Oxynitride glasses

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Abstract

Oxynitride glasses are silicates and alumino-silicates in which nitrogen atoms substitute for oxygen in the glass network. They are present as intergranular films and at triple points within the microstructures of silicon nitride-based ceramics as a result of the cooling of liquid phases formed by reaction of sintering additives with the nitride and surface silica. Oxynitride glass chemistry and volume fractions determine the type of microstructure developed and hence the properties of silicon nitride and sialons. In particular, they affect strength and fracture toughness and the control of high temperature creep behaviour. The desire to understand the nature of these grain boundary phases has resulted in a number of investigations on oxynitride glass formation, structure, properties and crystallisation which have shown that they have higher glass transition temperatures, elastic moduli, viscosities and values of hardness and lower thermal expansion coefficients than the corresponding oxide glasses. This paper reviews the development of oxynitride glasses and outlines the effect of glass composition, especially nitrogen content and also cation ratios, on properties and relates this to structural features within the glass. Nucleation and crystallisation studies are also outlined.
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Keywords: Glass; Sialon; Thermal properties; Mechanical properties

1. Introduction

In the current search for lighter, stiffer materials for use in modern communications equipment and to reduce energy usage, glasses are being investigated as potential candidates, especially those showing improved mechanical properties such as higher elastic moduli, hardness, strength and fracture toughness. Oxynitride glasses, essentially alumino-silicate glasses in which nitrogen atoms substitute for oxygen atoms in the glass network,[1–4] are the types of materials that could fulfil these requirements. It is now known that by substituting about one in five oxygen atoms by nitrogen in the network of alumino-silicate glasses, the Young's modulus is ∼25% higher than the equivalent oxide glass.[5,6] Other properties such as hardness, viscosity, glass transition temperature all increase with increasing nitrogen content.[3–6]

Oxynitride glasses were first discovered as grain boundary phases in silicon nitride-based ceramics.[7–9] In order to densify silicon nitride ceramics, additives, such as yttria or one of the rare earth oxides, plus alumina, are used to provide conditions for liquid phase sintering. The Y_2O_3 and Al_2O_3 react with silicon nitride and silica present on the nitride particle surface to form Y–Si–Al–O–N liquid phases which result in densification of the ceramics and transformation of the α-silicon nitride to the β form.[7–9] The liquid phases cool as intergranular oxynitride glass films[10] and triple points[10–12] and the content of the modifying cation (Y or RE) in these intergranular glasses, and the overall volume fractions of glass phase within the silicon nitride ceramic control the mechanical properties.[8,9,11,12] For example, as Y:Al ratio increases, fracture toughness also increases which is indicative of easier debonding at the silicon nitride grain interfaces.[11,12]

As progress was made in understanding the nature of silicon nitride ceramics, how additive chemistry controlled microstructure and how microstructure affected properties, there was a growing impetus to understand the nature of these intergranular oxynitride glass phases. This resulted in a number of investigations of oxynitride glass formation, structure, properties and crystallisation in various M–Si–O–N,[13–16] M–Si–Al–O–N[5,6,13,14,17–27] and M–Si–Mg–O–N[28,29] systems, where M is a modifying cation such as Mg, Ca, Ba, Sc, Y and the rare earth lanthanides.

2. Preparation and representation of oxynitride glass systems

Oxynitride glasses[4,5] are prepared by mixing the appropriate powders – silica, alumina, the modifying oxide(s) plus silicon

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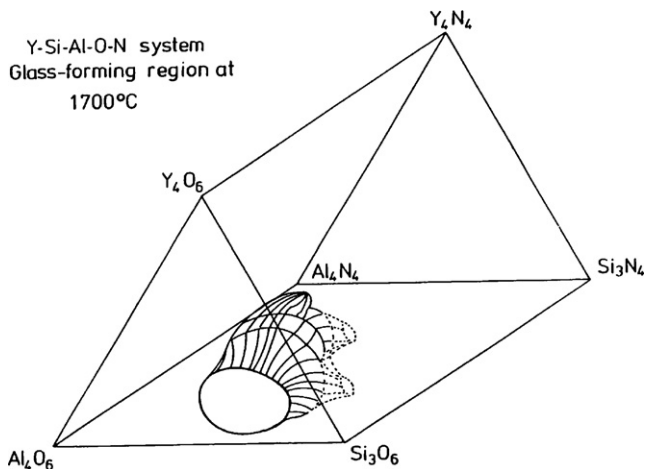Fig. 1. Jänecke's triangular prism representation of the Y–Si–Al–O–N system showing glass-forming region after melting at 1700 °C (after Drew et al.[13]).

nitride or aluminium nitride – in isopropyl alcohol in a ball mill with sialon milling media, followed by evaporation of the alcohol. Glasses (50–60 g) are melted in boron nitride lined graphite crucibles under 0.1 MPa nitrogen pressure at 1600–1750 °C for 1 h, after which it is quickly removed from the furnace and poured into a preheated graphite mould at ∼850–900 °C. The glass is annealed at this temperature for 1 h to remove stresses and then slowly cooled.

