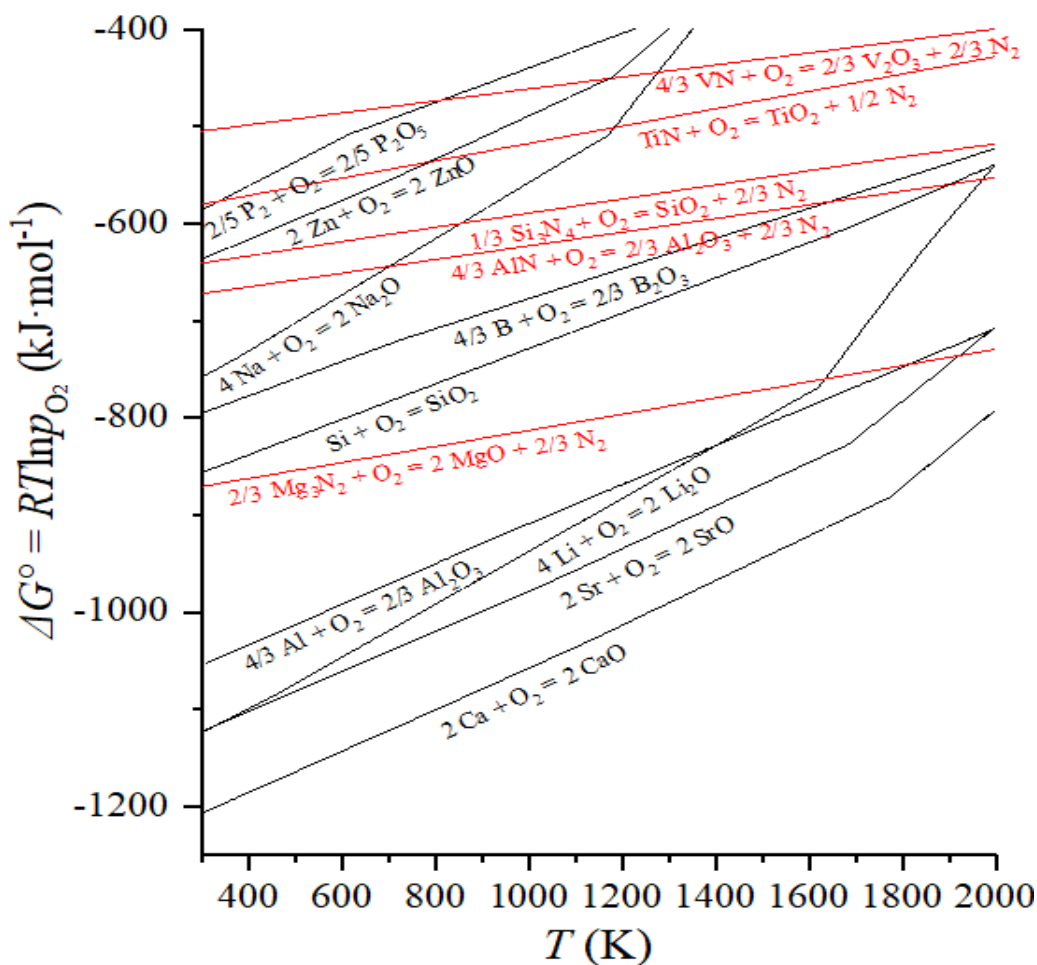


FIGURE 5 Gibbs free energies of various $\frac{2}{y} M + O_2 = \frac{2}{y} MO_y$ and $\frac{2}{y} AN_x + O_2 = \frac{2}{y} AO_y + \frac{x}{y} N_2$ reactions with increasing temperature, normalized to 1 mole O_2 .²²⁴⁻²²⁵ When a nitride can be oxidized into various oxide species (like VO, V_2O_3 , VO_2 or V_2O_5 in the case of vanadium), only the reaction showing the lowest Gibbs free energies in the temperature range is shown (as it is the one that will reduce the most oxides).

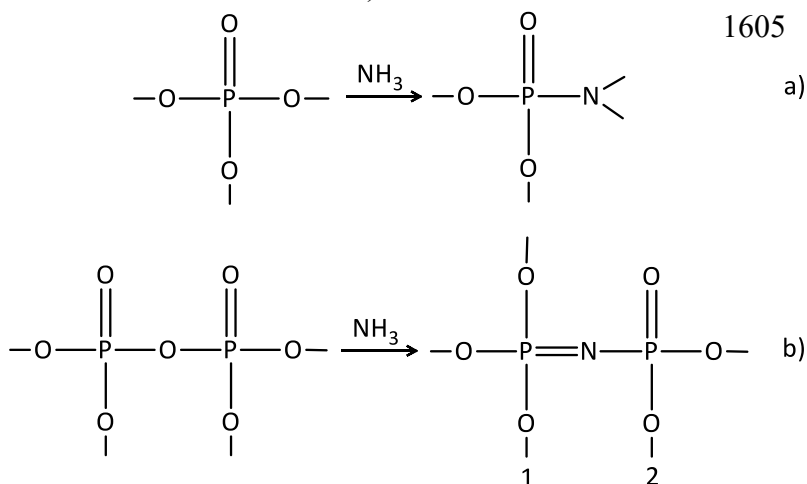


FIGURE 6 The substitution of oxygen by nitrogen with the formation of 2-fold and 3-fold coordinated nitrogen atoms in phosphate oxynitride glasses.⁴⁶

