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Preparation and Properties of Y—Si—Al—O—N Glasses

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SUMMARY

Y—Si—Al—O—N glass batches as large as 100 g were made by melting in BN crucibles at temperatures from 1600 to 1650°C in N_2 at 200 kPa. Chemical analysis of the glasses showed that their N contents from 6·3 to 15 atomic % were unchanged by melting. Density, glass transition temperature, thermal diffusivity, elastic modulus, microhardness, and fracture toughness are all higher for these oxynitride glasses than for oxide glasses; and all tend to increase with increasing N content. Bend strengths up to 215 MPa were obtained for a glass containing 15 atomic % N, and strength-controlling defects, where identifiable, were metallic particles and porous regions.

1 INTRODUCTION

Previous studies[1–9] of the preparation and properties of glasses in the system Y—Si—Al—O—N showed that such glasses exhibit some remarkable properties. Those results, although encouraging, indicated that further work was needed to define more completely the preparation and properties of Y—Si—Al—O—N glasses. Areas needing particular attention that the present investigation addresses include the preparation of large (>30 g) glass batches, further definition and optimization of glass-melting parameters, and further characterization of glass properties.

This investigation is an extension of earlier, preliminary work[7,8] on the preparation and characterization of relatively small (10–30 g) glass specimens in the system Y—Si—Al—O—N. As noted earlier,[7] some of those glasses contained crystalline β- or β′-Si_3N_4 that came from either incomplete melting or from the fact that some of the compositions may have

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contained excess Si_3N_4. A major objective of the present work has been to prepare large (100 g) batches of crystal-free glass for characterization studies that would complement and augment previous studies.[1-9]

2 EXPERIMENTAL PROCEDURES

2.1 Glass compositions and materials

The three glasses that were investigated in detail in this work contain, respectively, 6·3, 13·3 and 15·0 atomic % N. As illustrated in Fig. 1, the two lower N compositions ('a' and 'b') are in the AlN—SiO_2—Y_2O_3 ternary, while the third ('h') is slightly out of that ternary, occurring between it and the Si_3N_4 corner of the triangular prism that represents the Y—Si—Al—O—N system.[10] For reference, some of the crystalline phases in the ternary are also labeled in Fig. 1.

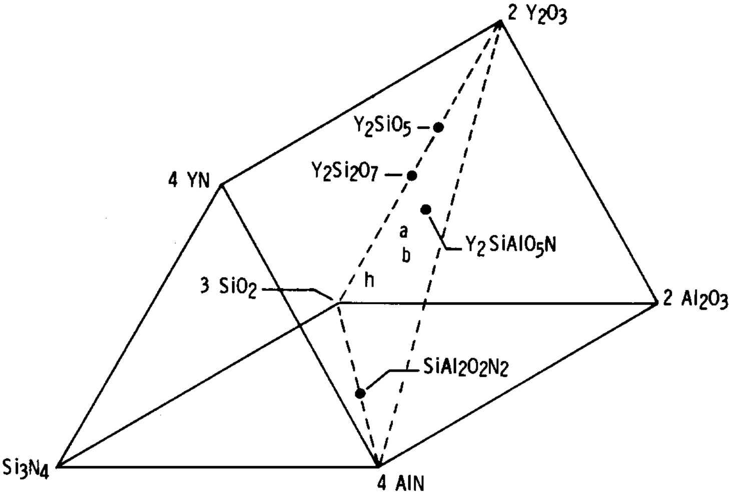

Fig. 1. Equivalent diagram showing compounds and experimental compositions in the system Y—Si—Al—O—N.

Nominal starting, and analyzed final compositions of the three glasses that were investigated, are given in Table 1. Batches were formulated from Al_2O_3,* Si_3N_4,** SiO_2,† and Y_2O_3†† powders weighed in the desired

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* 99·995% α-Al_2O_3 (Gallard Schlessinger Corp., Carle Place, NY).

** AME CP-85 Si_3N_4 (AME, Gateshead, UK).

† 99·5% high-purity fused SiO_2 (Thermo Materials Corp., Atlanta, GA).

†† 99·9% Y_2O_3 (Molycorp, NY).

