

Yttrium Oxynitride Glasses: Properties and Potential for Crystallisation to Glass-Ceramics

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Abstract

Silicon nitride-based ceramics contain oxynitride glass phases at the grain boundaries which can impair subsequent high temperature properties. Studies of bulk glasses in the Y–Si–Al–O–N system have been carried out and it has been shown that up to 10 atomic % N can be incorporated into these oxynitride glasses. Nitrogen increases the viscosity, hardness and glass transition temperature of the glasses. Heat treatments of Y–Si–Al–O–N glasses have been carried out and the crystalline phases formed are reported. Further improvements are possible if glass-ceramic processes using two-stage heat treatments are introduced. This paper reviews the development of oxynitride glasses, the effects of nitrogen on properties and reports on the glass-ceramic heat treatments.

Auf Siliziumnitrid basierende Keramiken enthalten Oxinitridglasphasen an den Korngrenzen, die die Hochtemperatureigenschaften verschlechtern können. Glasproben aus dem Y–Si–Al–O–N-System wurden untersucht und es konnte gezeigt werden, daß bis zu 10 At.% N in den Oxinitridgläsern enthalten sein kann. Stickstoff erhöht die Viskosität, die Härte und die Übergangstemperatur der Gläser. Die Y–Si–Al–O–N-Gläser wurden wärmebehandelt und die dabei entstandenen kristallinen Phasen werden im folgenden beschrieben. Weitere Verbesserun-

gen sind möglich, wenn eine zweistufige Wärmebehandlung durchgeführt wird. Der folgende Artikel beschreibt die Entwicklung der Oxinitridgläser, den Effekt von Stickstoff auf die Eigenschaften und die Glas-Keramik Wärmebehandlungen.

Les céramiques de type nitrure de silicium contiennent des phases vitreuses azotées aux joints de grains qui peuvent conduire à une détérioration des propriétés à haute température. Les études sur des verre massifs dans le système Y–Si–Al–O–N ont été menées et il a été montré qu'il était possible d'incorporer jusqu'à 10% atomique d'azote dans ces verres oxyazotés. La présence d'azote augmente la viscosité, la dureté et la température de transition vitreuse. Des traitements thermiques ont été effectués sur des verres de ce système et les phases cristallines formées sont rapportées. L'amélioration des vitrocéramiques obtenues est possible en effectuant le traitement thermique en deux étapes. Cet article passe en revue l'obtention des verres oxyazotés, les effets de l'azote sur les propriétés et décrit des traitements thermiques de céramisation.

1 Introduction

Glass-ceramics are an important class of materials that are formed by melting, shaping and subse-

quent controlled crystallisation of glasses. The possibility of producing glass-ceramics containing refractory oxynitride crystalline phases with particular beneficial properties has led to further studies of oxynitride glass formation and properties. Jack¹ reported preparing oxynitride glasses in the following systems: $\text{Si}_3\text{N}_4\text{-Al}_2\text{O}_3\text{-SiO}_2$, $\text{Si}_3\text{N}_4\text{-MgO-SiO}_2$ and $\text{AlN-Y}_2\text{O}_3\text{-SiO}_2$, with nitrogen levels up to 10 at.%. Changes in physical properties due to incorporation of nitrogen were not reported at this point.

Both Shillito *et al.*² and Loehman^{3,4} were among the first to report correlations between amounts of nitrogen incorporated into oxynitride glasses and changes in their physical properties. Shillito *et al.* reported a linear increase in hardness of a Y-Si-Al-O-N glass as the nitrogen content increased. Loehman produced more detailed results of changes in physical properties due to incorporation of up to 7 at.% nitrogen in these glasses. Glass transition temperature (T_g), microhardness and fracture toughness increased with increasing nitrogen content, while the thermal expansion coefficient decreased. IR spectroscopic analysis carried out by Loehman indicated that the incorporated nitrogen became chemically bonded to silicon in the glass network and, by substitution for oxygen, produced a more tightly and highly linked structure. While these results did show improvements in properties of glasses related to incorporation of nitrogen, these property changes could not be attributed solely to the incorporation of nitrogen, since it is well known that viscosities of these types of glasses will depend on the concentration of Al and/or Y.

Drew *et al.*⁵⁻⁷ carried out extensive studies on oxynitride glasses in M-Si-O-N and M-Si-Al-O-N systems. Glasses with varying nitrogen: oxygen ratios, with a fixed cation composition were prepared, to allow direct comparison between different M-Si-Al-O-N systems and the effect of replacing oxygen by nitrogen within each system. Drew *et al.* found that, for glasses with a constant cation ratio, incorporation of nitrogen resulted in increases in T_g . Viscosity, refractive index, dielectric constant and AC conductivity also increased with N content in all the Mg-, Ca-, Y- and Nd-sialon glasses investigated.

Ahn & Thomas⁸ carried out preliminary studies on crystallisation of Y-sialon glasses. They reported that appreciable crystallisation was only effected after glasses were doped with up to 5 wt% ZrO_2 which acted as a nucleating agent. They identified the main crystalline phase as $\text{Y}_2\text{Si}_2\text{O}_7$. Winder & Lewis⁹ carried out further work in this system and reported that low nitrogen: oxygen ratios again favour formation of yttrium disilicate

($\text{Y}_2\text{Si}_2\text{O}_7$), while the increased glass viscosity, associated with an increase in the nitrogen: oxygen ratio, favoured suppression of the crystallisation of $\text{Y}_2\text{Si}_2\text{O}_7$ and preferential formation at higher temperatures of yttrium garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$).

In a study of crystallisation of glasses in the $\text{Y}_2\text{O}_3\text{-SiO}_2\text{-AlN}$ system, Dinger *et al.*¹⁰ found that nucleation occurs heterogeneously on FeSi particles distributed in the glass. More extensive studies of crystallisation in Y-sialon glasses were carried out by Leng-Ward & Lewis.¹¹ They reported that on heat treatment at 1250°C the oxide glasses fully crystallised to yttrium disilicate, mullite and Al_2O_3 . Again with increasing nitrogen content, they found that the disilicate phase was progressively replaced by yttrium aluminium garnet and nitrogen was mainly incorporated into $\text{Si}_2\text{N}_2\text{O}$. They also reported that heat treatment of the nitrogen glasses at 1100°C produced partial crystallisation involving intermediate phases related to nitrogen wollastonite, notably B-phase. Leng-Ward & Lewis prepared glasses of constant Y: Si: Al atom ratio of 1.04: 1.27: 1.27 and equivalent nitrogen contents of 0, 10, 20 and 30 equiv.% and found the maximum nitrogen at this composition also to be about 28 equiv.%. Heat treatment of these compositions at 1100°C gave partial crystallisation of the 10 and 20 equiv.% N glasses to produce Al_2O_3 and a major intermediate phase with a Y: Si: Al atom ratio close to 3: 2: 1 or 5: 3: 2 and an X-ray pattern similar to, but distinct from, B-phase. This phase was labelled I_w . At 20 equiv.% N a small amount of an additional intermediate phase occurred with an atomic ratio of 2: 2: 1.