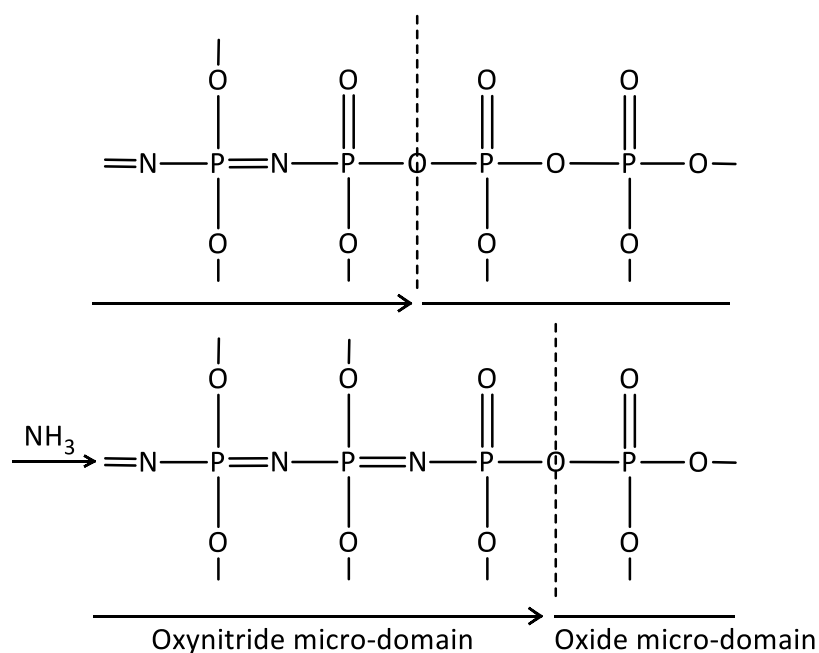


FIGURE 7 Preferential substitution of oxygen bridging $\text{PO}_4\text{-PO}_3\text{N}$ tetrahedra ¹⁴⁶.

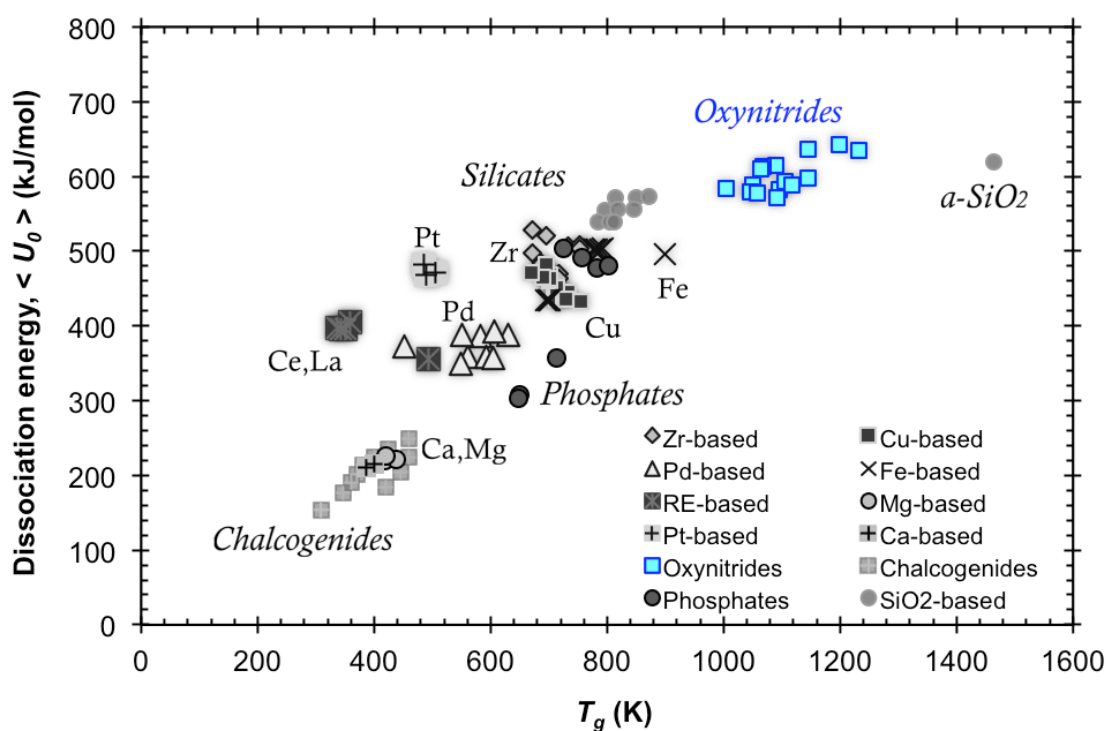


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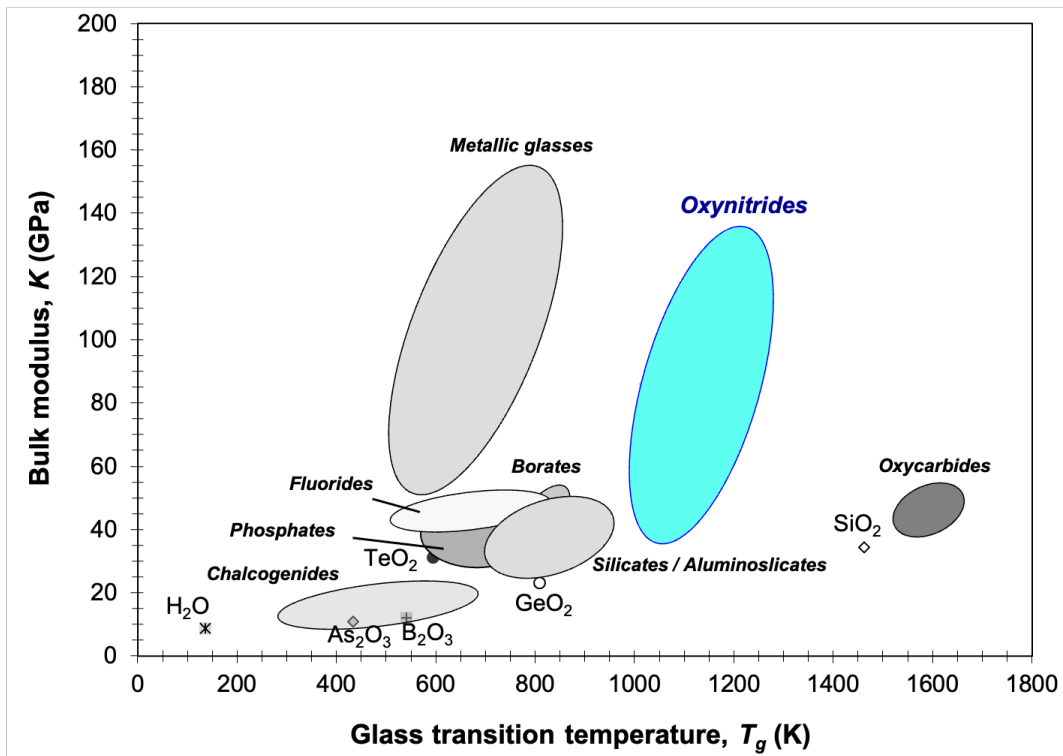