A number of investigations have outlined the limits of glass formation for the Mg–, Ca–, Y– and lanthanide RE–Si–Al–O–N systems.[3–5,13–16,28] Convenient methods of representing both Si–Al–O–N and M–Si–Al–O–N systems[7] involve the concept of reciprocal salt pairs. 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 introduction of a further cation gives a five-component system represented by Jänecke's triangular prism shown in Fig. 1 for the Y–Si–Al–O–N system in which the boundaries of the complete glass-forming region are outlined.[13,14]

The concentrations of all components are expressed in equivalents instead of atoms or gram-atoms. One equivalent of any element always reacts with one equivalent of any other element or species. The top right hand corner of the basal square represents one mole of Si_3N_4 and, moving from right to left, $3Si^{4+}$ is gradually replaced by $4Al^{3+}$ and, moving from top to bottom, $4N^{3-}$ is replaced by $6O^{2-}$. The corners of the square are thus Si_3O_6, Si_3N_4, Al_4O_6 and Al_4N_4. The prism representation allows the third "modifying" cation to be taken into account so that any point in the prism represents a combination of 12 positive and 12 negative valency units. The cations and anions are thus treated separately. The concentrations can be expressed as equivalent percentages (e/o) of either cations or anions as follows:

$$\text{equivalent\% (e/o) of Si} = \frac{4[\text{Si}] \times 100}{4[\text{Si}] + 3[\text{Al}] + V_M[\text{M}]},$$

where [Si], [Al] and [M] are, respectively, the atomic concentrations of Si, Al and the modifying cation M (in this case Y) in any composition and 4, 3 and V_M are their respective normal valencies. Any vertical plane within the prism has a constant nitrogen:oxygen ratio on which:

$$\text{equivalent\% (e/o) of nitrogen} = \frac{3[\text{N}] \times 100}{2[\text{O}] + 3[\text{N}]},$$

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

$$\text{equivalent\% (e/o) oxygen} = 100 - \text{e/o N}$$

The Y_2O_3–SiO_2–Al_2O_3 glass-forming region is plotted on the oxide face of the prism and the Y–Si–Al–O–N glass-forming region expands initially as nitrogen is introduced and then contracts above approximately 10 e/o N until the solubility limit for nitrogen is reached. In this case, it was found that ∼28 e/o of nitrogen could be substituted for oxygen (∼1 in 5 oxygen atoms) and still form a glass.

In M–Si–O–N systems, much smaller glass-forming regions are observed as can be seen from the small areas marked a and b in Fig. 1 showing that Al_2O_3 also extends glass formation in oxynitride systems as it does in silicates. The miscibility gap in various silicate binary systems extends into the equivalent M–Si–O–N system with consequent phase separation in some low alumina glasses.[15,16]

More recently, oxynitride glasses with greater than 65 e/o N in various M–Si–O–N systems[31,32] (M = Ca, Sr, Ba, La, Pr and Sm) have been prepared from mixtures of the electro-positive metal M, Si_3N_4 and SiO_2 powders which are heated in a nitrogen atmosphere at 1650–1800 °C. Glass formation depends strongly on the precursors used and proceeds via a strong exothermic reaction as low as 900–1100 °C, resulting in formation of amorphous and crystalline phases which melt upon further heating. Most glasses contained minor amounts of metal silicides. The anion content per Si atom is high,[32] ranging from 2.5 to 4, indicating that these glass structures may be quite different from those of previously reported oxynitride glasses with lower N contents.

3. Characterisation and properties of oxynitride glasses

3.1. Experimental methods

X-ray diffraction analysis is carried out in order to confirm that the glasses are totally amorphous. Scanning electron microscopy is used to confirm this and to assess homogeneity. Nitrogen content is determined on a number of glasses using a standard nitrogen analyser. The bulk densities are measured using an Archimedian technique.

Differential thermal analysis (DTA) is carried out in a flowing nitrogen atmosphere at a heating rate of 10 °C min^{-1}, using Al_2O_3 as a reference material, in order to detect the glass transition temperature (T_g) and crystallisation temperature (T_c). The onset point of an endothermic drift on the DTA curve corresponding to the beginning of the glass transition range is reported as T_g while the peak of the exotherm is taken as T_c. Errors in measurement are ±3 °C.

Thermal expansion coefficient is measured in a dilatometer in air at a heating and cooling rate of $5\,°C\,min^{-1}$ and the thermal expansion coefficient (α) is calculated between 200 and $600\,°C$. The inflection point of the expansion curve is taken as an indication of the glass transition temperature (T_{gDIL}), while the maximum is taken as the softening point (T_{ds}).

The elastic moduli (E; G) are calculated from measurements of the longitudinal, V_l, and transverse, V_t, ultrasonic wave velocities with a better than $10^{-3}\,m\,s^{-2}$ accuracy by means of 10 MHz piezoelectric transducers.[5] The Young's modulus, E, the shear modulus, G, and Poisson's ratio, υ, are derived from the following relationships:

$$E = \frac{\rho(3\,V_l^2 - 4\,V_t^2)}{(V_l/V_t)^2 - 1} \tag{1}$$

$$G = \rho V_t^2 \tag{2}$$

$$\upsilon = \left(\frac{E}{2G}\right) - 1 \tag{3}$$

where ρ is the density of the material. The accuracy of the measurement depends mainly upon the accuracy of the density measurement and the accuracy is then $\Delta E/E \sim 1 \pm 2\%$. Microhardness is measured using a standard Vicker's indentation technique.

