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BASIC RESEARCH ON OXYNITRIDE GLASSES

Final Report

Ronald E. Loehman

July 1982

Prepared for:

U.S. ARMY RESEARCH OFFICE
P.O. Box 12211
Research Triangle Park, NC 27709

Contract No. DAAG-29-79-C-0007

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. $AD-A118925$	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) BASIC RESEARCH ON OXYNITRIDE GLASSES		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER 8116 Final
7. AUTHOR(s) Ronald E. Loehman		8. CONTRACT OR GRANT NUMBER(s) DAAG-29-79-C-007
9. PERFORMING ORGANIZATION NAME AND ADDRESS SRI International 333 Ravenswood Avenue Menlo Park, California 94025		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE July 19, 1982
		13. NUMBER OF PAGES 50
14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)		15. SECURITY CLASS (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Glass, Nitrogen-containing glass, Silicon nitride, Nitrogen ceramics

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Nitrogen has been partially substituted for oxygen in a wide variety of silicate systems to produce oxynitride glasses with improved properties. Nitrogen contents as high as 12 at% have been achieved. The glass-forming regions in the Y-Si-Al-O-N, Mg-Si-Al-O-N, and Ca-Si-Al-O-N systems have been investigated in detail, and those in the Si-Al-O-N, La-Si-Al-O-N, Li-Si-Al-O-N, and Sc-Si-Al-O-N systems have been studied to a lesser extent. For all compositions there is a consistent variation in properties with nitrogen content.

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The glass transition temperature, hardness, fracture toughness, and density all increase, and the thermal expansion coefficient decreases with increased nitrogen content. Those data, together with infrared spectroscopic results, are consistent with a structural model in which trivalent nitrogen substitutes for bivalent oxygen to give a greater degree of cross-linking in the glass network. The improved properties afforded by nitrogen substitution may lead to commercial applications for oxynitride glasses as hardened windows, high modulus glass fibers, leach-resistant coatings, and as joining compositions for nitrogen ceramics.

FOREWORD

This document is a summary of work performed over a three-year period under sponsorship of the U.S. Army Research Office. Dr. John Hurt served as technical monitor. The objective of the research was to investigate the role of nitrogen substitution in oxide glasses, primarily by determining the conditions under which oxynitride glasses can be made and by discovering the influence of nitrogen incorporation on glass structure and properties. The report is organized as a comprehensive review of what is currently known about oxynitride glasses and, as such, it contains extensive descriptions of work done by others integrated with the presentation of the author's research.

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INTRODUCTION

The effects of nitrogen additions on the properties of oxide glasses have been investigated sporadically over the years. Mulfinger (1) studied the physical and chemical dissolution of N_2 and NH_3 in glass melts and found spectroscopic evidence that nitrogen was present as nitride or -NH groups. The nitrogen content reached a maximum of about 0.7 wt% after the melt was bubbled with NH_3 for 5 h at 1400°C. Elmer and Nordberg (2) introduced 3 wt% nitrogen into a porous borosilicate glass by heating in ammonia at higher temperatures. That level of nitrogen reduced the tendency of the glass to devitrify under electrolysis and increased its electrical resistivity and viscosity. Those property changes were correlated with infrared spectroscopic measurements showing the presence of -NH and -N- groups in the glass structure. Harding and Ryder (3) added Si_3N_4 to an amber container-glass to determine the effect of sulfate concentration on nitrogen solubility, but no properties other than solubility were reported.

During the past four or five years, there has been a considerable increase in research on nitrogen-containing glasses. The upsurge in interest in these glasses was originally motivated by their relevance to the processing of Si_3N_4-based ceramics (4, 5) when it was recognized that at least some of the intergranular phases in the ceramics are amorphous oxynitrides (6, 7). The discovery that nitrogen incorporation alters a wide range of glass properties (8, 9) shifted the focus of research to nitrogen-containing glasses themselves, independent of their role in ceramic processing.

Evidence is accumulating that the observed property alterations result from the direct substitution of trivalent nitrogen for bivalent oxygen in the glass structure. The extra degree of linkage afforded by the nitrogen produces a tighter, more highly cross-linked glass structure. Thus,

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nitrogen incorporation represents one of the few methods of achieving compositional substitution in the anion portion of oxide glass networks.

At this early stage it is not clear whether any nitrogen-containing glass will find wide commercial use. However, several areas of application are suggested by results obtained so far, among them refractory glass-ceramics, leach-resistant glasses, hardened optical windows, and joining compositions for ceramic-ceramic seals.

Oxynitride Glass Synthesis

The preparation of oxynitride glasses is more complex than preparation of conventional oxide glasses for a variety of reasons. Prime among them is the need to maintain reducing conditions while melting and homogenizing so as to enhance nitride solubility and to prevent nitrogen loss through sample decomposition. Typically, mixtures of oxide and nitride powders are melted under N_2 or Ar atmospheres (9, 10), although gel glasses have been nitrided in ammonia (11), and there is one report of oxynitride glass synthesis in air (12). In the case of the air melt, reducing conditions were probably maintained locally by use of a closed silica crucible.

Direct reaction of N_2 or NH_3 with silicate melts (1) does not seem as favorable a technique for oxynitride glass formation as melting of mixtures of oxide and nitride powders. In the former case, the gases apparently react with the melt only very slowly, and the levels of nitrogen attained are much lower than with other methods. Dancy and Janssen (13) studied the direct dissolution of N_2 in synthetic metallurgical slags made from mixtures of CaO, Al_2O_3, and SiO_2. Those melts, which were similar in composition to the oxide portions of some oxynitride glasses (10), dissolved between 0.25 and 2.5 wt% N_2 at 1550°C under 1 atm N_2. Incorporation of gaseous nitrogen was very slow, requiring about 24 h to reach apparent equilibrium. By contrast, when Si_3N_4 was added to the melt along with the N_2, reaction was rapid and much higher nitrogen contents were found (~ 4 wt%). Contrary to the authors' claim that the Si_3N_4 promotes gaseous N_2 dissolution by maintaining reducing conditions in the melt (13), the most
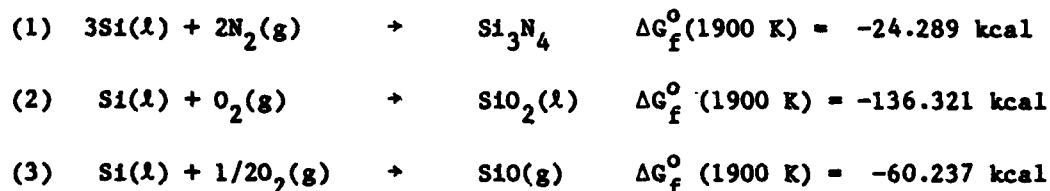
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likely explanation for the enhanced nitrogen content is simply that the Si_3N_4 itself dissolved in the melt.