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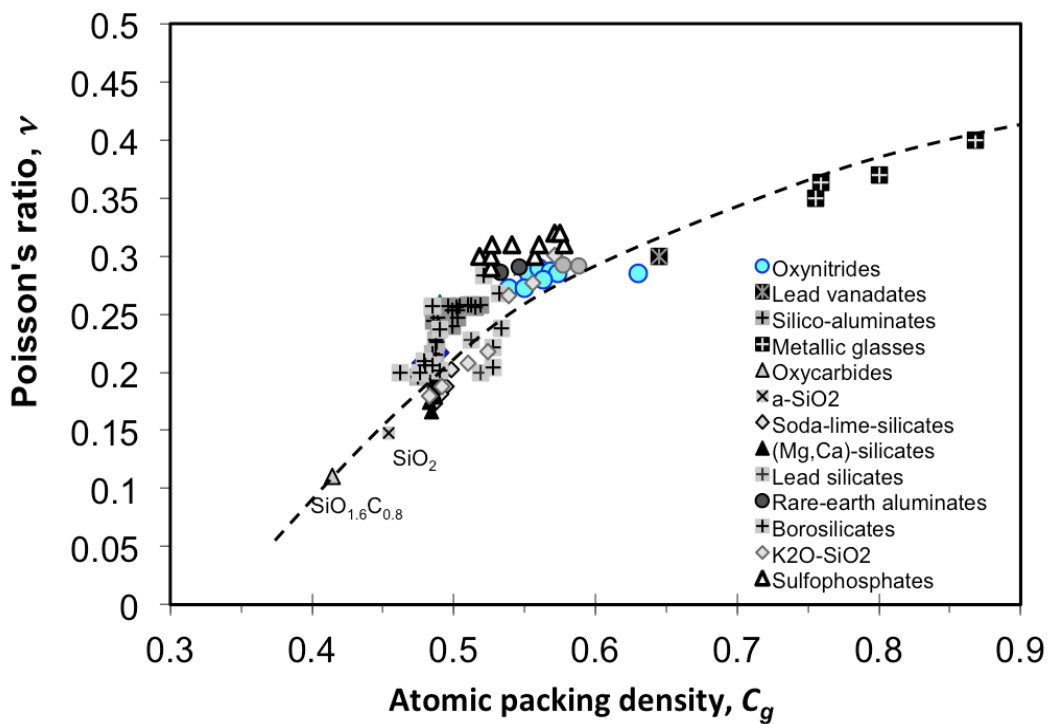


FIGURE 10 Poisson's ratio, ν , as a function of the atomic packing density, C_g (reprinted and adapted from ref. ²³).