TABLE 1

Chemical Analyses of Y—Si—Al—O—N Glasses

Element	*Composition (in weight %)*					
	'a'		*'b'*		*'h'*	
	Nom.	*Anal.*	*Nom.*	*Anal.*	*Nom.*	*Anal.*
Al[a]	6·0	6·5	12·6	12·7	9·1	9·6
Si[a]	18·9	18·0	13·2	13·2	14·3	14·3
Y[b]	39·8	42·6	41·5	43·0	45·1	45·4
O[c]	32·2	29·3	26·2	24·8	24·4	23·1
N[d]	3·2	3·3	6·6	6·4	7·1	7·2
Fe[b]	—	0·11	—	0·13	—	0·09
B[b]	—	trace ~0·1	—	trace ~0·1	—	trace ~0·1

[a] Average of emission spectroscopy and atomic absorption.

[b] Emission spectroscopy.

[c] Vacuum fusion, precision ±0·8%.

[d] Kjeldahl distillation, precision ±0·2%.

Nom. = nominal starting composition.

Anal. = analyzed glass composition.

amounts, and mixed overnight in polyethylene bottles containing Al_2O_3 balls. For consolidation, and for convenience in handling, the powder mixtures were then isostatically pressed at 140 MPa into compacts that weighed up to 100 g. The compacts were subsequently broken into coarse chunks that were used as feed material for glass-melting.

2.2 Glass preparation

Glasses were prepared according to the procedures given in Fig. 2. All melting was done in 25 mm i.d. × 70 mm high screw-top crucibles machined from hot-pressed BN (Grade HP, Carborundum Co., Niagara Falls, NY), and cleaned as indicated in Fig. 2; without that cleaning procedure, severe crucible–melt interactions occurred. After conclusion of this study, it was found that, as suggested by W. B. Crandall (pers. commun.), excellent results could be obtained by melting in inexpensive graphite crucibles slurry-coated with BN powder, a method now used exclusively.

Glass-melting was done in nitrogen at 200 kPa pressure in a cold wall vacuum furnace (Centorr Associates, Suncook, NH) having a tungsten mesh heating element. The premelting step shown in Fig. 2 was sometimes omitted

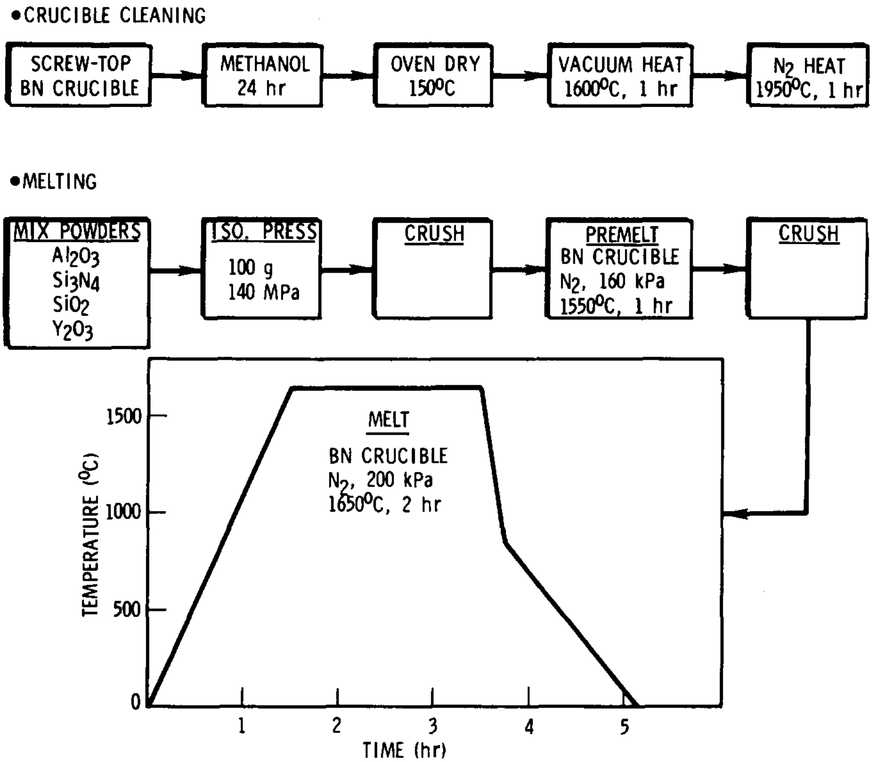


Fig. 2. Preparation of Si—Y—Al—O—N glasses.