The dissolution kinetics of $\beta-Si_3N_4$ in a Mg-Si-O-N liquid were investigated by Tsai and Raj (14). Their study is not directly applicable to oxynitride glass synthesis because the composition they chose (containing 38 wt% Si_3N_4) was outside the glass-forming region. Nevertheless, the results provide some insight into the preparation of oxynitride glasses using Si_3N_4. In Tsai and Raj's system, dissolution was driven by a chemical reaction that produced a crystalline species, i.e., $\beta-Si_3N_4(c)$ + $SiO_2(\ell) \rightarrow Si_2N_2O(c)$. The rate-limiting step in this process must be the slowest of three sequential steps: (1) interfacial reaction at the Si_3N_4-liquid interface (dissolution), (2) transport of silicon and nitrogen through the liquid, and (3) interfacial reaction at the Si_2N_2O-liquid interface (precipitation). Their analysis, which was based on X-ray diffraction and electron microprobe experiments and morphological examination of reactants and products using TEM, led Tsai and Raj to conclude that the kinetics were controlled by the rate of dissolution at the Si_3N_4-liquid interface. If that conclusion is correct, the experimentally determined activation energy for dissolution, $\sim$ 621 kJ mol^{-1}, is the sum of the heat of solution of $\beta-Si_3N_4$ in the liquid and the activation enthalpy for movement of atoms across the interface. So large a value for the activation energy is thought to result from a large endothermic heat of solution of Si_3N_4 in the Mg-Si-O-N liquid (15).

It is not clear how general this result is. Oxynitride glasses are made by dissolving a variety of nitrides, and even when Si_3N_4 is the nitrogen source, the amorphous or α-forms are usually chosen. Only the first two of the three steps discussed above, the Si_3N_4-liquid interfacial reaction and the transport of the Si and N through the liquid, occur when oxynitride glasses are made. If diffusion rates for Si and N do not vary greatly with liquid composition and if dissolution is not much affected by the crystalline form of the Si_3N_4, then the initial interfacial reaction would be rate-limiting in oxynitride glass synthesis using Si_3N_4.

Gel glasses, which below the sintering temperature are quite porous and contain high concentrations of hydroxyls, have been converted to oxynitride glasses by treatment with ammonia (11). Nitrogen concentrations have been achieved that are almost as high as those obtained by dissolving solid nitrides in silicate melts. The mechanism of nitrogen incorporation is believed to be condensation reactions of hydroxyl and alkoxy groups with ammonia to produce $-Si-NH_2$ groups and water (11). Further condensation between $-Si-NH_2$ and $OH-Si-$ groups leads to nitrogen that is threefold coordinated by silicon.

Oxynitride glass stability is affected by both the furnace atmosphere and by the composition of the melt. For example, the JANAF tables (16) list the Gibbs energies of formation for the following species that may be present during oxynitride glass synthesis.

(1) $3Si(\ell) + 2N_2(g)$ → Si_3N_4 $\Delta G_f^o(1900 \text{ K}) = -24.289$ kcal

(2) $Si(\ell) + O_2(g)$ → $SiO_2(\ell)$ $\Delta G_f^o(1900 \text{ K}) = -136.321$ kcal

(3) $Si(\ell) + 1/2O_2(g)$ → $SiO(g)$ $\Delta G_f^o(1900 \text{ K}) = -60.237$ kcal

The reactions can be combined to yield the overall reaction (4)

(4) $Si_3N_4 + SiO_2(\ell) + O_2(g)$ → $4SiO(g) + 2 N_2(g)$,
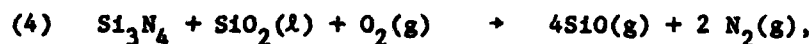
ΔG^o (1900 K) = -80.338 kcal

The ΔG^o values are given for the typical processing temperature of 1900 K. Reaction (4) shows that decomposition of oxynitride melts is promoted by increasing either the Si_3N_4 or SiO_2 concentrations or the oxygen partial pressure. Melting in flow systems in which $SiO(g)$ is continuously removed favors melt decomposition, whereas static atmospheres that maintain a high P_{SiO} tend to increase melt stability. Likewise, melting under high nitrogen overpressure favors compositional stability in the melt. Because of the very large negative ΔG_f^o values for CaO and

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Al_2O_3, those species will not participate in any oxidation-reduction reaction, and therefore they do not appear in the equilibrium expression.

At equilibrium $\Delta G^O = -RT \ln K$, where the equilibrium constant K for reaction (4) is given by

$$K = \frac{P_{SiO}^4 \, P_{N_2}^2}{A_{Si_3N_4} \, A_{SiO_2} \, P_{O_2}} = \exp(-\Delta G^O/RT)$$

The A's indicate activities and the P's are partial pressures in atmospheres.

To illustrate the effect of atmosphere, consider a CaSiAlON melt made from 50 wt% SiO_2, 10 wt% Al_2O_3, 20 wt% CaO, and 20 wt% Si_3N_4. Assuming that the mixture behaves ideally, $A_{Si_3N_4} = 0.0998$ and $A_{SiO_2} = 0.5821$. Suppose that the oxygen partial pressure in the furnace atmosphere is 10^{-3} atm and the P_{N_2} is set at 2 atm by an external nitrogen source. Solving the equilibrium expression gives $P_{SiO} = 12.6$ atm, indicating that under the given conditions the melt will decompose by outgasing considerable quantities of SiO. Because of the very large negative ΔG_f^O values for CaO and Al_2O_3, those species will not participate in any oxidation-reduction reactions; therefore, they do not appear in the equilibrium expression.

As a second example, consider the same melt composition, but this time assume that the oxygen partial pressure is 10^{-15} atm because of equilibrium between the furnace atmosphere and a hot graphite furnace element, and that $P_{N_2} = 20$ atm, a value attainable in some furnaces used in oxynitride glass synthesis. Solving the equilibrium expression for this example gives $P_{SiO} = 3.99 \times 10^{-3}$ atm, which is over four orders of magnitude less than in the first case. Thus, through proper control of the furnace atmosphere, an otherwise unstable composition can be prepared as a good oxynitride glass.

Chemical composition also strongly influences melt stability. From empirical studies, it is known that some combinations of ingredients make good oxynitride glasses, whereas other combinations are unsuccessful because they produce frothy melts. For example, Al_2O_3, MgO, or CaO in

combination with SiO_2 and Si_3N_4 can be formed into homogeneous, bulk glasses that contain only occasional bubbles. However, if TiO_2 or P_2O_5 is added to a melt containing Si_3N_4 or AlN, an extreme frothing reaction leads to foamed or cellular structures in the quenched products. These observations can be rationalized by considering the following oxidation reactions for Si_3N_4 and AlN (16):

(5) $Si_3N_4 + 3O_2(g) \rightarrow 3SiO_2(\ell) + 2N_2(g)$

$$\Delta G^o \ (1900 \ K) = -384.674 \ kcal$$

This overall reaction results from combining reactions (1) and (2), above. In a similar fashion, one obtains (1)

(6) $4AlN + 3O_2(g) \rightarrow 2Al_2O_3 + 2N_2(g)$

$$\Delta G^o \ (1900 \ K) = -203.926 \ kcal$$

for the oxidation of AlN. Only the ΔG^o (1900 K) values are quoted here for purposes of illustration. Gibbs energies at other temperatures can be obtained from tabulated data (16).

If reactions (5) and (6) are normalized so that the stoichiometry is expressed in terms of one mole of oxygen gas, their standard Gibbs energies can be plotted as functions of temperature on an Ellingham diagram (17), as illustrated in Figure 1. The oxidation or reduction tendencies of reactions can be determined by the relative positions of their ΔG^o values in Figure 1. For example, Mg is oxidized by Al_2O_3, but not by CaO. This can be seen by comparing the reactions at a given temperature, for example 1473 K.