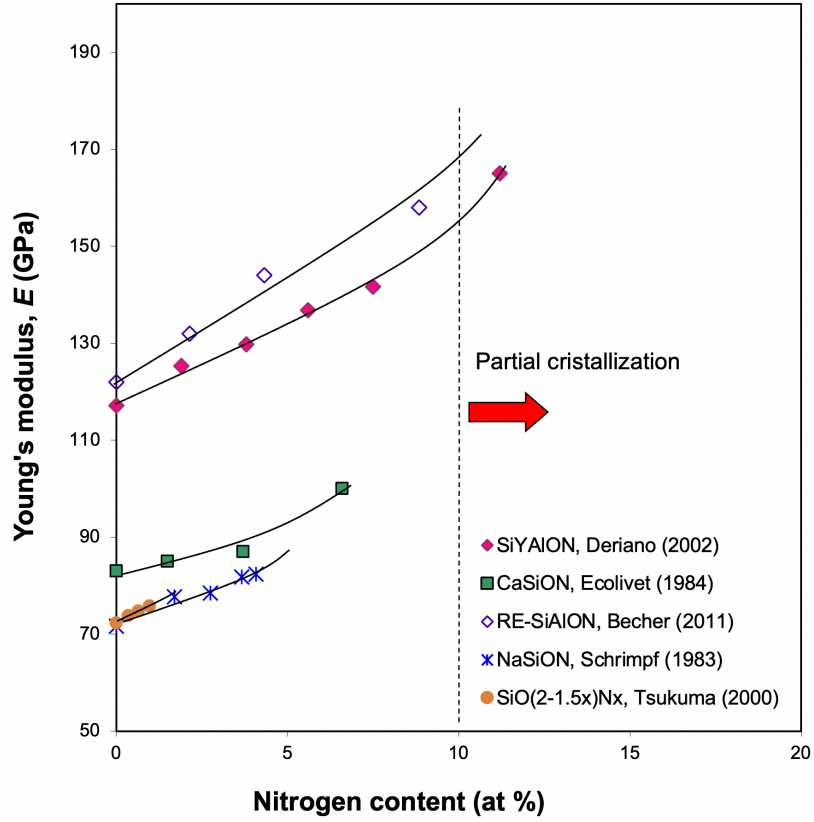


FIGURE 11 Young's modulus of oxynitride glasses with increasing nitrogen content

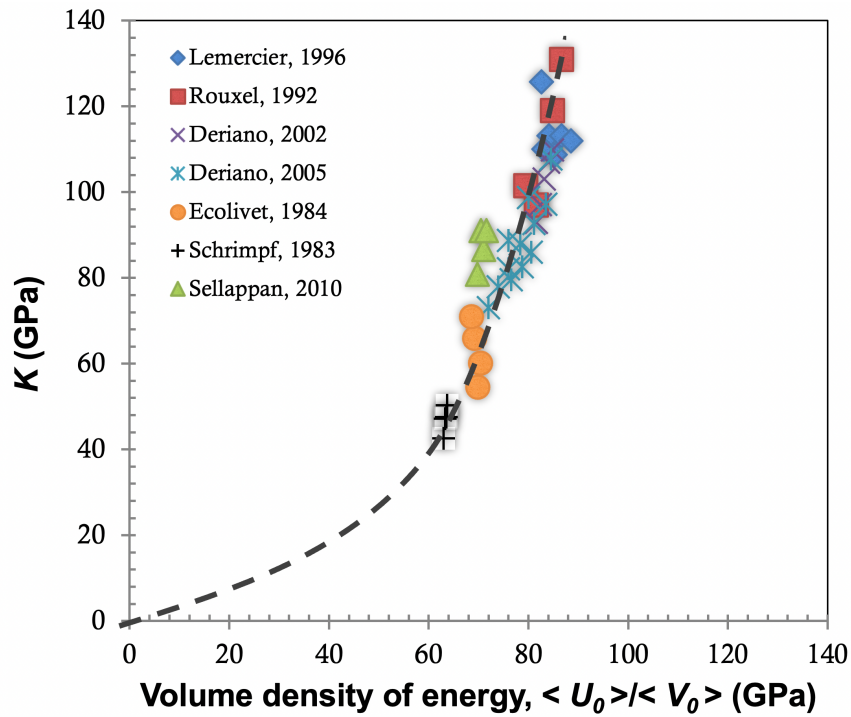
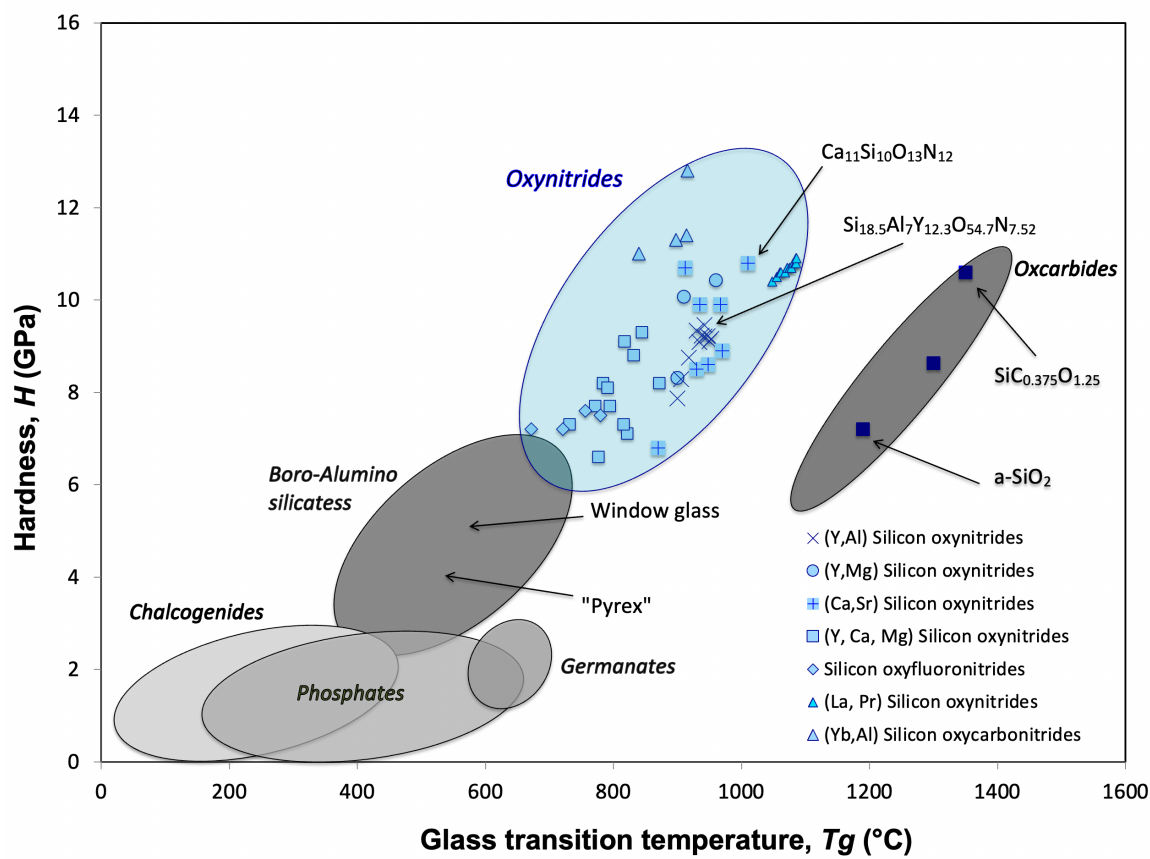