Empirical investigations of oxynitride glass systems¹²⁻¹⁷ and their crystallisation have already been carried out by the present authors. This has complemented more extensive studies of phase equilibria in M-Si-Al-O-N systems and the effects of vitreous phases on high-temperature properties of silicon nitride-based ceramics.¹⁸

The present work is part of a BRITE-EURAM collaboration between the authors' laboratories with the following objectives:

- (1) Study of the formation and characteristics of oxynitride-based glasses containing Y or rare earth cations such as Nd;
- (2) study of the effects of nitrogen and the cations on properties such as glass transition temperature, Young's modulus, viscosity, etc.;
- (3) study of the structure of these glasses and the formation of nuclei;
- (4) study of the optimisation of the controlled crystallisation of these glasses in order to

develop novel glass-ceramics with tailored properties.

The preparation procedure for different glasses in the YSiAlON system and the influence of nitrogen content and cation ratios on T_g , hardness, fracture toughness, viscosity and elastic moduli are now reported and studies on crystallisation will be described.

2 Materials

2.1 Representation of systems

Methods of representing both Si–Al–O–N and M–Si–Al–O–N systems¹⁸ have been developed. Five-component metal–sialon systems can be represented by a triangular prism. For example, the Y–Si–Al–O–N prism is shown in Fig. 1. The basal plane of the prism is a square which, in this case, represents the Si_3N_4 – Al_4N_4 – Al_4O_6 – Si_3O_6 system, that is, the oxides and nitrides of silicon and aluminium. The top left-hand corner is Si_3N_4 (3Si^{4+} , 4N^{3-}) and, if 12 positive and 12 negative valency units are maintained throughout, the other corners are then Si_3O_6 , Al_4O_6 and Al_4N_4 . Addition of a fifth component, such as Y, produces a prism with the right triangular face being a ternary oxide system and the left face the nitrides.

The concentrations of all components are expressed in equivalent units so that any point in the prism represents a combination of 12 positive and 12 negative valencies. As shown by Fig. 1, the distance x of any point P from the oxide face represents the concentration (in equivalent units) of nitrogen, and the distance y represents the equivalent concentration of oxygen, so that the equivalent concentration ratio of nitrogen = $x/(x+y)$ = $(3[\text{N}])/(2[\text{O}] + 3[\text{N}])$ where $[\text{O}]$ and $[\text{N}]$ are, respec-

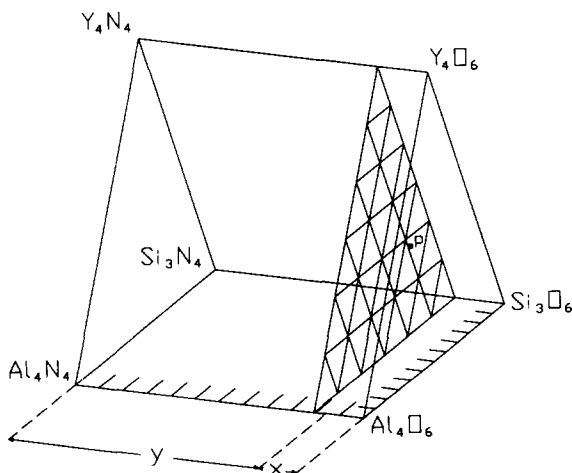


Fig. 1. The triangular prism representation of the Y–Si–Al–O–N system.

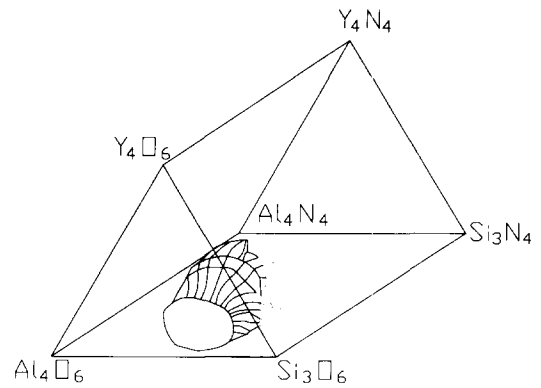


Fig. 2. Glass-forming region in the Y–Si–Al–O–N system (after Drew *et al.*⁵).

tively, the atomic concentrations of oxygen and nitrogen within any composition. The edge of the prism is scaled such that $x+y = 12$. The vertical plane is scaled such that each division is two valency units. The point P thus has a composition $\text{Y}^{3.36+\text{Si}^{6.72+\text{Al}^{11.92+\text{O}^{9.96-\text{N}^{2.04}}$ in valency units and hence $\text{Y}_{1.12}\text{Si}_{1.68}\text{Al}_{0.64}\text{O}_{4.98}\text{N}_{0.68}$ in atomic units. Compositions are then expressed as equivalent percent (equiv.%) so that this composition is 28Y, 56Si, 16Al and 83O, 17N.

This representation was adopted by Drew *et al.*⁵ to describe the limits of glass formation in different metal–sialon systems. The limits of the metal aluminosilicate glass regions were plotted on the oxide face of the prism and it was possible to observe how the glass region extended into the M–Si–Al–O–N prism on replacing oxygen by nitrogen. The three-dimensional representation of the complete glass forming region in the Y–Si–Al–O–N system is shown in Fig. 2.

2.2 Preparation of glasses

Parent glasses were prepared from mixtures of silicon nitride powder (Starck LC12) together with high purity (99.9%) oxides (Y_2O_3 , Al_2O_3 , SiO_2) to give the required chemical composition, in equivalent percent (equiv.%) cations/anions. Glasses with fixed cation compositions of 28 Y, 56 Si and 16 equiv.% Al and N levels from 0 to 25 equiv.% were prepared in order to determine the effect of nitrogen on properties (Table 1). A number of other compositions have been prepared with fixed O:N ratios from 0 to 25 equiv.% N and varying cation ratios in order to determine the extent of glass formation in the Y–Si–Al–O–N system (Tables 2 and 3).

Compositions were also selected, based on B-phase, $\text{Y}_2\text{SiAlO}_5\text{N}$, keeping the Y:Si:Al ratio constant and varying the nitrogen content (Table 4), together with compositions derived from K which has been shown to produce B-phase on heat treatment (Table 5). Finally a series was prepared,

Table 1. Standard cation compositions with varying nitrogen content

Equivalent %					Atomic %				
Y	Si	Al	O	N	Y	Si	Al	O	N
28	56	16	100	0	11.9	17.7	6.8	63.6	0
28	56	16	90	10	12.1	18.2	6.9	58.4	4.4
28	56	16	84	16	12.3	18.4	7.0	55.3	7.0
28	56	16	80	20	12.4	18.6	7.1	53.1	8.8
28	56	16	77	23	12.5	18.7	7.1	51.4	10.3

Table 2. Varying cation compositions in the Y-Si-Al-O-N system

Equivalent %					Atomic %				
Y	Si	Al	O	N	Y	Si	Al	O	N
28	72	0	90	10	12.3	23.8	0	59.5	4.4
28	68	4	90	10	12.3	23.3	1.8	59.2	4.4
28	64	8	90	10	12.2	21.0	3.5	59.0	4.3
28	60	12	90	10	12.2	19.6	5.2	58.7	4.3
28	56	16	90	10	12.1	18.2	6.9	58.4	4.4

Table 3. Varying cation compositions in the Y-Si-Al-O-N system

Equivalent %					Atomic %				
Y	Si	Al	O	N	Y	Si	Al	O	N
44	56	0	83	17	19.3	18.5	0	54.7	7.5
40	56	4	83	17	17.6	18.5	1.7	54.7	7.5
28	56	16	83	17	12.3	18.5	7.0	54.7	7.5
22	56	22	83	17	9.7	18.4	9.7	54.7	7.5
16	56	28	83	17	7	18.5	12.3	54.7	7.5
O	56	44	83	17	0	18.5	19.3	54.7	7.5