(7) $2Mg + O_2 \rightarrow 2MgO$ ΔG_f^o (1473 K) $\approx$ -209 kcal

(8) $2/3Al_2O_3 \rightarrow 4/3Al + O_2$ $-\Delta G_f^o$ (1473 K) $\approx$ + 192 kcal

TEMPERATURE (°K)

473   873   1273   1673   2073   2473

$\Delta G^\circ = RT\ln P_{O_2}$ (kcal)

$Mo + O_2 = MoO_2$

$6FeO + O_2 = 2Fe_3O_4$

$C + O_2 = CO_2$

$3/2 Fe + O_2 = \frac{1}{2}Fe_3O_4$

$2C + O_2 = 2CO$

$4/3 AlN + O_2 = 2/3 Al_2O_3 + 2/3 N_2$

$2/5 P_2 + O_2 = 2/5 P_2O_5$

$4Na + O_2 = 2Na_2O$

$2Mn + O_2 = 2MnO$

$4/3 B + O_2 = 2/3 B_2O_3$

$Si + O_2 = SiO_2$

$Ti + O_2 = TiO_2$

$O_2 + 1/3 Si_3N_4 = SiO_2 + 2/3 N_2$

$4/3 Al + O_2 = 2/3 Al_2O_3$

$2Be + O_2 = 2BeO$

$4Li + O_2 = 2Li_2O$

$2Mg + O_2 = 2MgO$

$2Ca + O_2 = 2CaO$
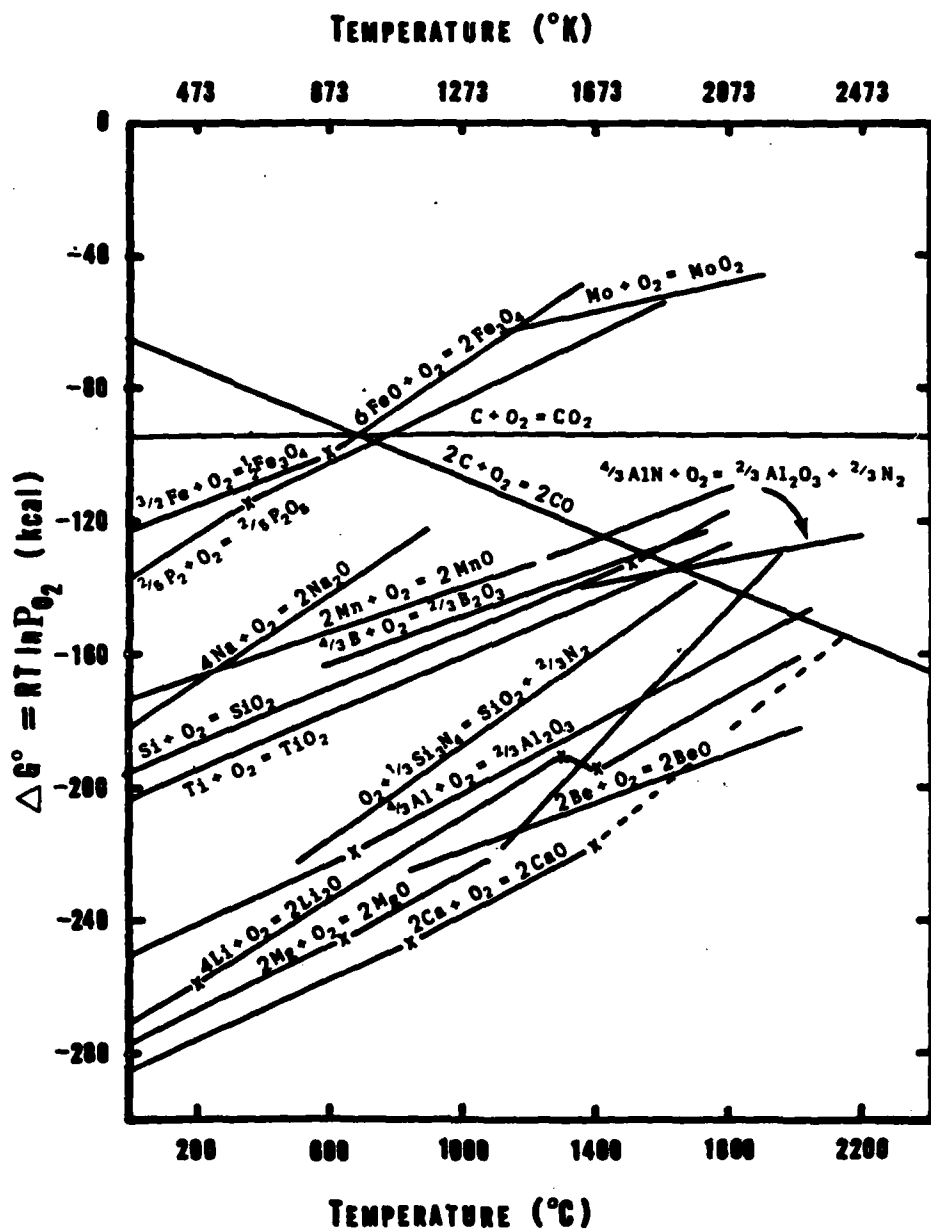
200   600   1000   1400   1800   2200

TEMPERATURE (°C)

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FIGURE 1   GIBBS ENERGIES FOR SELECTED REACTIONS AS A FUNCTION
OF TEMPERATURE

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Summing, $2/3Al_2O_3 + 2Mg \rightarrow 2MgO + 4/3Al$; $\Delta G_R^O \simeq -17$ kcal. The negative ΔG_R^O indicates that the overall reaction is favorable as written. A similar calculation for $Mg + CaO \rightarrow MgO + Ca$ gives a positive ΔG_R^O, indicating an unfavorable reaction as written.

The positions of the ΔG^O versus T lines for oxidation reactions (5) and (6) allow one to predict the stabilities of melts made from Si_3N_4 or AlN and various oxides. At a given temperature, any oxide whose ΔG_f^O lies above that for reaction (5) (i.e., any reaction with a less negative ΔG_f^O) will oxidize Si_3N_4, while at the same time being reduced by the Si_3N_4. Any oxide whose ΔG_f^O lies below that for reaction (5) (i.e., more negative ΔG_f^O) at a given temperature will be stable in contact with Si_3N_4.

Thus, Al_2O_3, Li_2O, CaO, and MgO will be favorable components for oxynitride glass synthesis according to this oxidation-reduction criterion (as has indeed been found experimentally). However, Fe_2O_3, TiO_2, P_2O_5, and MnO are predicted to oxidize Si_3N_4 in a melt, leading to frothing or bloating as N_2 is evolved. As already mentioned, such frothing has been observed experimentally in the case of TiO_2 and P_2O_5 additions to melts containing Si_3N_4 (18). A similar analysis can be made for other nitrogen sources such as AlN, Ca_3N_2, and Li_3N.

The suitability of various crucible materials for oxynitride glass preparation can be explained, in part, by these same thermodynamic argu- ments. In general, metal oxides will be reduced by the melt if their ΔG_f^O values are less negative than those of the oxynitride glass ingre- dients. Thus, the metals from which those oxides are formed are potential crucible materials, provided their melting points are greater than the glass processing temperature (about 1650°C for many compositions), and provided the metal will not react with the melt to form stable compounds. This analysis predicts, for example, that Mo, W, and Nb would be suitable crucible materials, whereas Ta and Zr would be oxidized by typical melts. Molybdenum crucibles, in fact, have been used extensively in oxynitride glass preparation, and limited tests on W and Nb indicate they also would serve (18). Tantalum, on the other hand, appears to be oxidized by oxyni- tride melts (18). All these results are as expected, based on the thermodynamic calculations of oxidation-reduction behavior.