Viscosity is deduced from creep tests performed in air between 750 and $1000\,°C$, either in 3-point bending[5] or in compressive mode.[27] The expression for viscosity, η is based on the strong analogy existing between the stress/strain relationships in an elastic solid and those governing a viscous fluid:

$$\eta = \frac{\sigma}{2(1+\upsilon)\dot{\varepsilon}} \tag{4}$$

where σ and $\dot{\varepsilon}$ are the applied stress and the creep rate and υ is Poisson's ratio.

Ground glass specimens are analysed using FTIR and FTRaman spectroscopy to assess the relative levels of Q_1, Q_2 and Q_3 units in the glass structure. Other structural studies have used MAS-NMR and XPS.

3.2. Effects of glass composition on structure and properties of oxynitride glasses

Loehman[17] 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 Si:(Y + Al) ratio and therefore the changes in properties are influenced by the cation concentrations and are not only due to changes in nitrogen content.

Further systematic investigations by Drew, Hampshire and Jack[13,14] measured the properties of glasses with fixed cation ratios and, thus, they were able to show, unambiguously, the
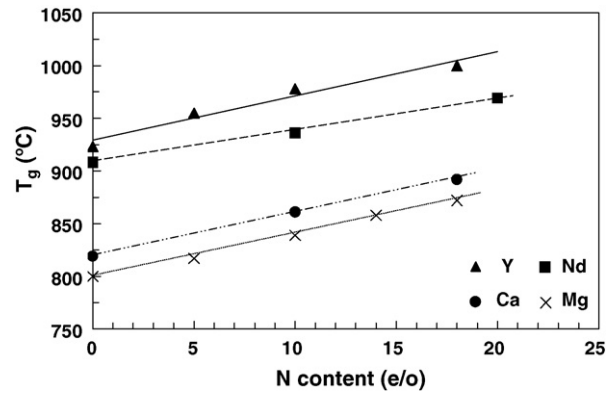

Fig. 2. Effect of N (e/o) on glass transition temperature (T_g) for glasses with fixed cation ratio of 28Y:56Si:16Al (after Hampshire et al.[14]).

effect of changes in N:O ratio on properties. For glasses in the Ca–, Mg–, Nd– and Y–Si–Al–O–N systems with fixed cation composition (in e/o) of 28Y:56Si:16Al, incorporation of nitrogen results in increases in glass transition temperature (T_g), shown in Fig. 2, and also microhardness, viscosity, resistance to devitrification, refractive index, dielectric constant and ac conductivity.

In a more extensive study of the Y–Si–Al–O–N system,[5] involving a number of European laboratories, it was confirmed that glass transition temperature (T_g), viscosity, microhardness and elastic moduli all increase systematically while coefficient of thermal expansion (CTE) decreases with increasing nitrogen:oxygen ratio for different series of glasses. These trends were also confirmed in a later study by Sun et al.[23] As shown in Fig. 3, values of Young's modulus increase by 15–25% as $\sim$17–20 e/o N is substituted for oxygen at fixed cation ratios.[5,23] The coefficient of thermal expansion (α) decreases as N content increases at fixed Y:Si:Al ratios[5,23] as shown in Fig. 4.

These effects 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.[5,14,18,23] However, some nitrogen atoms may be bonded to less than three Si atoms, as in:
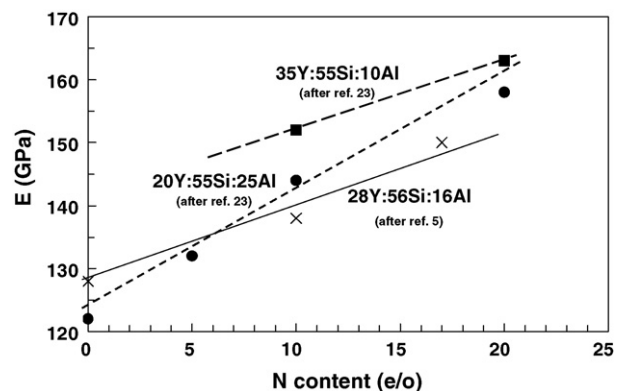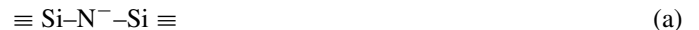
$$\equiv Si–N^{-}–Si \equiv \tag{a}$$