Table 4. B-Phase compositions

Equivalent %					Atomic %				
Y	Si	Al	O	N	Y	Si	Al	O	N
46.1	30.8	23.1	100	0	19.1	9.5	9.5	61.9	0
46.1	30.8	23.1	90	10	19.4	9.7	9.7	56.9	4.3
46.1	30.8	23.1	84	16	19.7	9.9	9.9	53.7	6.8
46.1	30.8	23.1	80	20	19.8	9.95	9.95	51.7	8.6
46.1	30.8	23.1	76.9	23.1	20	10	10	50	10

Table 5. K Compositions

Equivalent %					Atomic %				
Y	Si	Al	O	N	Y	Si	Al	O	N
35	45	20	100	0	14.7	14.1	8.4	62.8	0
35	45	20	90	10	14.95	14.5	8.35	57.7	4.3
35	45	20	84.1	15.9	15.2	14.6	8.7	54.6	6.9
35	45	20	80	20	15.3	14.7	8.75	52.5	8.75
35	45	20	77	23	15.4	14.9	8.8	50.8	10.1

Table 6. Compositions midway between B-phase and K compositions

Equivalent %					Atomic %				
Y	Si	Al	O	N	Y	Si	Al	O	N
40.6	37.8	21.6	100	0	16.9	11.8	8.9	62.4	0
40.6	37.8	21.6	90	10	17.2	12.0	9.2	57.3	4.3
40.6	37.8	21.6	84	16	17.4	12.2	9.3	54.2	6.9
40.6	37.8	21.6	80.5	19.5	17.6	12.3	9.4	52.3	8.4
40.6	37.8	21.6	77	23	17.7	12.5	9.4	50.4	10.0

based on a composition lying exactly half-way on a line between B-phase and K (Table 6).

The powders were blended in isopropanol for 10 min using a Janke and Kunkel Ultra-Turrax T25 homogeniser. The alcohol was then evaporated off and the powder mixture dry-mixed for a further 2 min before pressing into pellets. Large batches (60 g) were melted in a boron nitride lined graphite crucible under 0.1 MPa nitrogen at 1700°C for 1 h in a vertical tube furnace, after which the crucible was withdrawn rapidly from the hot zone, lifted from the furnace and poured into a pre-heated graphite mould at 900°C and annealed for 1 h at 850–900°C prior to slow furnace cooling.

3 Experimental methods for glass characterisation

3.1 X-Ray analysis and SEM

X-Ray analysis was carried out using a Hägg-Guinier focusing camera or a Phillips X-ray powder diffractometer (Cu K_{α} radiation) in order to detect any crystalline phases present in the glasses. Crystallisation products were also identified using the same techniques. Scanning electron microscopy was used to assess homogeneity.

3.2 Microhardness testing

Microhardness tests were carried out on the polished glass samples using a Leco microhardness tester. A load of 300 g was applied to the sample for 15 s. The resulting indentation diagonals were measured to give an estimation of the hardness of the glass.

3.3 Thermal analysis

Simultaneous differential thermal analysis/thermogravimetry was carried out using a Stanton-Redcroft STA-780 simultaneous TG/DTA analyser to determine glass transition (T_g) and crystallisation (T_c) temperatures.

3.4 Thermal expansion

Thermal expansion coefficient was measured in a Setaram TMA92 dilatometer under an Argon at-

mosphere at 0.1 MPa pressure. The temperature was increased at a rate of 5°C/min. Values for glass transition temperatures were deduced from the dilatometric curves.

3.5 Viscosity

Viscosity η was determined using three-point bending creep tests—its expression is based on the strong analogy existing between the stress-strain relation in an elastic solid and those governing a viscous fluid:^{19,20}

$$\eta = \sigma/[2(1 + \nu)\dot{\epsilon}] \quad (1)$$

where σ and $\dot{\epsilon}$ are the applied stress and the creep rate on the outer tensile fibre respectively and ν is Poisson's ratio.

3.5.1 Elastic moduli

At room temperature the 'Pulse Echo Overlap' technique allows the measurement of the compressional, V_L , and shear V_S , ultrasonic wave velocities with a better than 10^{-3} accuracy. The elastic moduli, E and G , and hence V , are derived from the relations

$$E = \rho[3V_L^2 - 4V_S^2]/[(V_L/V_S)^2 - 1] \quad (2)$$

$$G = \rho V_S^2 \quad (3)$$

where ρ is the density.

High-temperature measurements require the thermal insulation of the transducer. The principle of the method is to use magnetostrictive transducers to generate ultrasonic short pulses in long thin wave guides.²¹ The ultrasonic line is composed of a thin tungsten wave guide coupled to the sample via an alumina wave guide. The different parts of the ultrasonic line are attached together with a refractory cement. In the 'long-beam' mode approximation, Young's modulus is directly related to the compressional wave velocity, V_C , by the relation

$$E = \rho V_C^2 \quad (4)$$

Lateral dimensions, d , must be smaller than the wavelength by a factor of at least 5 (i.e. $d/\lambda \leq 0.2$). The time separating two successive echoes is related to the propagation velocity by $\tau = 2L/V_C$ where L is the length of the sample. To avoid the error due to phase shifts introduced at the interfaces, the ultrasonic signal was analysed by Fourier analysis. Software has been developed and, with a high-speed 486 microprocessor, a time of about 1 min is sufficient to undertake the spectral analysis of all the signal, and to give the propagation time from the three main echoes. This allows the rapid acquisition of reliable, precise results on very small samples ($L \sim 20$ mm).

Table 7. Analysis of standard compositions

Composition (Y:Si:Al:O:N; equiv.%)	X-Ray analysis	Observations on melting
28:56:16:100:0	Amorphous	Brown glass bar
28:56:16:90:10	Amorphous	Grey glass bar
28:56:16:84:16	Amorphous	Black glass bar
28:56:16:80:20	Amorphous	Transparent grey glass
28:56:16:77:23	Amorphous	Very difficult to melt grey in colour, not glassy in appearance

3.6 Crystallisation heat treatments

Heat treatment was carried out under nitrogen at selected temperatures in the range 800 to 1400°C in order to crystallise the glasses. Comparisons have been made with results from the ultrasonic investigations.

4 Results and discussion

4.1 Glass formation

Table 7 shows the X-ray analysis and observations on melting for the different series of Y-sialon glasses with increasing nitrogen contents from 0 to 23 equiv.%. Table 8 shows the results for the series with fixed nitrogen: oxygen ratio and varying cation compositions.

The (28Y-56Si-16Al) compositions formed homogeneous glasses which were grey to black in colour up to 20 equiv.% N. However, the 23 equiv.% N composition proved very difficult to melt with very vigorous frothing occurring during melting.