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Boron nitride is another crucible material that has been used for oxynitride glass synthesis. The ΔG^O calculated from published data (16) for the reaction

(9) $4/3BN + O_2 \rightarrow 2/3B_2O_3 + 2/3N_2$

is ΔG_R^O (1900 K) = -104.60 kcal, where the value at 1900 K has been chosen to allow comparison with the examples given in reactions (1) through (6). In the temperature range of interest, Si_3N_4, AlN, and most oxides that have been used successfully in oxynitride synthesis have ΔG_f^O values more negative than that for reaction (9), which explains why, in neutral or reducing atmospheres, BN can be used as a container for oxynitride melts. Note that some grades of hot-pressed BN contain a few percent free B_2O_3 or calcium borate that can dissolve into the melt during heating. Whether this is a problem, of course, depends on the glass composition and its intended use.

Other candidate crucible materials are suggested by the data in Figure 1. For example, graphite appears suitable for melts containing SiO_2 at temperatures below 1550°C, but above 1550°C the reaction $SiO_2 + 2C \rightarrow Si + 2CO(g)$ is favorable. Wusirika and Chyung (19) reported using graphite crucibles at temperatures as high as 1800°C. However, tests in our laboratory showed that graphite reacts strongly at 1600°C with oxynitride melts (10). The origin of the discrepancy is not known.

Compositional Systems

A wide variety of oxynitride compositions have been made by the technique of reacting a solid nitride with a silicate-based melt. Some of those that have been reported are listed below.

|		
Ca-Si-O-N	Ca-Si-Al-O-N	Na-Ca-Si-O-N
La-Si-O-N	La-Si-Al-O-N	Na-B-Si-O-N
Mg-Si-O-N	Mg-Si-Al-O-N	Ca-B-Si-Al-O-N
Si-Al-O-N	Li-Si-Al-O-N	Sc-Si-Al-O-N
Na-Ba-Al-P-O-N	Y-Si-Al-O-N	

All but one of these systems have Si, O, and N in common, and about half also contain Al. The occurrence of Si, O, and N in those glasses is a reflection of the structural similarity of SiO_2 and Si_3N_4 on a local atomic scale. In both compounds, the local atomic arrangement consists of four anions tetrahedrally coordinated around each Si atom. The main difference is in the coordination of the anions: in SiO_2, the oxygens are each linked to two silicons, whereas in Si_3N_4, the nitrogens are each bonded to three silicons. Figure 2 illustrates this point by means of a schematic representation of the crystal structure of $\beta-Si_3N_4$, in which the full circles represent silicon and the open circles represent nitrogen.

The simplest oxynitride glass would be a Si-O-N composition that might be made by reacting a mixture of SiO_2 and Si_3N_4. Direct melting of the compounds is difficult because, temperatures greater than 1800°C are necessary for SiO_2 to be fluid enough for Si_3N_4 dissolution and for the reaction to be practicable. Above 1800°C the decomposition pressure of Si_3N_4 is very high and the melt is unstable. Under reducing conditions at those temperatures, SiO_2 decomposes to give SiO(g) and O_2, further destabilizing the melt. For example, a mixture of Si_3N_4 and SiO_2 powders heated between 1850° and 1900°C in an open Mo crucible under a 2-atm static N_2 atmosphere gives an inhomogeneous, frothy, cellular mass on quenching (18). A similar result was reported by Wusirika and Chyung (19). Decomposition can be suppressed by using high overpressures of nitrogen if SiO(g) loss also is prevented.

Alternatively, it is conceivable that a sol-gel method might be devised to prepare a Si-O-N glass that would permit densification at temperatures lower than required for direct melting. However, no such glass has been reported to date.

The oxynitride glasses that are next simplest from a compositional standpoint contain Si, O, N, and one other cation. Examples are Si-Al-O-N (19,21), Ca-Si-O-N (10), Mg-Si-O-N, (10,22) and La-Si-O-N (23). They all have been made successfully by reacting the relevant metal oxide with SiO_2 and Si_3N_4 or AlN. One function served by the metal oxide in these systems is to react with SiO_2 to form a eutectic liquid in which the nitride can
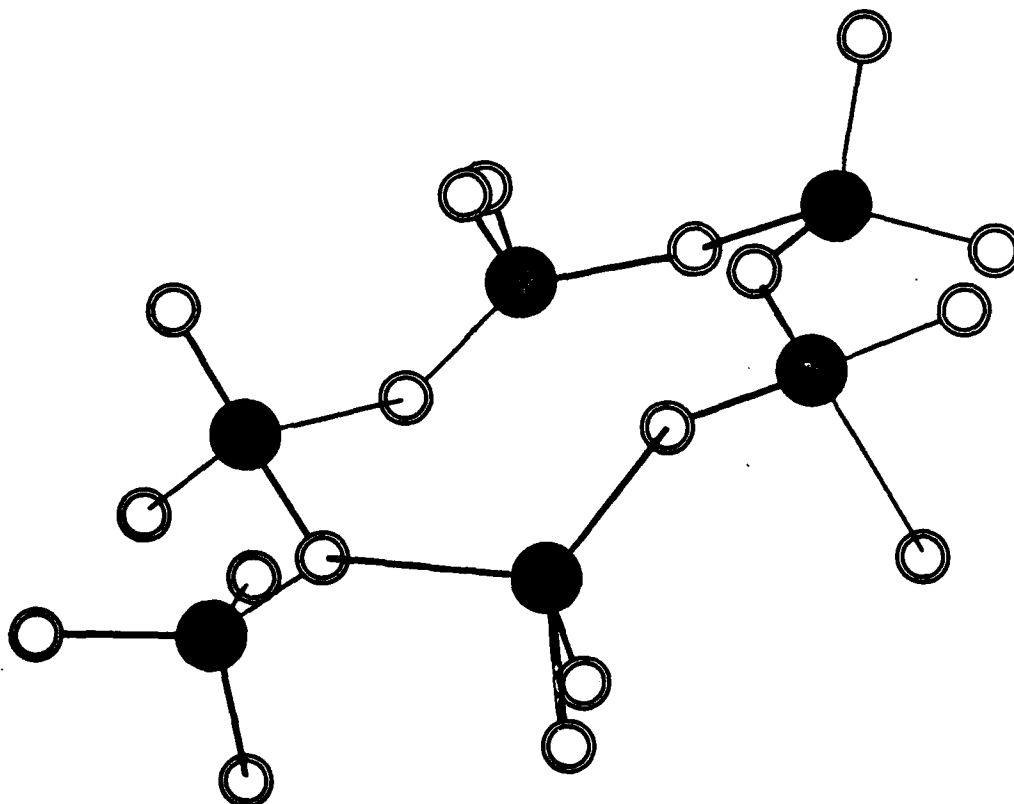
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FIGURE 2   SCHEMATIC REPRESENTATION OF THE β-Si$_3$N$_4$ STRUCTURE

Filled circles are Si;   open circles are N.

dissolve without decomposing. The nitride, in turn, seems to promote glss formation. For example, quenching of $CaO-SiO_2$ or $MgO-SiO_2$ melts at rates common in ordinary glass preparation gives a crystalline product. Dissolution of 10 to 20 wt% Si_3N_4 in either melt, followed by the same quench, produces stable oxynitride glasses that contain up to 7 at% nitrogen (10). This is direct evidence for the stabilization of glass network structures by silicon nitride. The Ca-Si-O-N and Mg-Si-O-N glasses are milky because of phase separation on a fairly coarse scale. Their microstructural features are discussed in a later section.