Fig. 3. Effect of N (e/o) on Young's modulus (E) for glasses with fixed Y:Si:Al ratios (data from Hampshire et al.[5]; Sun et al.[23]).
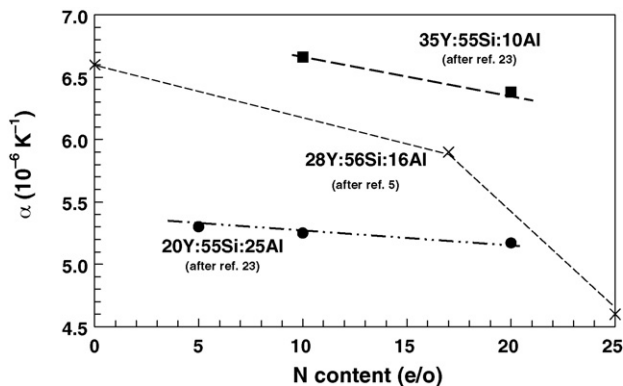
Fig. 4. Effect of N (e/o) on coefficient of thermal expansion (α) for glasses with fixed Y:Si:Al ratios (data from Hampshire et al.[5]; Sun et al.[23]).

$$\equiv Si-N^{2-} \qquad\qquad (b)$$

This suggests that "non-bridging" nitrogen atoms may also be present. The local charge on the non-bridging nitrogen ions is balanced by the presence of interstitial modifying cations in their local environment. In the case of silicate (oxide) glasses, non-bridging oxygen atoms replace bridging oxygen atoms at high modifier contents. For (a) above, while the N atom links two silicon atoms rather than three, it is still effectively a "bridging" ion.

The glass network contains tetrahedral structural groups: SiO_4, SiO_3N and SiO_2N_2. Amorphous SiO_2 containing only $[SiO_4]^{4-}$ groups has a completely balanced network with each tetrahedron having 4 bridging oxygen atoms. The $[SiO_3N]^{5-}$ group requires the presence of an extra positive charge locally to balance the extra negative charge from the N anion and therefore the situation is very similar to that for an $[AlO_4]^{5-}$ tetrahedron within the network, which also requires an extra positive charge to make it isoelectronic with the SiO_4 tetrahedron. Therefore, oxynitride glasses containing SiO_3N groups can accommodate more modifiers in "charge compensating" sites than the equivalent oxide glasses without creating non-bridging oxygen species.

Fig. 5 shows the viscosity–reciprocal temperature relationships for a series of glasses[5] with composition (in e/o) of $28Y:56Si:16Al:(100-x)O:xN$ ($x = 0$, 10, 17). It can be seen that viscosity increases by almost 3 orders of magnitude simply by replacing 17 e/o oxygen by nitrogen in the Y–Si–Al–O–N glasses. Similar trends have been reported for other Y–Si–Al–O–N glasses with different cation ratios.[27]

The effect of fixed Si:Al and Y:Al ratios on properties of glasses with constant O:N ratio were also investigated.[5,23,27,33] As Si:Al ratio increases, T_g and viscosity increase while elastic moduli, hardness and thermal expansion coefficient decrease. With increasing Al:Y ratio, elastic moduli and thermal expansion coefficient decrease while the T_g and viscosity decrease to a minimum (at 16 e/o Al) and then increase with further increase in Al content.

Fig. 6 shows the viscosity–reciprocal temperature relationships observed as a function of Y:Al ratio for Y–Si–Al–O–N glasses with a fixed N content of 17 e/o and fixed Si content of 56 e/o. As Y content decreases, there is a reduction in viscos-
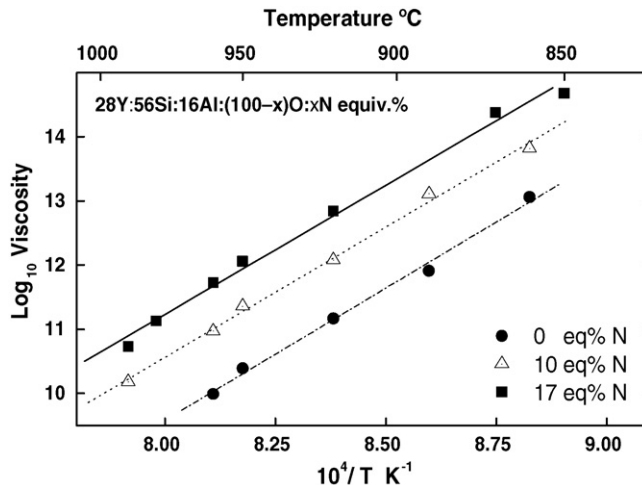
ity of greater than 1 order of magnitude as Al content increases from 4 to 16 e/o Al and then, with further increase in Al to 22 e/o, viscosity increases again. Overall, these effects can be assumed to be related to changes in the density of the glass network and the numbers of non-bridging oxygens as Al changes its coordination. At higher Al:Y ratios, when 4 co-ordinated Al is prevalent, enhancement of the cross-linking of the glass network occurs, caused by the formation of more Al–O–Si linkages as Raman spectroscopy analyses would indicate.[34] Fig. 7 shows the viscosity–reciprocal temperature relationships observed as a function of Al:Si ratio for Y–Si–Al–O–N glasses with a fixed N content of 17 e/o and fixed Y content of 28 e/o. As Al content increases from 12 to 16 e/o, 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.