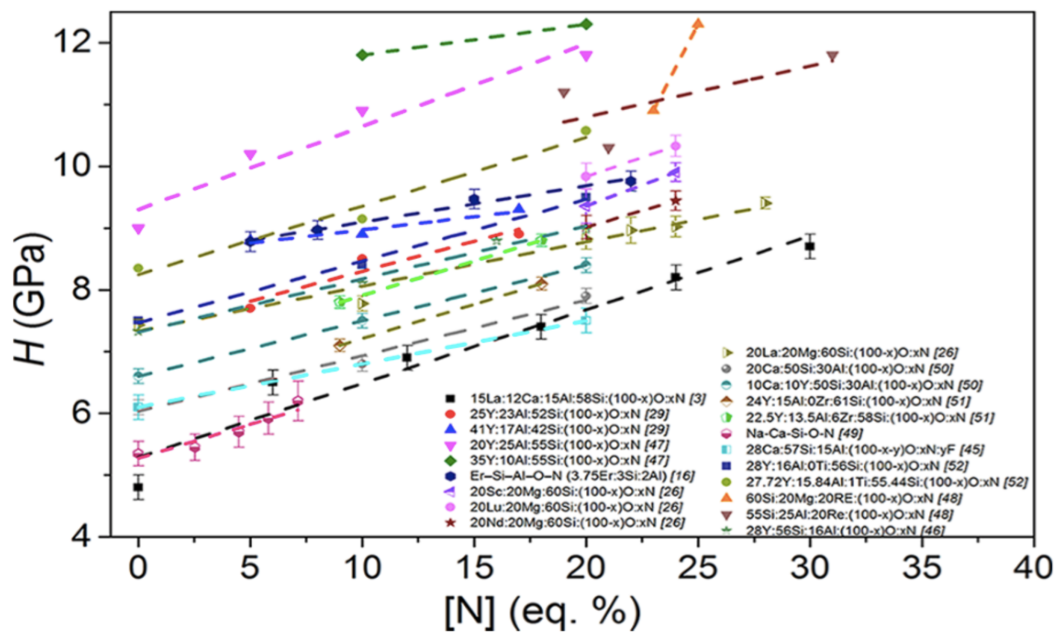
FIGURE 12 Bulk modulus, K , as a function of the volume density of energy $\langle U_0 \rangle / \langle V_0 \rangle$. Data from refs.

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1646 **FIGURE 13** Hardness (mostly from Vickers indentation tests) as a function of the glass
1647 transition temperature (reprinted and adapted from ref. ²³).



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1649 **FIGURE 14** Hardness of silicon oxynitride glasses as a function of the nitrogen content in eq.
1650 % N. Reprinted with permission from ¹⁸⁵.