The B-phase cation compositions on firing do not produce glasses but an opaque crystalline product varying in colour from white to grey. The B-phase (Y_2SiAlO_5N) starting composition lies outside the glass-forming region in the

Table 8. Analysis of varying cation compositions

Composition (Y:Si:Al:O:N; equiv.%)	X-Ray analysis	Observations on melting
28:72:0:90:10	SiO ₂ (large flower like crystals)	Opaque white material formed
28:68:4:90:10	SiO ₂ (large flower like crystals)	Opaque white material formed
28:64:8:90:10	Amorphous	Black glass disc
28:60:12:90:10	Amorphous	Black glass disc
28:56:16:90:10	Amorphous	Black glass disc
44:56:0:83:17	Apatite	Grey opaque material
40:56:4:83:17	Amorphous	Black glass
28:56:16:83:17	Amorphous	Black glass
22:56:22:83:17	Amorphous	Black glass
16:56:28:83:17	Amorphous	Black glass
0:56:44:83:17	β -Si ₃ N ₄	Unmelted sintered pellets

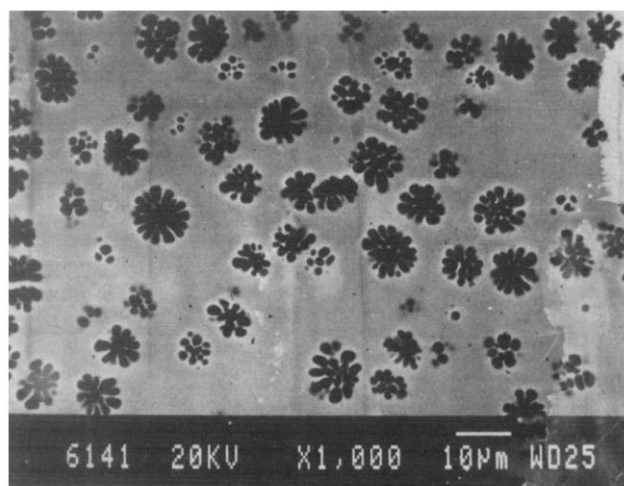


Fig. 3. Scanning electron micrograph showing SiO_2 crystals in the 28:72:0:90:10 (Y:Si:Al:O:N) glass.

Y-Si-Al-O-N system and Fig. 2 shows glass-forming regions as found by Drew *et al.*⁵ The oxide composition contained only yttrium aluminium garnet (YAG). Low nitrogen compositions were found to contain Y-N apatite, and traces of B-phase were found in the composition with 16 equiv.% nitrogen. However, as the nitrogen content increases, another phase is observed to replace Y-N apatite. The peaks of this unknown phase almost match those of $\text{X}_2\text{-Y}_2\text{SiO}_5$ and intensities increase with nitrogen content, being very weak at 16 equiv.% N but becoming much stronger at 23.1 equiv.% N.

K (35Y-45Si-20Al) compositions formed homogeneous glasses over the entire nitrogen range examined. The colour of the glass melt varied from brown to black for nitrogen contents from 0 to 20 equiv.% N with the 23 equiv.% N composition forming a transparent glass.

For the (40.6Y-37.8 Si-21.6Al) series, dark brown to black homogeneous glasses were formed at 0, 19.5 and 23 equiv.% N contents. The 10 and 16 equiv.% N compositions did not form homogeneous glasses but white crystalline products which on X-ray analysis showed traces of the unknown phase found in the 16, 20 and 23.1 equiv.% N B-phase cation compositions. For varying Si:Al ratios, homogeneous glasses were formed from the compositions containing 8, 12 and 16 equiv.% Al. The 28:72:0:90:10 (Y:Si:Al:O:N) composition shows evidence of residual crystallinity in the form of coarse flower-like crystals of SiO_2 , as shown in Fig 3. The 28:68:4:90:10 composition shows evidence of phase separation and residual SiO_2 .

For the Al:Y series, with constant Si and N content, a melting temperature of 1700°C was not high enough to melt the SiAlON glass composition without yttrium. At the other extremity, the composition with no aluminium produced a par-

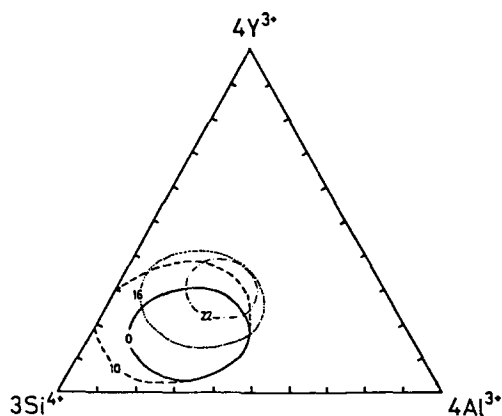


Fig. 4. Triangular section through Jänecke prism showing glass-forming regions at 0, 10, 16 and 22 equiv.% N.

tially crystalline grey opaque material containing N apatite. Homogeneous glasses, however, were formed by the other compositions and all these appeared black in colour.

From all of this information, glass-forming regions have been mapped out and Fig. 4 shows a triangular section through the Jänecke prism with equivalents 4Y^{3+} , 3Si^{4+} and 4Al^{3+} at the apices and the glass-forming regions for 0, 10, 16 and 22 equiv.% N. The regions are similar to those found by Drew *et al.*⁵ except for the region at 22 equiv.% N which does not extend into the more Y-rich compositional range reported by them. This discrepancy may be due to differences in weight losses as a result of nitrogen evolution.

4.2 Influence of nitrogen content on properties

Figure 5 illustrates the influence of nitrogen content on microhardness. Microhardness increases with nitrogen content for all the series of glasses. Of the three series, glasses belonging to the series based on the B-phase/K intermediate composition have by far the lowest values, whereas the K glass has the highest overall hardness value.

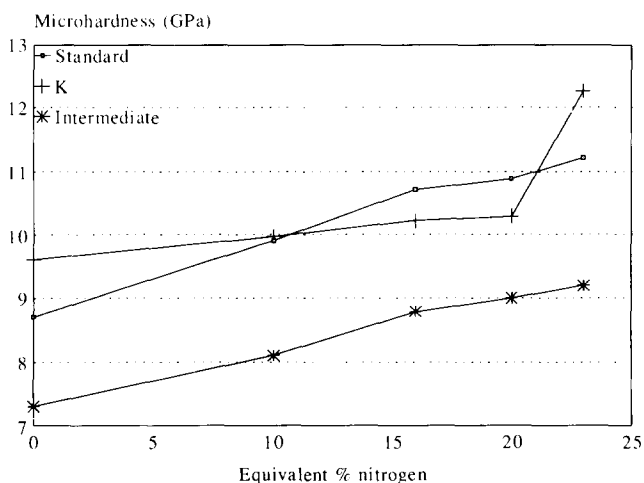


Fig. 5. Effect of N content on microhardness of glass compositions.

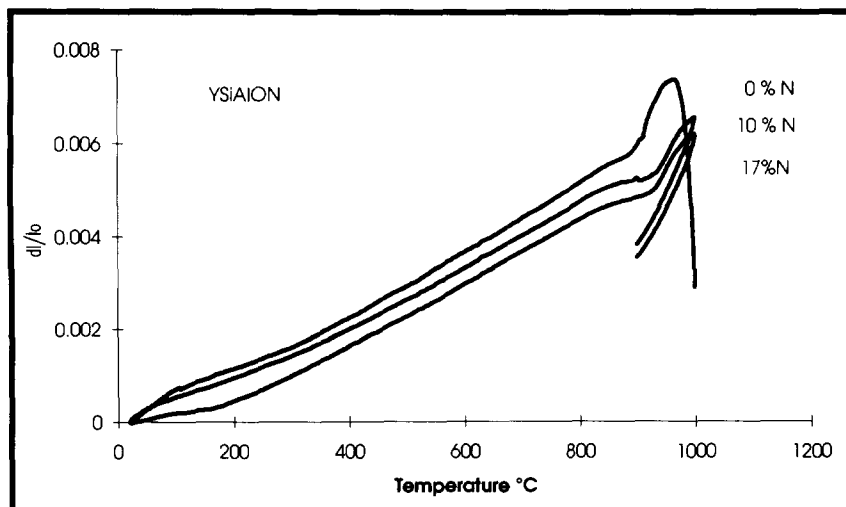


Fig. 6. Expansion of standard cation composition Y-sialon glasses with temperature.