Fig. 5. Viscosity–reciprocal temperature relationships for a series of glasses with composition (in e/o) of $28Y:56Si:16Al:(100-x)O:xN$ ($x = 0$, 10, and 17) (data from Hampshire et al.[5]).
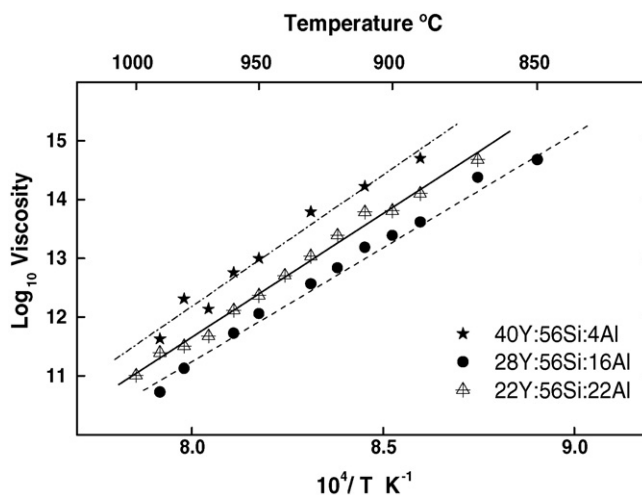

Fig. 6. Viscosity–reciprocal temperature relationships of Y–Si–Al–O–N glasses as a function of Y:Al ratio (fixed N = 17 e/o, fixed Si = 56 e/o) (data from Hampshire et al.[5]).
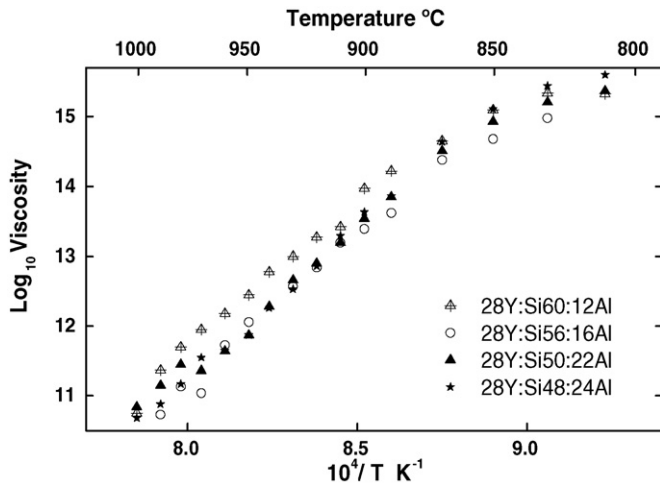
Fig. 7. Viscosity–reciprocal temperature relationships of Y–Si–Al–O–N glasses as a function of Al:Si ratio (fixed N = 17 e/o, fixed Y = 28 e/o) (data from Hampshire et al.[5]).

Fig. 9. Viscosity–reciprocal temperature relationships for a series of RE–Si–Al–O–N glasses with cation ratio (in e/o) of 28RE:56Si:16Al (fixed N = 17 e/o).

Properties of various RE–Si–Al–O–N glasses have been reported.[21,24–27] As the atomic number of the lanthanide ion increases, glass transition temperature (T_g), viscosity, Young's modulus and hardness increase almost linearly with increases in cation field strength,[24–26] CFS (where CFS = v/r^2, v is valency and r is ionic radius). Fig. 8 shows the linear change in elastic modulus as a function of RE cation field strength for glasses with a fixed cation ratio (35RE:45Si:20Al) and fixed nitrogen (17 e/o) content.[25,35] This trend suggests that the glass network is tightened inversely to the rare earth cation radius and cross-linking is a function of the nitrogen content. The exception is Europium. As can be seen, the value of CFS for Eu^{2+}, rather than Eu^{3+}, falls on the line. Eu^{3+} is known to reduce to Eu^{2+} in alumino-silicate glasses and de Graaf et al.[36] have also shown that both Sm and Yb can undergo a reduction from the trivalent state in the oxides to the divalent state in oxynitride glasses, the degree of conversion depending on melting time. Emission spectra of Sm-containing glasses show the presence of both Sm^{3+} as well as that of Sm^{2+}, which is also reflected in the data for
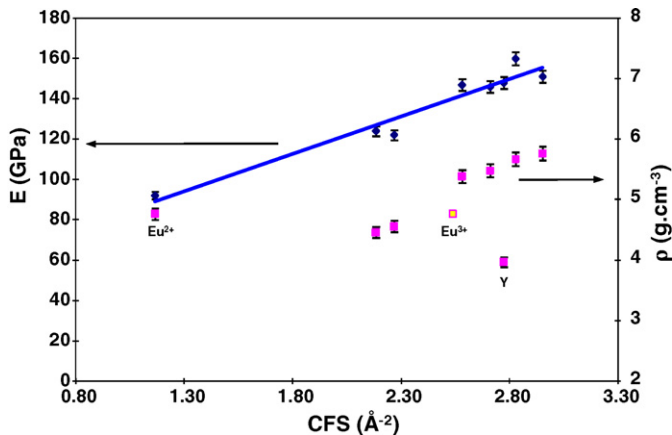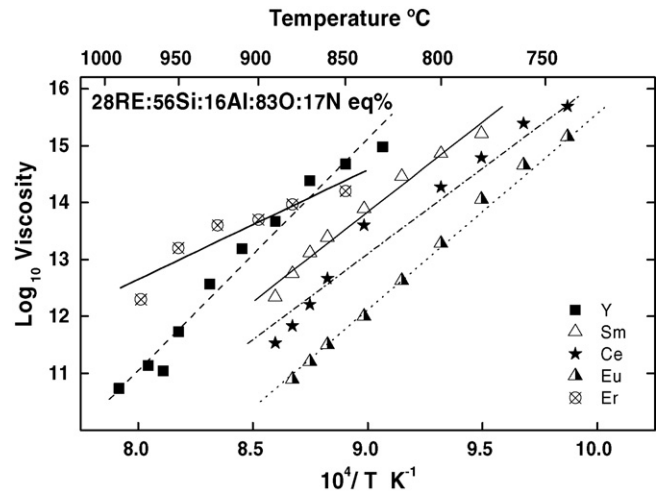