with no obvious bad effects. Melting temperatures for the 'b' and 'h' compositions were as shown (1650°C), while the 'a' composition melted at a lower temperature, 1600°C. In most cases, the glass ingots came out of the crucible with only gentle tapping. In certain instances, however, crucible–melt interactions were so severe as to require destruction of the crucible for ingot removal. That problem has been eliminated by the current practice of using graphite crucibles internally coated with BN.

2.3 Glass characterization

As discussed in this section, a number of techniques were used to characterize the chemical and physical properties of the three Y—Si—Al—O—N glasses that were investigated.

The elemental compositions of the glasses were determined by the various chemical analysis techniques noted in Table 1. Densities were measured by the Archimedes technique, and glass transition temperatures (T_g) by differential thermal analysis (DTA). Thermal diffusivities[11] were measured by the flash method.[12] Details of measurements of elastic moduli and microhardness were reported previously.[8] Fracture toughness was measured by the indentation technique.[13]

Fracture stresses were determined in four point bending on specimens 2·79 mm wide × 2·16 mm high × 50 mm long. Specimen edges were chamfered at 45° angles to a depth of 0·09 mm (measured perpendicular to the chamfered surface), and all surfaces were ground lengthwise to an 8 μm RMS finish. Outer and inner spans were, respectively, 30·5 and 15·25 mm, and the cross-head speed was 0·13 mm/min. All fracture surfaces were examined by optical microscopy to determine where fracture originated, and some fracture surfaces were further examined in the scanning electron microscope.

3 RESULTS AND DISCUSSION

Figure 3 shows polished disks 25 mm i.d. × 1 mm thick that were machined from ingots of the three glasses investigated in this study. The glasses range from light grey and very transparent ('a') to dark grey and barely translucent ('h'). Work reported previously[14] attributed the grey color to the presence of Si precipitates from thermal decomposition during melting. Despite the discoloration, however, all of the glasses in Fig. 3 gave amorphous X-ray diffraction patterns.

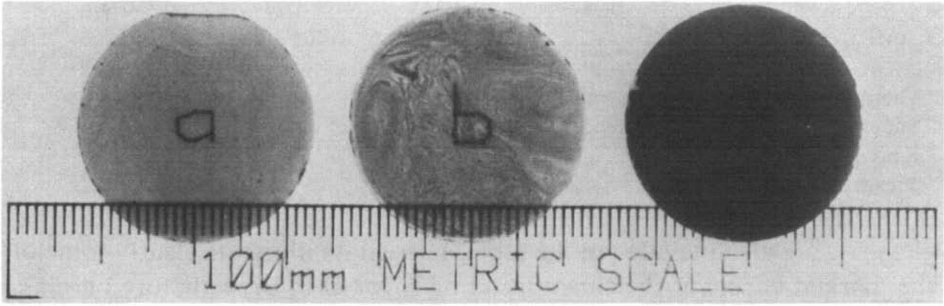


Fig. 3. Appearance of polished disks (1 mm thick) of oxynitride glasses (Y—Si—Al—O—N) (left to right): 'a', 'b', and 'h', Although all are X-ray amorphous, glass 'h' is only slightly translucent optically.

The chemical analysis data shown in Table 1 illustrate several significant points. That the N contents of the glasses are the same before and after melting, while the O contents decrease, is consistent with prior work[14] indicating that thermal decomposition proceeds via loss of O-containing vapor species. The small increases in Al and Y are also consistent with decomposition processes in which SiO (g) is the main product.[14] Of further interest is that, although B (from the BN crucible) was expected to be a significant contaminant, little, if any, B appeared in the glasses. Also noteworthy with regard to the chemical analysis results is that the Fe impurity must have come from the Si_3N_4 batch component; the remaining batch components were all very pure.