Thermal expansion curves for the pure glass grades of the (28-56-16) series are shown in Fig. 6. During the first period of heating and up to 200°C a very slight curvature is observed. Above this temperature, the curves are quite linear, although there is a continuous increase in the expansion coefficient up to the softening temperature point. The mean thermal expansion coefficients between 200 and 800°C, α , are reported in Table 9 which shows that α decreases when nitrogen content increases.

Figure 7 shows the changes in viscosity with temperature and compares these with results of Rouxel *et al.*¹³ on previous batches and with earlier work by Hampshire *et al.*²¹ The agreement is excellent for 0 equiv.% N. The viscosity is slightly higher for 17 equiv.% N, very likely because of

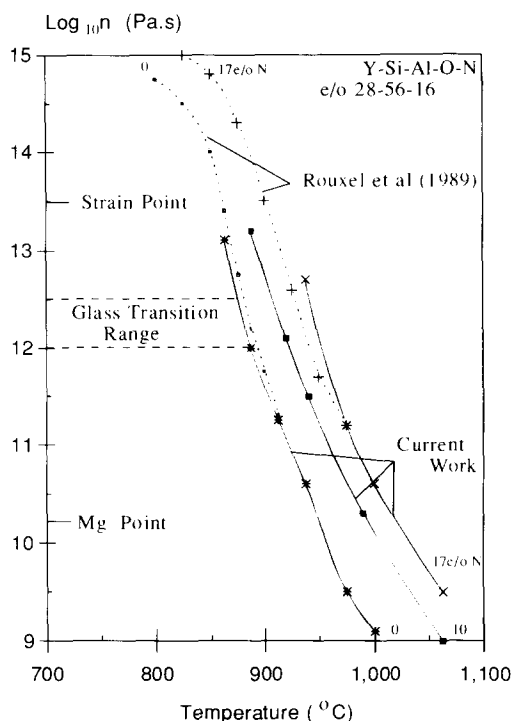


Fig. 7. Variation of viscosity with temperature for the standard cation composition Y-sialon glasses.

evolution of nitrogen during fabrication of the previous batches. The viscosity increases with nitrogen content. Assuming an Arrhenius-type relationship between viscosity and temperature, the activation enthalpy for viscous flow is estimated to be in the range 800–1000 kJ/mol at temperatures between the strain point ($10^{13.5}$ Pas) and the dilatometric softening point (Mg, $10^{11.2}$ Pas). This is close to the range of activation enthalpy for creep in silicon nitride based ceramics sintered with Y_2O_3 and Al_2O_3 .

Room-temperature values of the elastic moduli are reported in Table 9. As for hardness and viscosity, Young's modulus and shear modulus increase with nitrogen content, whereas Poisson's ratio remains very nearly constant.

The glass transition temperature (T_g) and crystallisation temperature (T_c) determined by thermal analysis show the same trend, that is, they both increase with increasing nitrogen content (Fig. 8). With lower Si content, the K series of glasses have lower T_g .

Hardness, viscosity, elastic moduli and glass transition temperature are higher for nitrogen

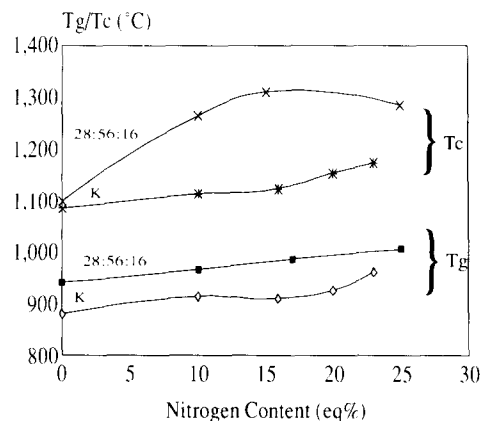
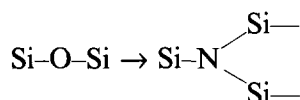


Fig. 8. Effect of N content on the T_g and T_c of standard cation composition glasses and K composition glasses in the Y-sialon system.

Table 9. Physical properties of (28 : 56 : 16) glasses

N content (equiv.%)	$\alpha (\times 10^6)$	E_0 (GPa) R-T	G_0 (GPa) R-T	ν R-T	T_g (°C)			T_c (°C) n
					DTA	n	Dil	
0	6.64	113	44	0.28	940	885-995	910	1 095
10	6.09	133	51	0.295	965	910-925	935	1 280
17	5.67	147	57	0.29	990	925-955	945	1 315

containing glasses than for the pure oxide analogue, whereas the thermal expansion coefficient is lower. This supports Mulfinger's theory²² that the replacement of some oxygen by nitrogen must lead to a higher average coordination of the non-metal atoms as in



thus leading to a more rigid glass network as a result of increased crosslinking. Si-N bonds have been proved to exist in oxynitride glasses using techniques such as IR,²³ XPS, NMR²⁴ or neutron-diffraction spectroscopy.²⁵ However, incorporated nitrogen atoms may also form one-fold (Si-N²⁻) and two-fold (Si-N⁻-Si) linkages to silicon. For instance, Jin *et al.*²⁵ found that only 42% of nitrogen atoms were bonded to three silicons in a Na-Si-O-N glass and that the presence of one-fold nitrogen cannot be ruled out. Also, in a Y-Si-Al-O-N glass, Kruppa *et al.*²⁶ calculated that 80% of nitrogen atoms were three-fold co-

ordinated to silicon and 20% two-fold. So, the enhancement in interconnectivity might not be a monotonic function of nitrogen content. Nevertheless, the present results suggest that, for the nitrogen range studied, the increase in crosslinking augments with nitrogen content.

For the (28-56-16) series, glass transition temperature were also deduced from dilatometric measurements and viscosity determination. The results are compared with those from thermal analysis in Table 9. The glass transition range usually corresponds to a viscosity range of 10^{12} - $10^{12.5}$ Pas. The temperature ranges determined in this way are somewhat lower than the results determined by thermal analysis. On the other hand, they are close to the temperatures derived from the dilatometric curves. One explanation may be that in dilatometric measurements, T_g is associated with onset of the glass softening, whereas in thermal analysis T_g is chosen at the maximum of the endothermic peak.