Fig. 8. Effect of CFS on Young's modulus and density of glasses with compositions (in e/o) 35RE:45Si:20Al:83O:17N. Data in increasing order of CFS correspond to RE = Eu^{2+}, La, Ce, Gd, Dy, Y, Er, and Yb (after Menke et al.[25]).

Young's modulus and density. A broad absorption band of Yb^{2+} characterizes the reflection spectra of Yb-containing glasses, indicating a similar reduction, while a second absorption band suggests the presence of some remnant Yb^{3+}. The other properties of these glasses also appear to confirm a mixed Yb oxidation state. These effects have been attributed to the reducing power of chemically incorporated nitrogen (N^{3-}) in the glass matrix, as also clearly demonstrated for Eu–Si–Al–O–N glasses.[35] With a change from Eu^{3+} to Eu^{2+}, the luminescence characteristics change to give an extended range of emission up to longer wavelengths (500–650 nm)[36,37] which is ascribed to a combination of energy transfer between the different sites and change of the Eu^{2+} site distribution.

Fig. 9 demonstrates the effects of different rare earth lanthanide cations (RE = Ce, Sm, Eu, and Er) on viscosity–reciprocal temperature relationships for RE–Si–Al–O–N glasses with fixed cation ratio of 28RE:56Si:16Al.[33] At any temperature (for example, in the range 825–900 °C), viscosity decreases by ∼3 orders of magnitude in the order: Er ≥ Y > Sm > Ce > Eu. As indicated previously, Eu is in the +2 state which is a much larger ion than Eu^{3+}. Viscosity, as with other properties, increases almost linearly with increase in cation field strength of the RE ion. Viscosities of RE–Si–Al–O–N liquids, containing Sm, Ce, Eu, where the ionic radii are larger than that of Y, are less than those of the equivalent Y–Si–Al–O–N liquids and this will have implications for easier densification of silicon nitride ceramics. However, there will also be consequences for high temperature properties, particularly creep resistance. Liquids and glasses containing RE cations with ionic radii smaller than Y (Lu, Er, Ho, Dy, Yb) have been shown to have higher viscosities than the Y-containing glasses and, in silicon nitride these RE cations will form grain boundary glasses with higher softening temperatures.

As shown previously, Al content has a significant effect on viscosity. Becher and Ferber[27] reported viscosity plots for alumina-free La–Si–O–N glasses and showed that these are shifted by approximately +50 °C on the temperature scale com-

pared with La–Si–Al–O–N glasses, which represents more than 1 order of magnitude increase in viscosity at a fixed temperature. Thus, reducing the alumina content of these oxynitride glasses results in more refractory glasses with higher viscosities.

The effects on properties of changes in silicon nitride grain boundary glass chemistry, as a result of changes in sintering additives, can be summarised as follows[27,33]:

(1) As 17 e/o N is substituted for oxygen at a fixed cation ratio, viscosity increases by >2 orders of magnitude.
(2) At a fixed N content, increasing the Y:Al ratio of the glass results in a further slight increase in viscosity.
(3) Changing the rare earth cation from a larger ion, such as La or Ce, to a smaller cation, such as Er or Lu, increases viscosity by a further 3 orders of magnitude.

Overall, a change of almost 6 orders of magnitude in viscosity can be achieved by increasing N and modifying the overall cation ratio and the type of rare earth ion.

Observations of intergranular films in silicon nitride have shown that their thickness decreases as RE ion radius decreases.[8,10] Viscous flow of these films contributes to the initial stage of tensile creep deformation in silicon nitride ceramics.[38] Larger RE ions, such as La and Ce, have a greater preference for N than the smaller RE ions, such as Er or Lu, and remain concentrated in close proximity to silicon nitride prism faces[39] in the IG films while smaller RE ions (Lu, Er) will tend to segregate at the triple points. Creep behaviour of silicon nitride is thus dependent on viscosities of both the intergranular oxynitride glass films and the triple point glasses.

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.[40,41] As expected, nitrogen substitution for oxygen at a fixed cation ratio results in linear increases in Young's modulus, glass transition temperature and dilatometric softening temperature.