The various glass characterization data that were obtained are summarized in Table 2. For comparison, data on some Y—Si—Al oxide glasses[15] are also included in the table. These data illustrate clearly some of the marked effects of the substitution of N for O in the structure on glass properties. The trends shown are consistent with results in the literature[16] on the effects of the substitution of N for O in any number of glass systems; density, T_g, hardness, and elastic modulus all increase with increasing N content. Although the properties in Table 2 would also be expected to show some dependence upon cation composition, Hampshire *et al.*[9] have shown that the same trends with N content are obtained even for glasses with the same cation composition.

TABLE 2

Characterization of Y—Si—Al—O—N Glasses

Glass	*'a'*	*'b'*	*'h'*	*Y—Si—Al*[b] *oxide glass*
N content (a/o)	6·3	13·3	15·0	0·0
ρ (kg/m^3)	3 820	3 920	4 000	3 572,[15] 3 830[3]
T_g (°C)	944 ± 11	956 ± 19	958 ± 15	830,[3] 918[3]
α (cm/s)[a]	0·004 95	0·005 25	0·005 74	—
Microhardness (GPa)	9·01 ± 0·65[c]	10·37 ± 0·55[c]	10·37 ± 0·47[c]	~8[9d]
E (GPa)	141	157	186	115[15]
ν	0·288	0·315	0·291	—
K_{IC} (MN m$^{3/2}$)	0·95	1·44	1·27	0·60[3]
σ_f (MPa)	—	154 ± 27	165 ± 48	—

[a] Thermal diffusivity data from ref. 11.
[b] Superscript nos. indicate references from which data were obtained.
[c] Knoop, 0·98 N load.
[d] Vickers, 0·98 N load.

As shown in Table 2, oxynitride glass densities (ρ) are slightly higher than densities for equivalent oxide glasses. In support of this conclusion, an oxide glass prepared in this study with approximately the same cation composition as 'a' had a measured density of 3670 kg/m^3 vs. the value of 3820 kg/m^3 given in Table 2 for the oxynitride glass. The glass transition temperatures (T_g) reported herein are similar to those given by other workers[4-6,9] for similar, but not identical, glasses, and considerably higher than T_g for oxide glasses.

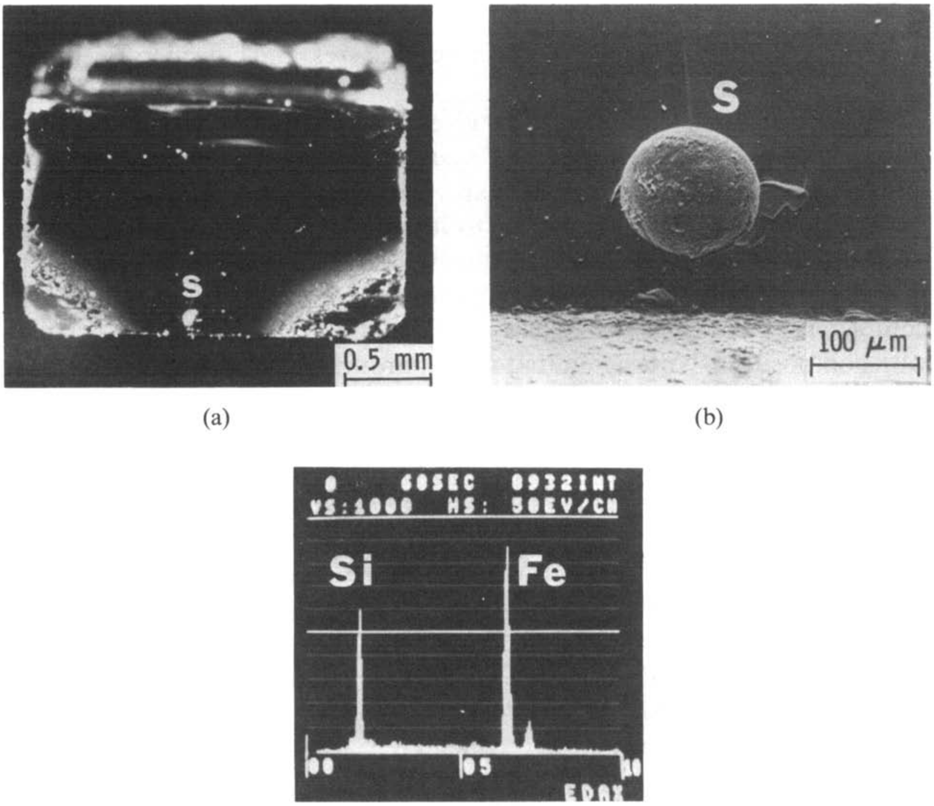
The thermal diffusivity (α) data given in Table 2 are the first known measurements on glasses in the system Y—Si—Al—O—N. Thermal diffusivities are somewhat higher than values for typical oxide glasses, and, as shown in the table, they appear to increase with increasing N content.