Change in the relative modulus (E/E_0) with temperature for the (26-56-16) glass with 17 equiv.%

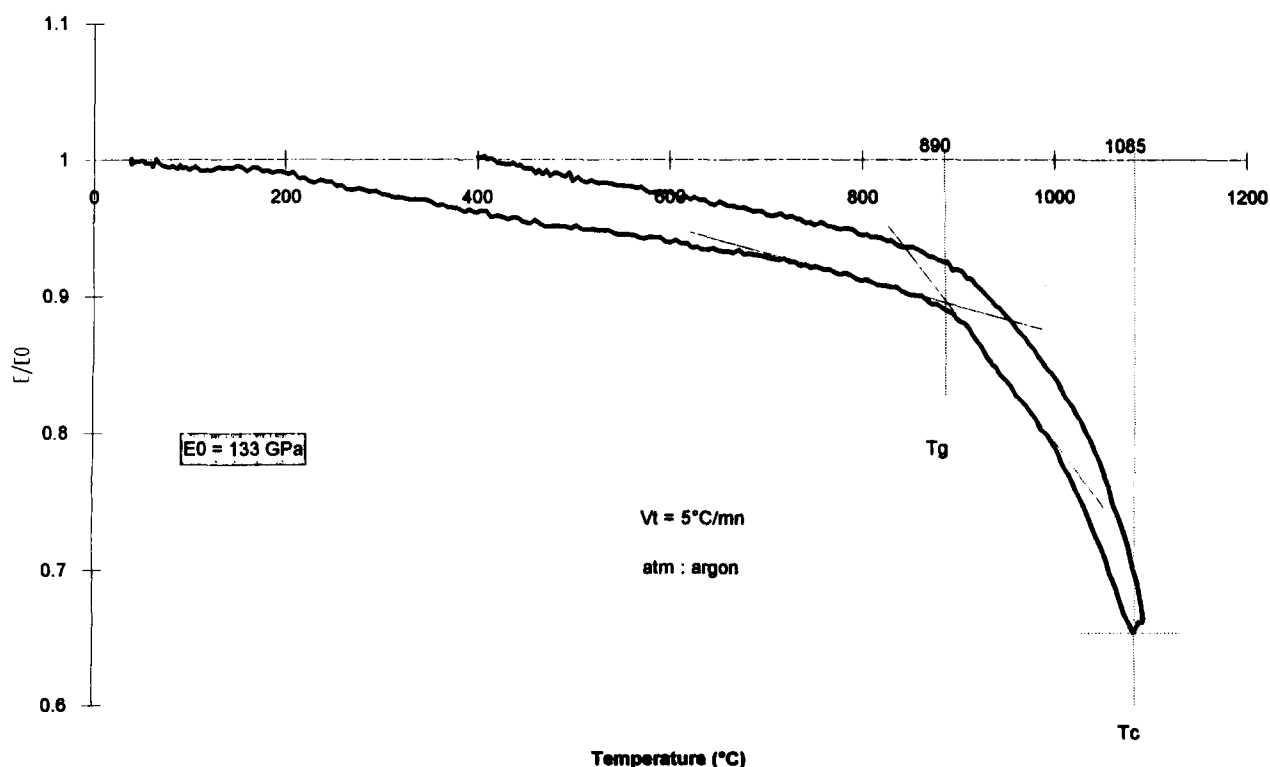


Fig. 9. Change in relative modulus (E/E_0) for the standard cation composition Y-sialon glass containing 17 equiv.% N.

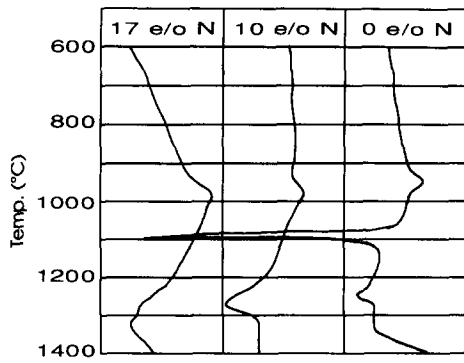


Fig. 10. DTA traces for standard cation composition Y-sialon glasses with 0, 10 and 17 equiv.% N.

N is shown in Fig. 9. The relative modulus decreases linearly up to 890°C at a rate of $10^{-2}K^{-1}$. Above this temperature, it decreases rapidly up to 1085°C where it starts increasing as crystallisation commences. When crystallisation has occurred, even partially, Young's modulus, after cooling to room temperature, is superior to that of the initial glass. Comparison with the results of viscosity determination (Fig. 7) shows that the change in slope corresponds to the viscosity associated with the strain point ($10^{13.5}$ Pas). Young's modulus proves to be sensitive at the very beginning of the softening of glass. Concerning the progression of crystallisation, these measurements indicate that the onset of the lowest crystallisation range occurs at 1085°C, whereas thermal analysis shows clearly only the main exothermic peak at 1315°C (Fig. 10) but with a progressive change commencing at approximately 1200°C.

4.3 Influence of varying Al/Y ratios

Contrary to the monotonic influence of nitrogen

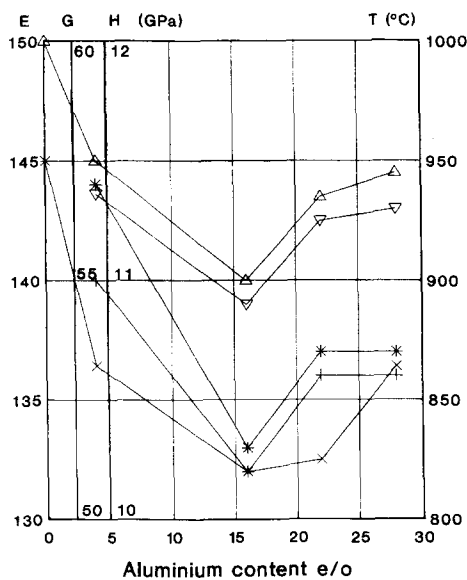


Fig. 11. Effect of Al:Y ratio (constant Si and N) on hardness, elastic modulus and glass transition temperatures of Y-sialon glasses.

on hardness, elastic moduli and glass transition temperature, varying Al/Y ratio leads to a minimum in all these characteristics at 16:28 equiv.% Al:Y (Fig. 11). This result suggests that an optimum might exist for the ratio of Y_2O_3/Al_2O_3 used in the densification of silicon nitride ceramics. The ratio corresponding to the lowest viscosity could lead to an optimum lower sintering temperature and also have a beneficial influence on the ability to undergo superplastic deformation.

Y^{3+} is likely to be considered as a modifying cation because of its size but the role of Al^{3+} is more ambiguous. It has been reported by Sato *et al.*²⁷ using MAS-NMR that in a SiAlON glass (approximately 84:16:97.5:2.5 equiv.% Si:Al:O:N), aluminium appears in four-, five- and six-fold coordination with oxygen, whereas only four- and six-fold coordination are observed in the corresponding nitrogen-free glass. Quantitative work on the spectrum indicated that $Al(O,N)_x$ species may be present but were not visible as distinct peaks. The ability to 'freeze in' five-fold coordinated Al sites into the oxynitride glass was attributed to increased viscosity arising from the higher coordination of nitrogen. Much more systematic work, particularly using MAS-NMR

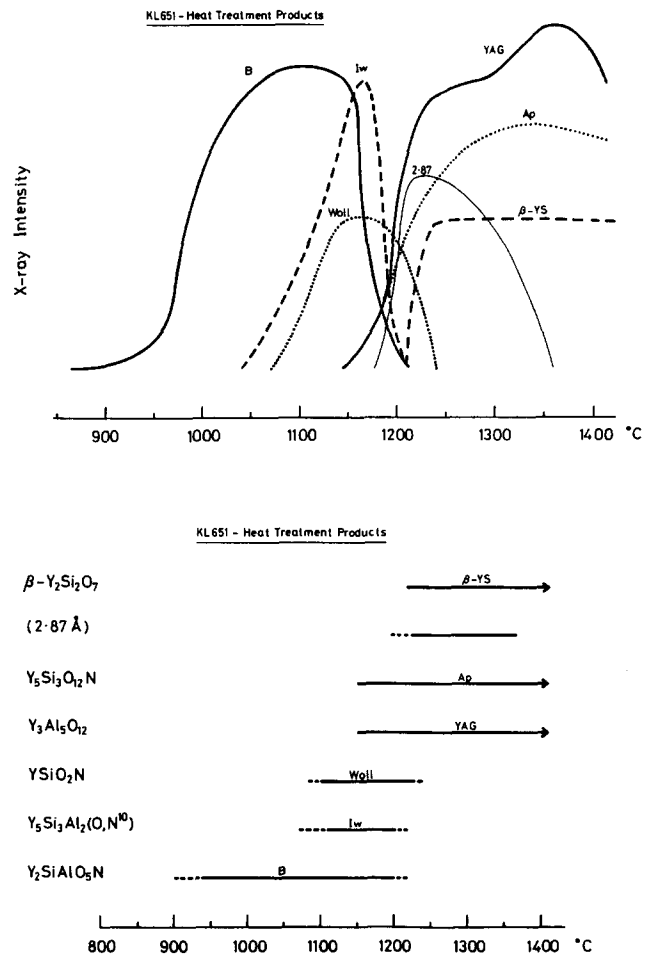


Fig. 12. Crystallisation products and their stability ranges following heat treatments of the K composition Y-Sialon glass with 23 equiv.% N.

would be useful to clarify the exact roles of aluminium and yttrium in the glass network.