For fixed nitrogen contents, replacement of Mg by Y causes non-linear increases in glass transition temperature and dilatometric softening temperature but has little effect on elastic modulus. The effects of anion replacement (N for O) and modifier cation replacement (Y for Mg) on properties are independent of each other and additive, rather than synergistic.

Studies of properties and structure of RE–Si–Mg–O–N glasses[29,30] (RE = Sc, Y, La, Nd, Sm, Gd, Yb and Lu) have also been undertaken and show similar trends to those found for RE–Si–Al–O–N glasses. Hardness, elastic modulus, viscosity, thermal expansion coefficient, glass transition temperature and softening temperature increase linearly with increasing cation field strength, F, as found for RE–Si–Al–O–N glasses.

In these glasses, nitrogen modifies the glass structure by increasing the content of SiO_3N tetrahedra with extra bridging corners at the expense of SiO_4 units sharing only two corners, as found also in Er–Si–Al–O–N glasses.[42] In the RE–Si–Mg–O–N glasses, this depends on the rare earth cation; Lu was found to be more effective in formation of SiO_3N units than La.[29] Replacing La by Lu results in approximately 1 order of magnitude increase in viscosity.

The subcritical crack growth (SCG) resistance in water of Y–Si–Al–O–N glasses and their oxide equivalents have been reported using different loading configurations[43,44] but the same relationship between crack velocity, v, and the applied stress intensity, K_I:

$$v = A(K_I)^n \tag{5}$$

where A is a constant and n is the power-law exponent. de Graaf et al.[44] found that n for a Y–Si–Al–O–N glass containing ∼7 at.% N was significantly higher (63) than for a Y–Si–Al–O glass (21), while Coon[43] reported, for a Y–Si–Al–O–N glass containing 18 at.% N, subcritical crack velocities in the range 5×10^{-7} to 6×10^{-5} m/s, obtained for stress intensities ranging from 0.675 to 0.686 MPa m$^{0.5}$, respectively, and an even higher value of n (142).

Optical properties of oxynitride glasses have been studied. The refractive index of all the glasses was found to increase with increasing nitrogen content,[13,45] due to its high ionic polarisability. When nitrogen substitutes for oxygen, IR transmission is significantly improved, whereas UV transmission was found to be impaired because of impurities in the glass.[13]

4. Crystallisation of oxynitride glasses to form glass–ceramics

As with other silicate glasses, oxynitride glasses may be heat treated at the appropriate temperatures to crystallise as glass–ceramics.[1,5,38,46–51] The conventional process to produce a glass–ceramic involves two steps: a lower temperature heat treatment of glasses to induce nucleation, generally just above the glass transition temperature, followed by heating to a second higher temperature, the so-called crystallisation temperature, to allow growth of the pre-formed nuclei. The crystalline phases formed depend on both the composition of the parent glass and the heat-treatment process. The glass–ceramic transformations in a glass of composition (in e/o) 28Y:56Si:16Al:83O:17N have been studied[49] using both classical and differential thermal analysis techniques and these two methods were found to be in close agreement. Optimum nucleation and crystallisation temperatures were determined in relation to the glass transition temperature. The major crystalline phases present are mixtures of different forms of yttrium disilicate and silicon oxynitride. Bulk nucleation was observed to be the dominant nucleation mechanism. The activation energy for the crystallisation process was found to be 834 kJ/mol.

For a glass of composition (in e/o) 35Y:45Si:20Al:77O:23N, crystallisation results in formation of B-phase (Y_2SiAlO_5N), Iw-phase ($Y_2Si_3Al(O,N)^{10}$) (i.e. ∼10 e/o N) and wollastonite ($YSiO_2N$) at temperatures below 1200 °C while α-yttrium disilicate ($Y_2Si_2O_7$), apatite ($Y_2Si_3O_{12}N$) and YAG ($Y_3Al_2O_{12}$) are formed at higher temperatures.[5] At relatively low heat treatment temperatures of ∼950–1100 °C, the nucleation and growth of N-wollastonite ($YSiO_2N$) and the intermediate phases B and Iw are kinetically favoured over that of the more stable equilibrium phases YAG and Si_2N_2O. B-phase has the pseudo α-wollastonite structure. Normally, it might be expected that this structure would consist of layers of Y^{3+} and rings of

$(Si,Al)(O,N)_4$ tetrahedra but it was shown that the formation of these rings is suppressed by the incorporation of nitrogen.[50]

Further studies, by analytical transmission electron microscopy, including electron spectroscopic imaging, have shown that B-phase forms after crystallisation heat treatment at 1050 and 1150 °C of Er– and Y/Yb–Si–Al–O–N glasses.[51,52] The crystals take up a wide range of composition; the erbium cation percentage varies around that of the expected B-phase composition (Er_2SiAlO_5N), but aluminium content is slightly lower and silicon content higher than this. In addition, Er content is strongly anti-correlated with Si content. A comparison of B-phase compositions after crystallisation of equivalent glasses formed with either yttrium, erbium or ytterbium shows that the B-phase solid solution range depends on the particular cation radius. As a consequence of this, the degree of crystallisation and the composition of the residual glass will, for equivalent glasses, also depend on the cation radius. In addition to crystal growth, the crystallisation heat treatment results in a phase separation of the residual glass whereby smaller Si- and N-rich amorphous features form. These features are effectively pinning the boundaries of growing crystals.