The La-Si-O-N glasses were made using a 30-atm overpressure of N_2 to suppress melt decomposition while heating at 1700°C (23). A nitrogen content of 18.2 at% was reported for one La-Si-O-N glass (23), a value more than double that attained for oxynitride glasses prepared without high nitrogen overpressures.

Small batches of Si-Al-O-N have been found to froth extensively when melted in open crucibles under one or two atm N_2 (10). Figure 3 shows the compositions attempted, superimposed on the behavior diagram of Naik et al. (20). All the numbered compositions in the figure were liquid at 1650°C, and the frothing did not seem to vary with composition. Some of the same compositions have been reported to give good dense glasses when confined by a hot-press die during melting (4). Wusirika and Chyung (19) prepared 500 g specimens of Si-Al-O-N glass without evidence of excessive decomposition by melting and casting into graphite molds under N_2. In particular, they list a glass similar to composition 9 in Figure 3 . The greater stability of larger melt volumes can be understood if decomposition and frothing occur primarily at the free surface of the melt. As the mass of the glass batch increases, the ratio of the surface area to the volume of the melt decreases, so the decomposition per unit mass of the melt is proportionally less with larger batches. The importance of minimizing the free surface of oxynitride melts is shown by the observation that the concentration of bubbles in a Mg-Si-Al-O-N glass was greater when it was made in a wide, shallow crucible than when it was prepared in a narrow, deep container (18).

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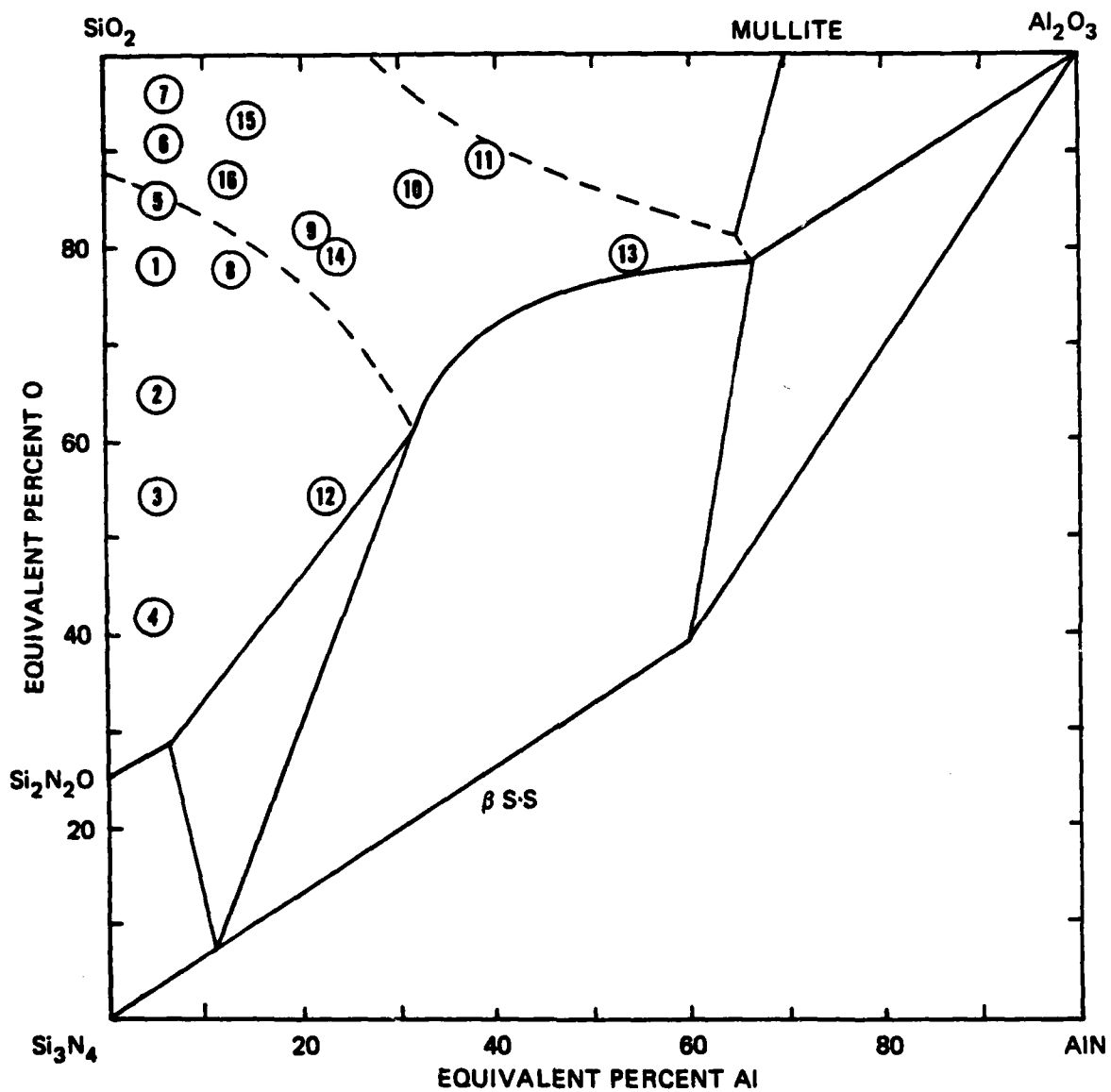
FIGURE 3   OXYNITRIDE GLASS COMPOSITIONAL STUDIES IN Si-Al-O-N SYSTEM SUPERIMPOSED
ON BEHAVIOR DIAGRAM OF NAIK et al. (Reference 20)

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Inclusion of Al_2O_3 in oxynitride compositions seems particularly to favor glass formation. In almost all cases, the effect of adding Al_2O_3 to a M-Si-O-N melt (where M indicates a cation other than Al or Si) is to increase the nitride solubility and to widen the glass-forming region. The chemical and structural compatibility of Al_2O_3 and Si_3N_4 is also demonstrated by the easy substitution of Al^{3+} and O^{2-} in the silicon nitride structure to form β'-SiAlON, $Si_{6-x}Al_xO_xN_{8-x}$, where $0 < x < 4.2$ (24). Part of the explanation for the favorable effect of Al_2O_3 on oxynitride glass formation may be the similar sizes of the SiN_4 and AlO_4 tetrahedra, which must allow them to substitute easily for each other. [The Si-N bond distance and the tetrahedral Al-O bond distance are each 1.75 Å (21)]. As already mentioned, the aluminum-free Ca- and Mg-oxynitride glasses are phase separated; addition of a few wt% Al_2O_3 suppresses the phase-separation and gives clear glasses.