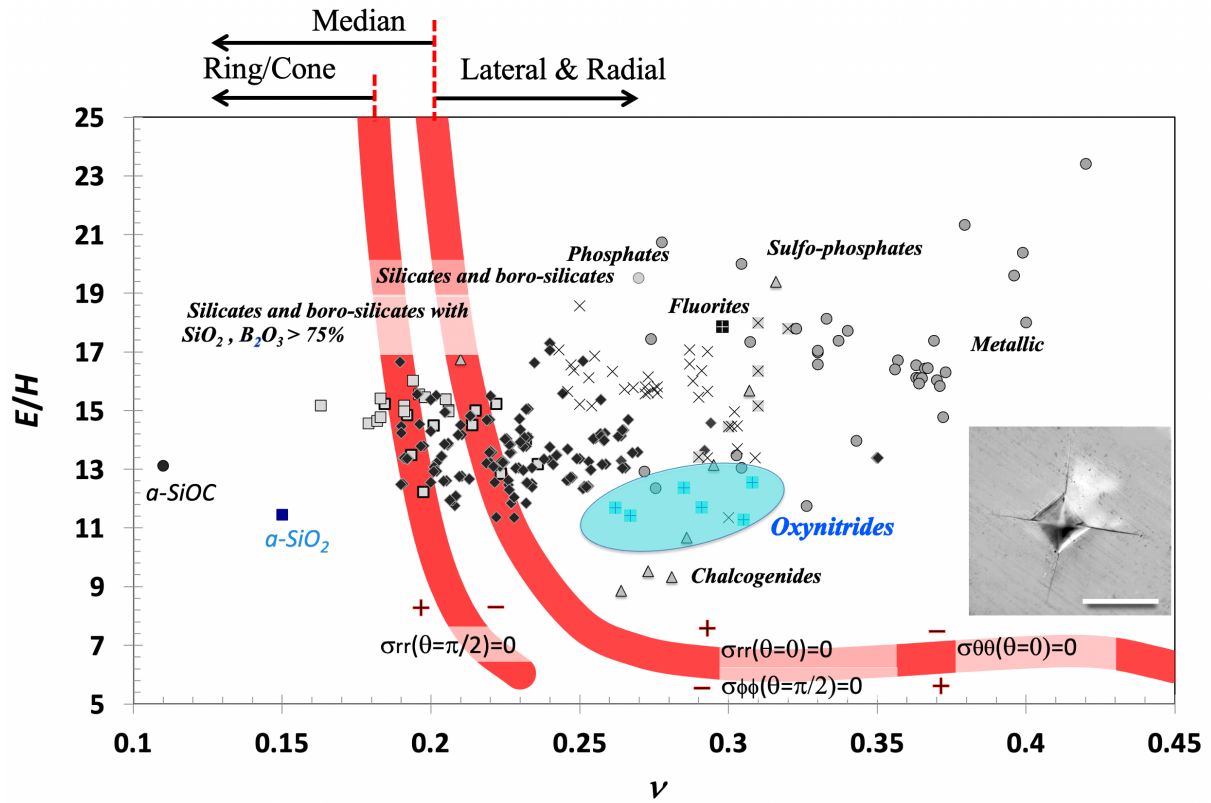


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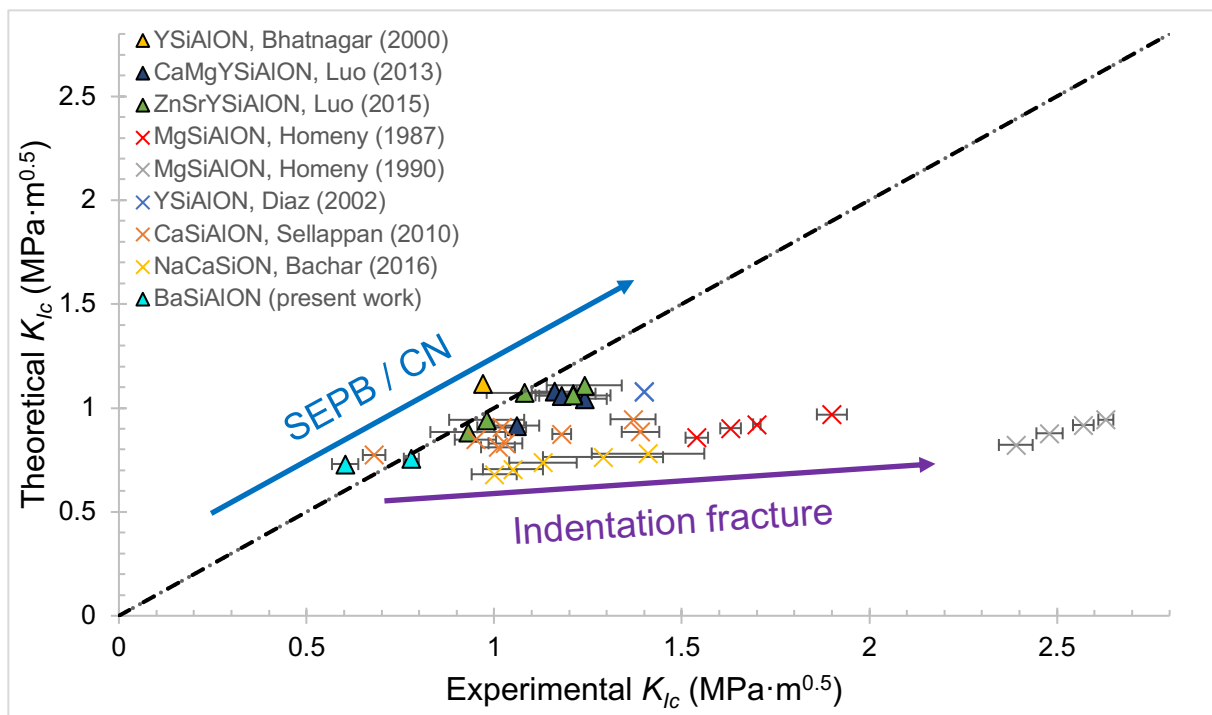


FIGURE 16 Measured and calculated fracture toughness of various oxynitride glasses. Round dots indicate fracture toughness measured by chevron notched specimen technique, and squared dots indicate fracture toughness measured by indentation or other techniques.