The properties of the glass–ceramics are significantly higher than those of the parent glasses with, for example, values of elastic modulus greater than 200 GPa.

5. Effects of addition of fluorine to oxynitride glasses on glass formation and properties

Fluorine as a non-bridging anion in glasses acts as a powerful network disrupter which substitutes for bridging oxygen ions. Fluorine reduces the glass transition temperature, viscosity and refractive index, aids crystallisation and increases the potential for phase separation.[53] The effect of fluorine addition on the structure of silicate or alumino-silicate glasses has been investigated[54,55] and it has been shown that fluorine can bond to silicon as Si–F, to Al as Al–F, and to Ca as Ca–F. Fluorine loss occurs under conditions where the Si–F bond is favoured. The bonding of fluorine to aluminium prevents fluorine loss as SiF_4 from the glass melt and explains the reduction in the glass transition temperature.[54] When fluorine is introduced into the Ca–Si–Al–O–N system, fluorine extends the glass-forming region in the Ca–Si–Al–O–N–F system[56] and considerable reductions of the liquidus temperatures are observed (up to ∼800 °C at more Ca-rich compositions). The compositional limits for glass formation at 5 e/o F have been mapped out. Fluorine also facilitates the solution of higher amounts of nitrogen (up to 40 e/o N) into glasses compared with the Ca–Si–Al–O–N system.[56] Fluorine has the effect of lowering glass transition temperature in these glasses but has no effect on the elastic modulus or microhardness.[57]

6. Phosphorus oxynitride glasses

The introduction of nitrogen into phosphate-based glasses has been investigated with the aim of improving their chemical resistance and optical properties through a similar cross-linking process to that found in silicate-based oxynitride glasses.[58–64]

The decomposition of melts containing P_2O_5 and N restricts their processing to much lower temperatures (<900 °C) than the silicates. Si-free phosphorus oxynitride glasses have been successfully produced by introduction of nitrogen into the melt using metal nitrides (mostly AlN) or by re-melting phosphate glass frits with the general formula $MPO_{3-3x}N_{2x}$ (M = Li, Na, K) under anhydrous ammonia. Nitridation in these systems reaches a stability limit around 800–900 °C, and above this temperature range phosphorus is lost from the melt.[59–61] The appearance of phosphine, PH_3, and a yellowish colouration of the glasses are indicative of melt instability. Phosphine formation is believed to be the result of P reduction from P^V to P^{III} and subsequent volatilisation and reaction with atmospheric moisture.

The structural units in phosphorus oxynitrides are similar to those in silicon oxynitrides; the substitution of nitrogen for oxygen in PO_4 gives structural units which vary in substitution from PO_4, to PO_3N and PO_2N_2 tetrahedra depending on N/P ratio. The proportion of the different $P(O,N)_4$ tetrahedra and the ratio between two and three coordinated nitrogen in the structure depends on the nature of the modifying cations present in the glass and on the level of nitridation reached in the final product.[60–63]

As in the case of the silicate-based oxynitride glasses, viscosity, glass transition temperature, dilatometric softening point, refractive index, Young's modulus and micro-hardness all increase with increasing nitrogen content while thermal expansion coefficient decreases. Nitrogen improves the chemical durability of phosphate glasses,[64] the dissolution mechanism changes from a rapid aqueous attack to a slow direct chemical reaction between H_2O and P–O–P or P–N=P bonds.

7. Conclusions

Oxynitride glass formation occurs in a number of M–Si–O–N, M–Si–Al–O–N and M–Si–Mg–O–N systems and, using normal melting processes, up to ∼30 equiv.% nitrogen can be dissolved in the glass. A novel approach, using metal precursors, allows much more N to be dissolved into some M–Si–O–N glasses. As nitrogen content increases, properties such as glass transition temperature, elastic modulus, viscosity, hardness and slow crack growth resistance increase while thermal expansion coefficient decreases as a result of increased cross-linking of nitrogen within the glass network. For a constant cation composition, viscosity increases by more than 2 orders of magnitude as 18 e/o oxygen is replaced by nitrogen. For rare earth oxynitride glasses with constant nitrogen content, viscosity, Young's modulus and T_g and other properties increase linearly with increasing cation field strength (decreasing ionic radius). Spectroscopic studies have identified the structural features of glasses and the role of nitrogen as a network "former".

Many studies on crystallisation of oxynitride glasses have been carried out which have identified suitable two stage heat treatments for nucleation and growth of crystal phases, including B-phase (M_2SiAlO_5N; M = Y, Er, Y + Yb), to form glass ceramics with significant increases in strength and elastic modulus over the parent glasses.

Addition of fluorine extends glass formation in oxynitride systems and allows dissolution of higher levels of nitrogen into glasses. Fluorine lowers glass transition temperature but does not have any effect on elastic modulus or microhardness.

Nitrogen may be dissolved into phosphate glasses with consequent improvements in chemical durability and increases in many physical and mechanical properties.

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