Figures 4 and 5 show the Mg-Si-Al-O-N and Ca-Si-Al-O-N glass-forming regions superimposed on their respective oxide ternary phase diagrams. The amount of Si_3N_4 that will dissolve in a given $MgO-Al_2O_3-SiO_2$ or $CaO-Al_2O_3-SiO_2$ composition to produce the illustrated glass-forming regions is about 10 to 15 wt%. However, much higher Si_3N_4 solubilities (up to 30 wt%) are observed for compositions in the low-SiO_2 portions of the phase diagrams. Figures 4 and 5 show that the glass-forming regions roughly correspond to the region of the given oxide ternary that is liquid at 1600°C and below. That correspondence is a fairly general result; i.e., oxynitride glasses form in many silicate systems that are liquid below about 1600°C and in which Si_3N_4 (or some other nitride) dissolves without significant decomposition. In the low-SiO_2 portions of Figures 4 and 5, the glass-forming regions extend into compositions that would not be liquid below 1800° or 1850°C if no Si_3N_4 were present. This is because, in those low-SiO_2 regions, Si_3N_4 substitutes for SiO_2 to maintain approximate equivalence in the liquidus temperature.

Two effects are found for compositions outside the boundaries of the glass-forming regions. In the direction of decreasing SiO_2 content, eventually a point is reached at which crystallization occurs, even for large

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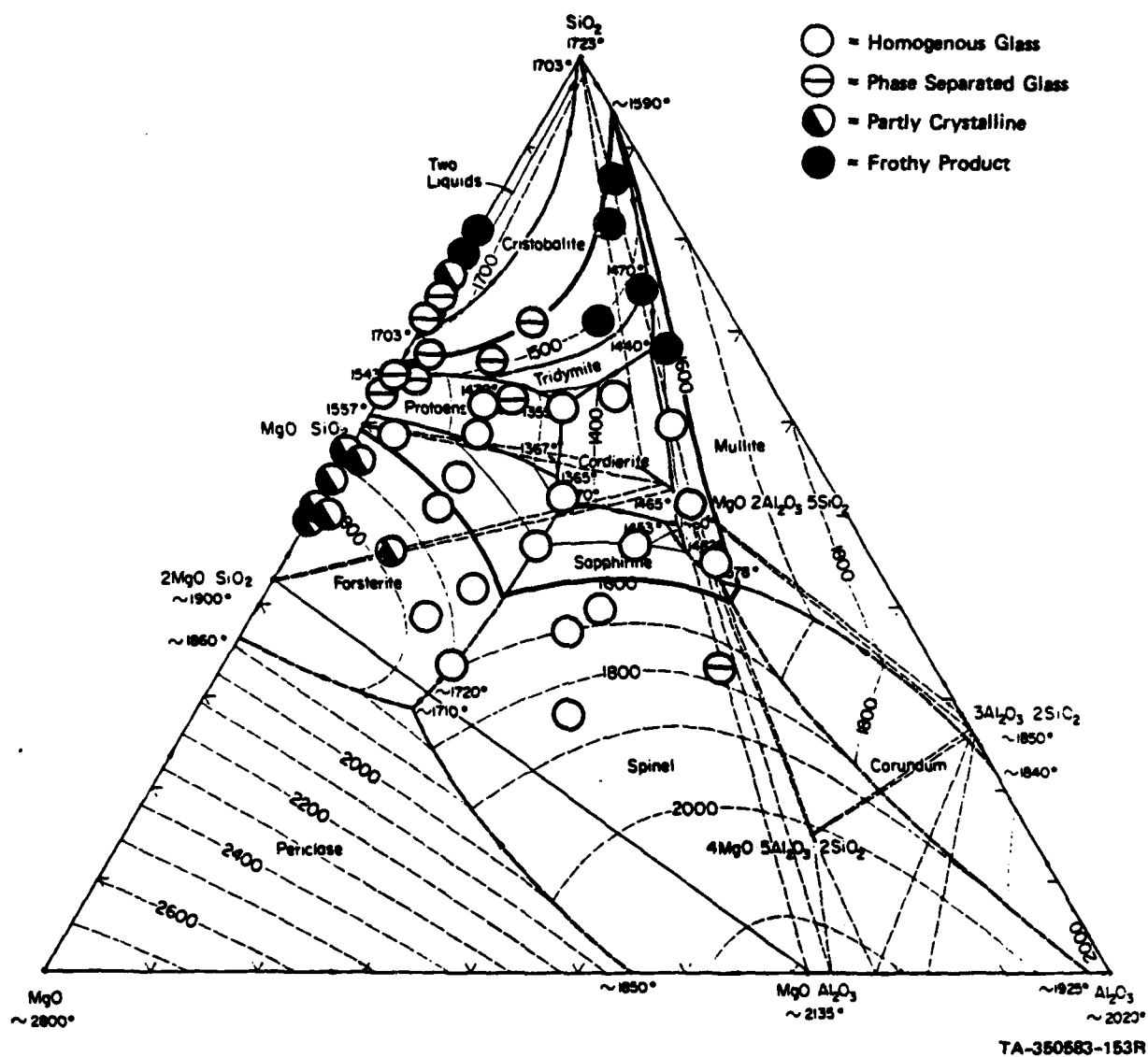FIGURE 4   GLASS-FORMING REGION IN THE Mg-Si-Al-O-N SYSTEM (Reference 10)
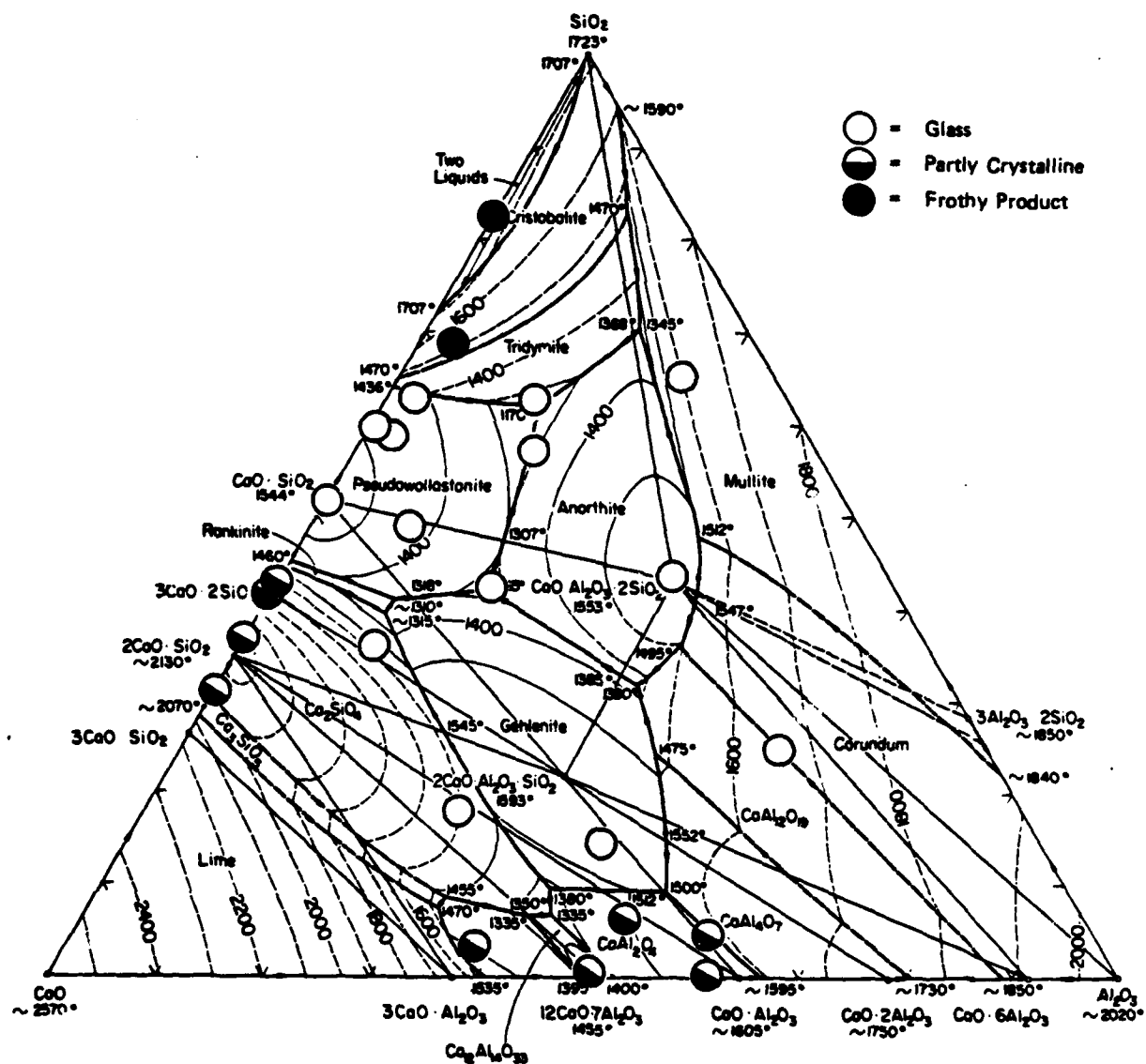All compositions contain 10 wt% Si_3N_4.