4.4 Potential for crystallisation to single-phase glass-ceramics

A first approach to obtain high-performance glass-ceramics is to use compositions leading to a single-phase, fully crystalline product. In the YSiAlON system, the only single phase in the glass-forming region is U-phase ($Y_3Si_3Al_3O_{12}N_2$) but, contrary to what is observed in the lanthanide systems, yttrium U-phase is very unstable. An alternative was tried with compositions leading to B-phase as the major phase. The original K composition, (Y:Si:Al:O:N) = (35:45:20:77:23) in equiv.%, formed a transparent glass with the highest hardness of all the compositions studied. Figure 12 shows the crystallisation products and their stability ranges following a series of heat treatment experiments. Clearly, there is a total decomposition of the low-temperature phases (B-phase: Y_2SiAlO_5N ; I_w : $Y_5Si_3Al_2(O,N)_{10}$; wollastonite: $YSiO_2N$) around $1200^\circ C$ so that two completely different phase assemblages are observed above and below $1200^\circ C$. Heat treatments at temperatures up to $1050^\circ C$ produce B-phase + glass only, but, due to the critical sensitivity of the results to small temperature changes, the reproducibility of a pure B-phase + (minimum) glass is poor. A glass-ceramic containing B-phase + wollastonite is more easily formed and may be an acceptable alternative to a single-phase product.

4.5 Optimisation of glass-ceramic processing

The conventional glass-ceramic process involves heating the as-prepared glass to an initial heat treatment temperature at which internal nucleation occurs followed by heating to a second higher temperature to allow crystal growth of the nuclei. The first temperature is usually about $50^\circ C$ above the annealing temperature. Morrissey *et al.*²⁸ identified process parameters for selected oxynitride glass-ceramics and, in a further study,²⁹ the same authors reported the process parameters controlling the preparation of oxynitride glass-ceramics in the Nd-Mg-Si-O-N system.

In this work, the (Y:Si:Al:O:N) = (28:56:16:83:17) composition was selected to study the crystallisation behaviour. Since, according to the changes observed in Young's modulus, the first crystallisation range was around $1085^\circ C$, an isothermal ultrasonic experiment was carried out at this temperature to estimate the time for complete crystallisation. The soaking temperature was reached in 3.5 h, so some nucleation might have taken place during heating. Crystallisation appeared to proceed in three stages (Fig. 13). During the first hour, the rate of change of Young's modulus, which mimics that of the crystallisation was very fast; then it levelled off before starting to increase further after 5 h. The rate of change was slow and sigmoidal during this second stage which was followed by a third stage with very similar kinetics. After 25 h, Young's modulus remained constant. The sample was then cooled down to

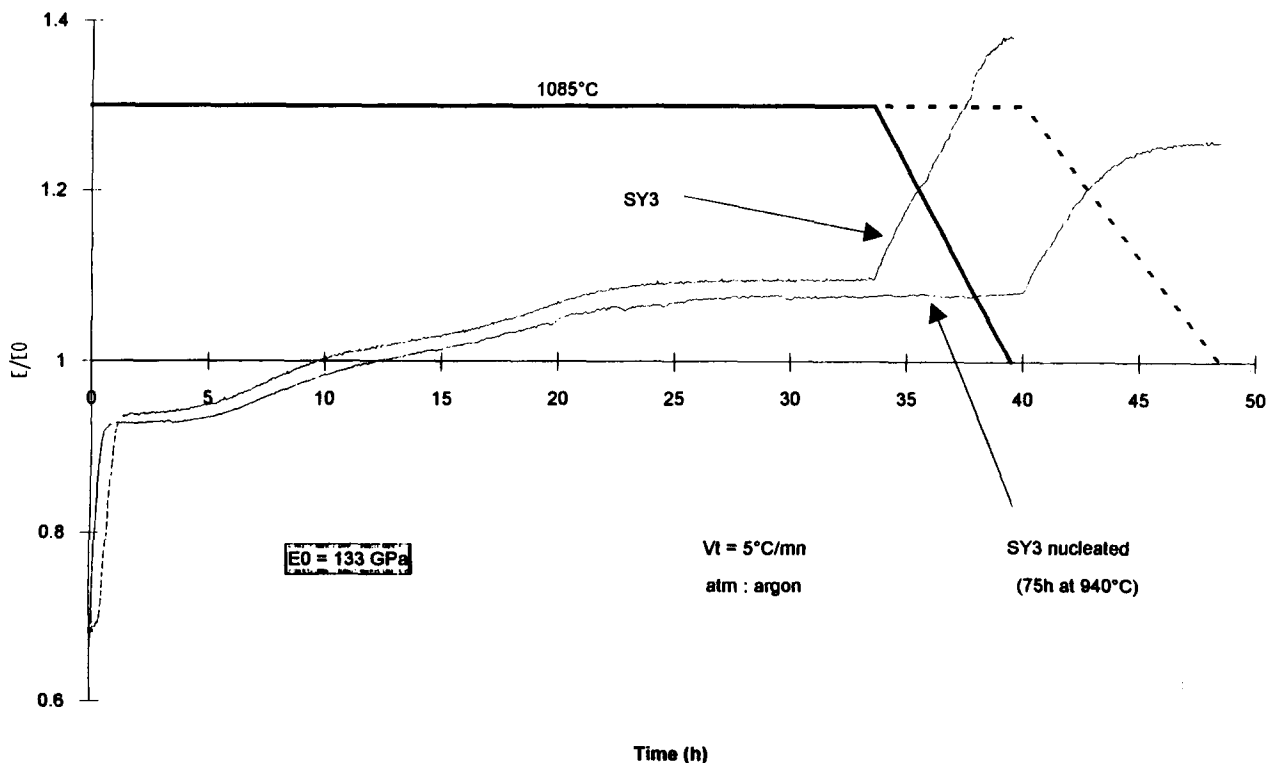


Fig. 13. Change in Young's modulus with time at the crystallisation temperature, ($1085^\circ C$) for the standard cation composition Y-sialon glass with 17 equiv.% N (SY3).