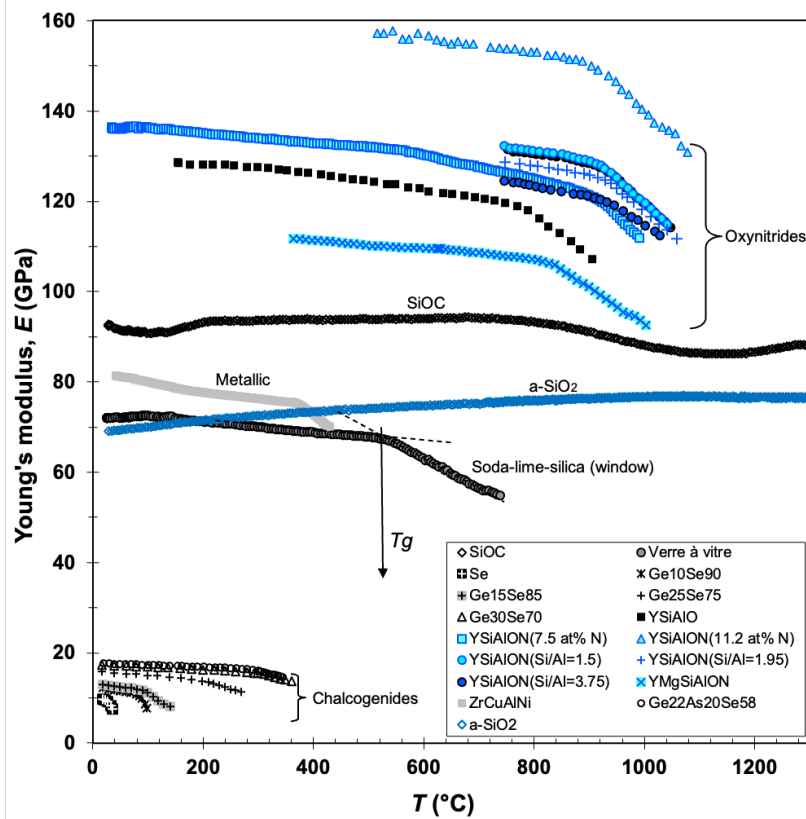


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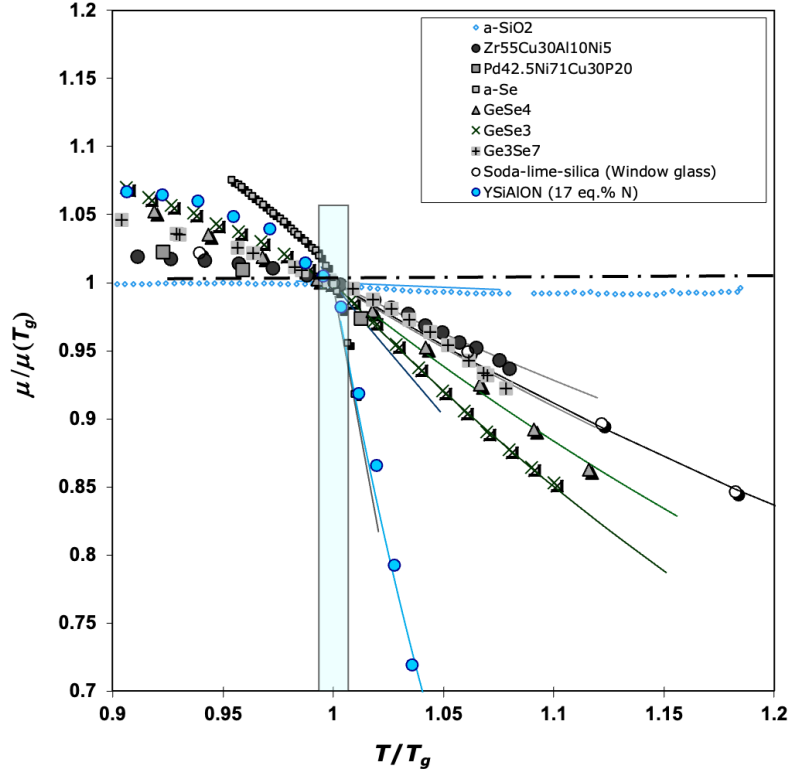


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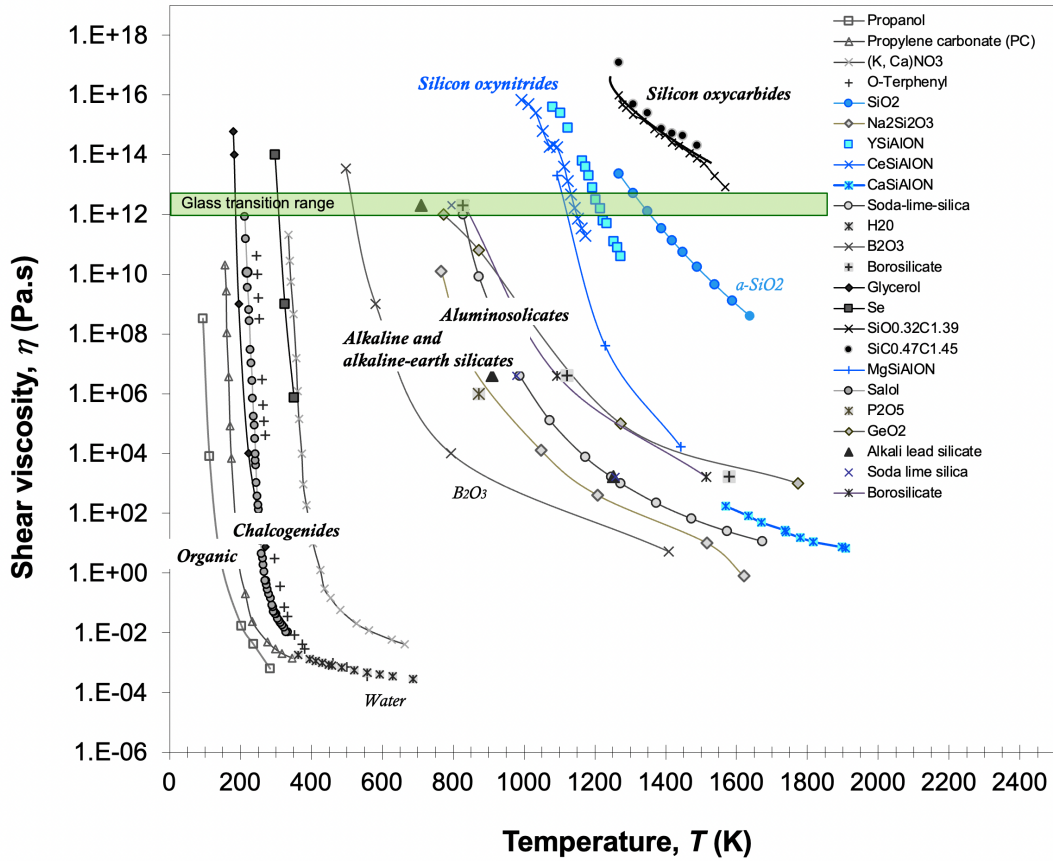
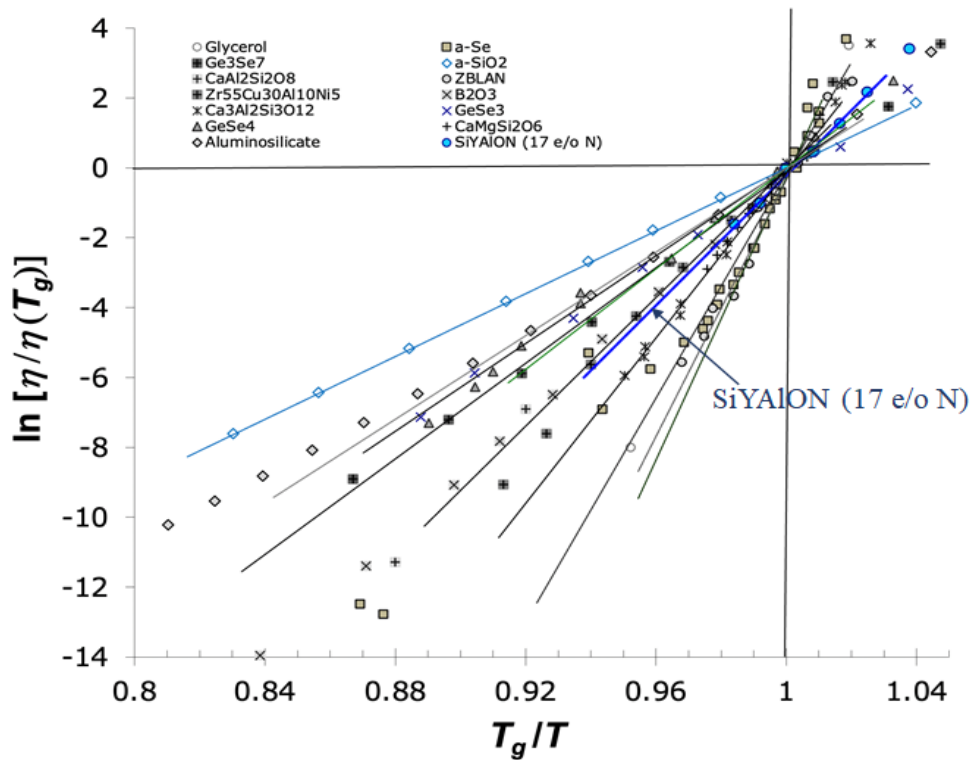