The data on microhardness, elastic modulus (E), and Poisson's ratio (ν), discussed in detail in an earlier publication,[8] are included herein for completeness and to give an overall picture of how glass properties change with composition. Note again that microhardness and elastic modulus both increase with increasing N concentration in the glass.

The fracture toughness (K_{IC}) values in Table 2 are the first reported for these particular glass compositions, two of which ('b' and 'h') are much higher in N (13–15 atomic %) than those (6–7 atomic % N) reported earlier by Loehman.[3,6] The indentations that were obtained in our glasses yielded practically ideal crack patterns that made crack-size measurements relatively easy. As with other measurements, the K_{IC} values listed in Table 2 are higher than for typical oxide glasses ($K_{IC} = 0{\cdot}7\text{–}0{\cdot}8\,\mathrm{MN\ m^{-3/2}}$), but lower than for dense, crystalline Si_3N_4 ($K_{IC} = 5\,\mathrm{MN\,m^{-3/2}}$). Although K_{IC} may increase somewhat with N content, further measurements would be needed to establish that point convincingly.

The bend test results in Table 2 are the first ever reported for glasses in the system Y—Si—Al—O—N, probably because previous investigations[1-9] dealt with relatively small amounts of material. The figures given in the table are means of ten measurements on specimens of each composition. The modulus of rupture values are very high for glasses, and it is notable that four specimens of the 'h' glass failed at impressively high stresses from 209 to 214 MPa (30 to 31 ksi).

As reflected in the standard deviation values in Table 2, the range of fracture stresses was greater for the 'h' glass than for the 'b' glass, suggesting that obvious defects limited the strength of the 'h' material. While careful examination of fracture surfaces revealed such obvious defects at fracture origins in the 'b' glass, similar defects were absent in the 'h' specimens. A typical fracture-inducing defect in the former glass is shown in Fig. 4. The Si sphere at the fracture origin is believed to have resulted from thermal decomposition during glass melting, and the Fe in it is thought to be a consequence of Fe impurities in the Si_3N_4 powder used in making the glass.[14] Surprisingly, fracture stresses on specimens failing from such defects were not particularly lower than on specimens that failed from other defects resembling porous or devitrified regions. Although this subject clearly



(a) (b)

(c)

Fig. 4. Defect in oxynitride glass bend specimen; (a) and (b) show metallic sphere at which fracture initiated, and (c) indicates that it contains Si and Fe.

requires further investigation, the potentially outstanding properties of Y—Si—Al—O—N glasses suggest that they may find extensive use in demanding structural applications.

4 CONCLUSIONS

In summary, it may be concluded that

- (a) Large (100 g) ingots of good quality Y—Si—Al—O—N glass can be readily fabricated by melting at low N_2 overpressures (200 kPa).
- (b) The N contents of the glasses are essentially the same as the N contents of the starting batches.
- (c) Among the properties that increase with increasing N content are:

density, glass transition temperature, thermal diffusivity, hardness, elastic modulus, and fracture toughness.

(d) The glasses have high transverse rupture strengths (up to 215 MPa).

(e) The demonstrated feasibility of fabrication and outstanding properties of Y—Si—Al—O—N glasses make them attractive candidate materials for demanding applications such as transparent armor and high modulus fibers for composites.

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