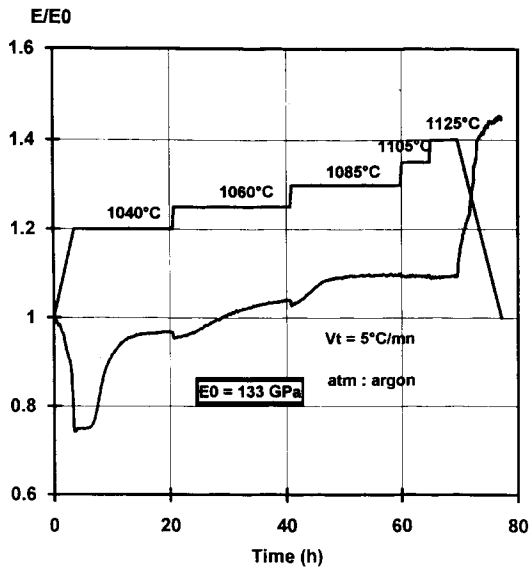


Fig. 14. Change in Young's modulus of SY3 glass on heat treating at 1040°C, 1060°C and 1085°C for 20 h at each temperature.

room temperature and re-heated up to 1150°C. During this run, Young's modulus decreased slowly and linearly over the entire temperature range and no longer exhibits a sudden decrease on reaching the glass transition range. This behaviour was reversible on cooling and it was concluded that heat treatment at 1085°C had led to a fully crystallised glass-ceramic with no residual glass. If glass films do remain along grain-boundaries in the glass-ceramic, they must be very thin, since the intergranular residual glassy phase (~7%) in silicon nitride ceramics is normally clearly evident by ultrasonic measurements³⁰ and shows the more abrupt change in modulus at a temperature corresponding to T_g for the intergranular glass.

In order to optimise the microstructure of the glass-ceramic, a nucleation stage has to be introduced, and so heat treatments for 2.5 h were carried out at 1015, 1035 and 1065°C. The samples were still amorphous after treatment at the two lower temperatures, but partially crystalline for 1065°C. An ultrasonic experiment was then performed consisting of 20–25°C incremental temperature steps of 20 h each, starting at 1040°C (Fig. 14). At 1040°C, Young's modulus started to increase after an incubation period of about 2 h and levelled off after 15 h. Subsequent increases in temperature led to modulus increases up to 1085°C.

Isothermal treatments with different durations were also conducted at 1100°C and the phases formed were identified by XRD. The relative heights of the main peaks of each crystalline phase are reported in Fig. 15. The first phase to precipitate is γ -Y₂Si₂O₇ which partially converts to δ after 24 h. After the same period of time, Y₂SiO₅ and yttrium aluminium garnet (YAG) are also

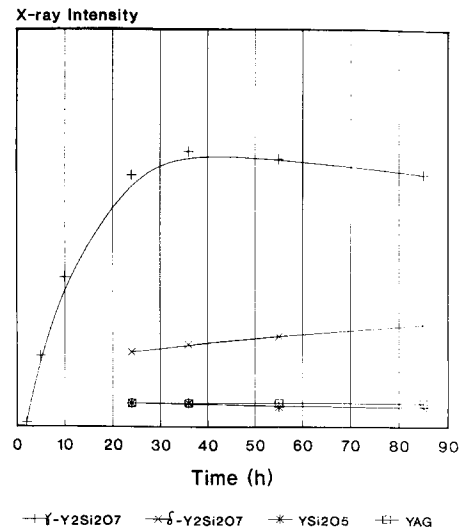


Fig. 15. Crystallisation of SY3 glass at 1100°C showing X-ray intensities of major phases.

present, but not Si₂N₂O. For longer times, the sum of the peak intensities remains almost constant, which is consistent with complete crystallisation as concluded from the ultrasonic experiment. Quantitative analysis of the change in Young's modulus with time (see Rouxel *et al.*³¹ for details) showed that about 70% of the glass is crystallised within 5 h and 80% within 10 h, which is far more than derived from diffraction peak heights. (Diffraction peak areas were impossible to measure due to the complexity of the diagram.) An explanation could be that ultrasonic measurements are sensitive to the whole crystalline volume, whereas XRD is insensitive to very small crystallites. So, ultrasonic techniques allow access to the complete glass fraction, but cannot distinguish between the different varieties of yttrium disilicates because their Young's moduli are too close.

Samples of the same glass were heat treated at various temperatures from 1000 to 1300°C for different times up to 36 h. The results are shown in Fig. 16. At 1000°C, the samples were still amorphous. They were partially crystallised at 1050°C and almost fully crystalline at 1100°C and above. With increasing temperatures, γ -Y₂Si₂O₇ transforms into δ which in turn converts into β above 1200°C. YAG and Y₂SiO₅ are detected at 1100°C and Si₂N₂O at 1200°C. However, caution is required in inferring from these results an accurate picture of the crystallisation sequence and the changing composition. In a previous study¹⁶ on a similar glass, it has been shown that Si₂N₂O was detected by Raman spectroscopy at a temperature 100°C lower than the first detection of this phase using XRD. For higher temperatures no further changes were observed. From these results it was inferred that a nucleation stage of 2.5 h at 1035°C (that is $T_g + 50^\circ\text{C}$ as measured by DTA) was suitable and that the minimum temperature lead-

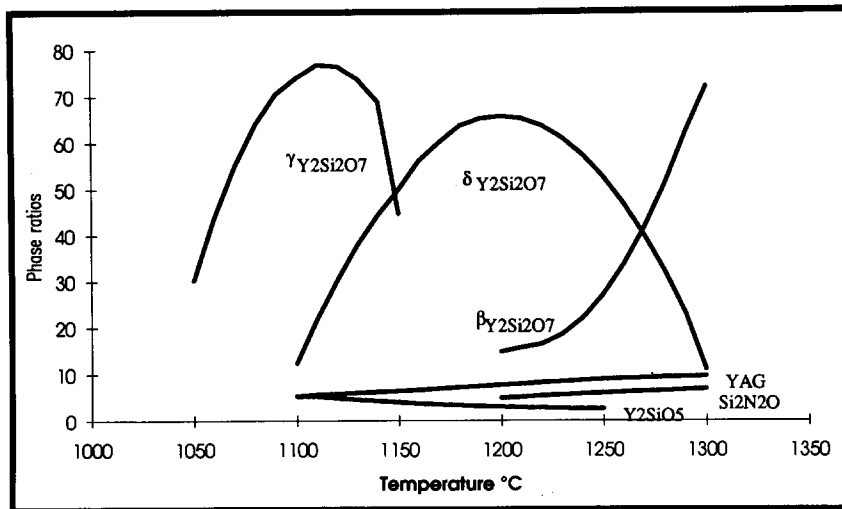


Fig. 16. Crystallisation of SY3 glass showing quantities of phases present after 36 h heat treatment at various temperatures.

ing to a fully crystalline product was 1085°C. Finally, a two-stage heat treatment, a nucleation stage at $T_g + 50^\circ\text{C}$ followed by a crystallisation stage at 1250°C, was tested and produced a glass-ceramic with a fine microstructure and a Vickers microhardness of 11.5 GPa. Some preliminary results in this system have been reported elsewhere.³² Further two-stage heat treatments are under investigation.

5 Conclusions

Homogeneous glasses have been prepared in the Y-Si-Al-O-N system with up to 23 equiv.% N. Assessment of the glass-forming regions have been made. Incorporation of N increases the hardness, elastic moduli and glass transition temperature, whereas varying the Al/Y ratio at constant nitrogen concentration leads to a minimum in these properties.

Crystallisation of Y-Si-Al-O-N glasses at different temperatures has been carried out and two distinct phase assemblages are observed below and above 1200°C. Crystallisation can be monitored using an ultrasonic technique for determination of Young's modulus. Y-Sialon glass-ceramics have been produced using a nucleation stage.

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