FIGURE 19 Shear viscosity coefficient, η , of glasses from different chemical system.

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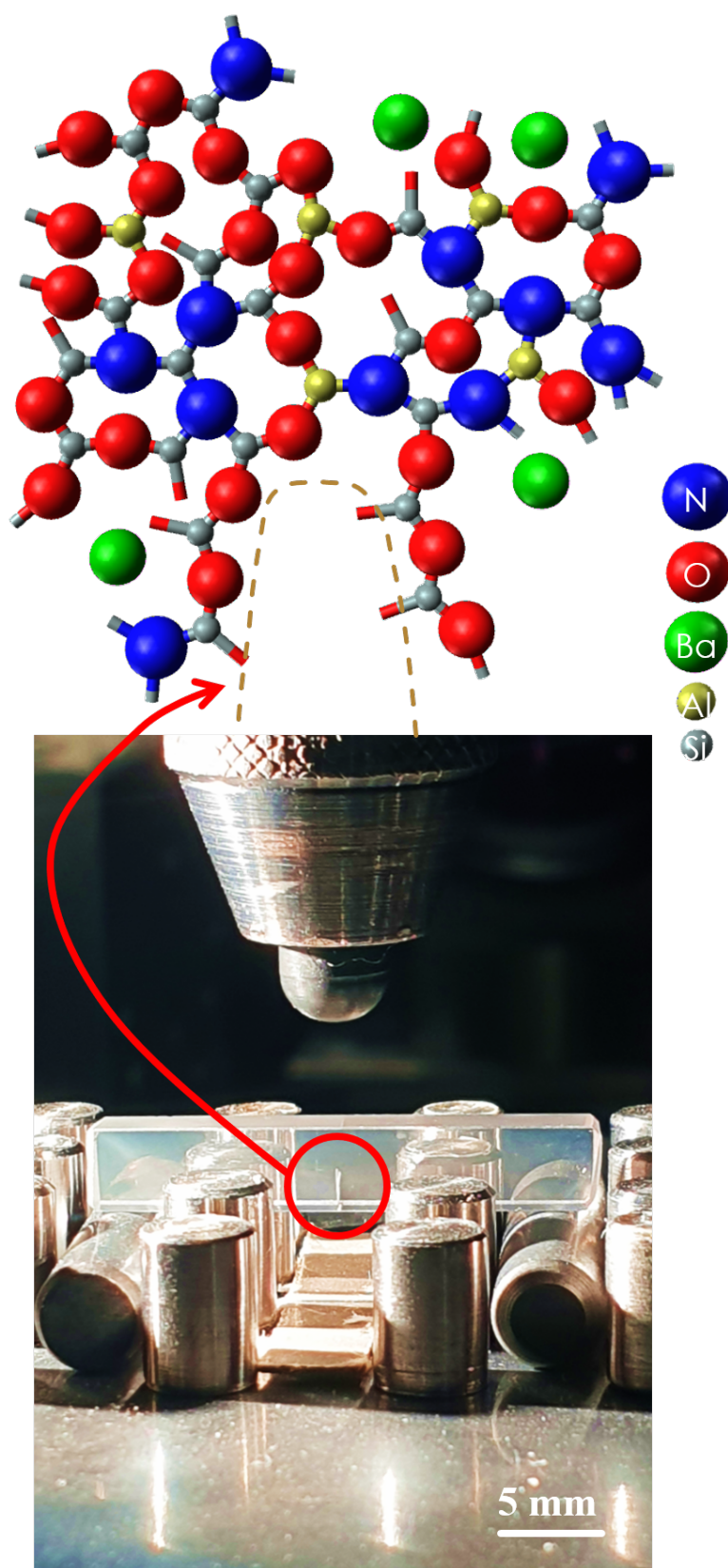
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FIGURE 20 T_g -scaled logarithm of the shear viscosity coefficient (η) in the transition range from which the activation energy for flow as well as the fragility index are straightforwardly derived from the slope of the linear intercepts (reprinted and adapted from ref. ¹⁹⁹).



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1682 Additional figure (COVER) – $\text{Ba}_{0.135}\text{Si}_{0.231}\text{Al}_{0.02}\text{O}_{0.589}\text{N}_{0.025}$ pre-cracked parallelepipedic bar
 1683 for the measurement of K_{Ic} by means of the SEPB method, and schematic drawing of the atomic
 1684 structure at the vicinity of a crack front.