15

FIGURE 5   GLASS-FORMING REGION IN THE Ca-Si-Al-O-N SYSTEM
All compositions contain 10 wt% Si_3N_4.

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Si_3N_4 additions. Frothing and melt instability, however, are observed in compositions in which the SiO_2 + Si_3N_4 content is high. The filled circles in Figure 4 which indicate frothing, are for specimens that contained 10 wt% Si_3N_4. For Si_3N_4 concentrations greater than 20 wt%, frothing is observed further into the center of the glass-forming region delineated in the diagram.

Fairly extensive compositional studies also have been done on the Y-Si-Al-O-N system (9,25). Compared with Ca-Si-Al-O-N and Mg-Si-Al-O-N glasses, those containing yttrium soften at higher temperatures, the glass-forming region is less extensive, and not as much nitrogen can be incorporated [up to 7 at% N (8-10)]. Those differences probably occur because the Y_2O_3-Al_2O_3-SiO_2 system is more refractory than either MgO-Al_2O_3-SiO_2 or CaO-Al_2O_3-SiO_2, and thus the compositional region liquid below 1650°C is less extensive. Figures 6 and 7 are two representations of the glass-forming region in Y-Si-Al-O-N. Figure 6 contains actual compositions as reported in reference 9. Figure 7 portrays the glass forming region in a different compositional space, which relates the Y-Si-Al-O-N glasses of Figure 6 to other compositions that have been studied. A number of properties measurements have been made on the Y-Si-Al-O-N glasses; they are discussed in a later section.

Other M-Si-Al-O-N glasses that have been made are La-Si-Al-O-N (10), Li-Si-Al-O-N (10), Ba-Si-Al-O-N (10), and Sc-Si-Al-O-N (18). None of them has been investigated as thoroughly as have the Y-, Mg-, and Ca-Si-Al-O-N glasses. The La- and Sc-Si-Al-O-N glasses resemble those made with yttrium, and because they are all are fairly refractory, it is somewhat difficult to make them with nitrogen contents greater than about 7 at% using only moderate furnace overpressures. The Li-Si-Al-O-N glasses, on the other hand, more nearly resemble those made from Ca and Mg.

Preparation of oxynitride glasses containing sodium and boron, either singly or in combination, presents some common problems. The Gibbs energies of formation of Na_2O and B_2O_3 are considerably less negative than the ΔG_R^o for the oxidation of Si_3N_4 [Eqn (5) and Figure 1]. Thus on thermodynamic grounds, we would expect Si_3N_4 in the melt to be oxidized to
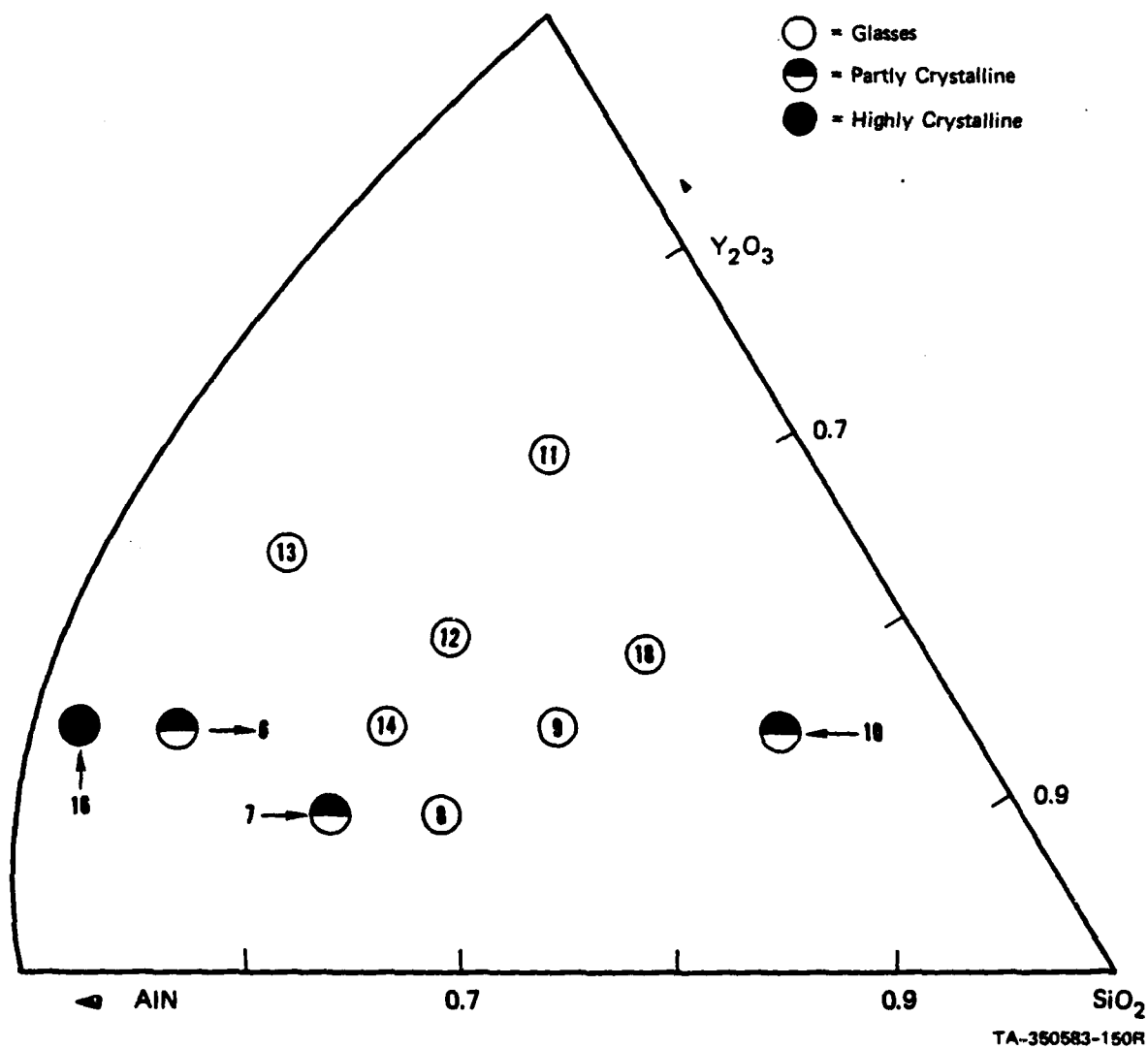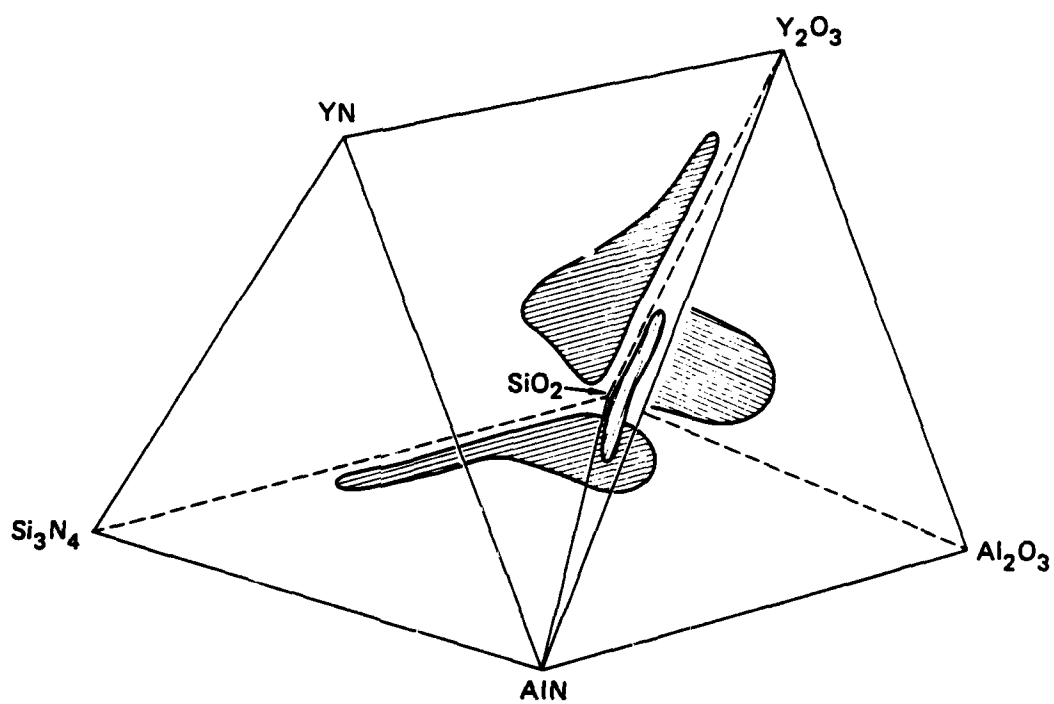
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FIGURE 6   GLASS-FORMING REGION IN THE Y-Si-Al-O-N SYSTEM (Reference 9)

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FIGURE 7   SCHEMATIC OF THE GLASS-FORMING REGION IN THE Y-Si-Al-O-N SYSTEM
(Reference 10)

SiO_2, and the Na_2O and B_2O_3 to their respective elements. We should observe Na loss from the melt because of its high vapor pressure (1 atm at about 890°C) and possibly loss of $SiO(g)$ if the Si_3N_4 is only incompletely oxidized. Jankowski and Risbud (22) observed severe outgasing when B_2O_3, SiO_2, and Si_3N_4 were heated directly in a graphite crucible under N_2. Decomposition was less severe when they presynthesized a sodium borosilicate glass in air, ground it to a powder, and then heated a mixture of the glass and Si_3N_4 in a Mo crucible. However, vigorous bubbling occurred during melting, and analysis showed that the resulting glass contained less nitrogen, sodium, and boron than the starting mixture.

Frischat and Schrimpf (26) developed a three-step melting procedure for preparing Na-Ca-Si-O-N glasses that compensated for alkali loss during heating. They first made a Na_2O-CaO-SiO_2 glass and then melted a mixture of that glass powder and Si_3N_4 under Ar. The melt was quenched, chemically analyzed, and then the composition was adjusted for alkali loss by adding the necessary ingredients. The mixture was remelted at 1150°C under vacuum to remove bubbles. The relatively low temperature of the last melting was probably responsible for the greater level of alkali retention. No mention is made in the paper (26) of nitrogen loss as a result of either of the last two meltings, but nitrogen contents as great as 6 at% are reported.

The Na-Ba-Al-P-O-N glass prepared by Wilder (27) deserves special mention. As far as the writer is aware, it is the only oxynitride glass made to date that does not contain any silicon. As discussed previously, because of structural similarities between SiO_2 and Si_3N_4, there is easy substitution of nitrogen for oxygen in silicates, and it appears likely that in those materials nitrogen enters the glass network. Phosphorus pentoxide-based glasses have as their fundamental structural unit a PO_4 tetrahedron in which one of the phosphorus-oxygen links is a double bond (28). The question, then, is how nitrogen might substitute into such a structure.

A little investigation reveals that there is a large and rich chemistry of compounds that contain P-N and P=N bonds in which the phosphorus-nitrogen double bond length is about 1.55 to 1.61 Å, and the single bond

length is 1.75 to 1.80 Å (29). In compounds such as the polyphosphazenes a single phosphorus can be linked to both nitrogen and oxygen, so there might be a structural analogy between $Si(O,N)_4$ and $P(O,N)_4$ units. However, the analogy is imprecise because the anions are not tetrahedrally coordinated to phosphorus in the polyphosphazenes. Furthermore, those compounds decompose at temperatures below 1000°C. A more likely explanation for the stability of the phosphorus oxynitride glass (27) is that it contains aluminum. Aluminum phosphate (β-berlinite) is isostructural with silica and contains alternately linked AlO_4 and PO_4 tetrahedra in which all corners are shared (30). The existence of a large number of Si-Al-O-N compounds based on the AlN Wurtzite structure (4) in which oxygen and nitrogen are tetrahedrally coordinated to aluminum suggests that, in the Na-Ba-Al-P-O-N glass, nitrogen is bonded to aluminum rather than to phosphorus to give a connected assembly of $Al(O,N)_4$ and PO_4 tetrahedra.

Chyung and Wusirika (12,19) reported over forty different oxynitride glass compositions based on M-Si-Al-O-N in which the M-component varied from one to three different cations. Most also were made using AlF_3 as a fining agent. The only exceptional difference between their glasses and the simpler materials already discussed was that some of Chyung and Wusirika's (12,19) melts were done in air in closed silica crucibles.

Oxynitride Glass Properties

The first extensive studies (8-10) of oxynitride glass properties revealed that very significant changes are produced by nitrogen incorporation. Since then, investigations have been extended to other systems, giving results that essentially confirm the original observations.

Specifically, addition of nitrogen to form oxynitride glasses has been found to increase the glass transition temperature (Tg), the hardness, and the fracture toughness in amounts proportional to the nitrogen concentration. The thermal expansion coefficient (α) exhibits a decrease with increasing nitrogen content, although the effect is not as great in all compositions that have been examined. Figure 8 (8) shows that the microhardness of a group of Y-Si-Al-O-N- glasses increases by about 30% as

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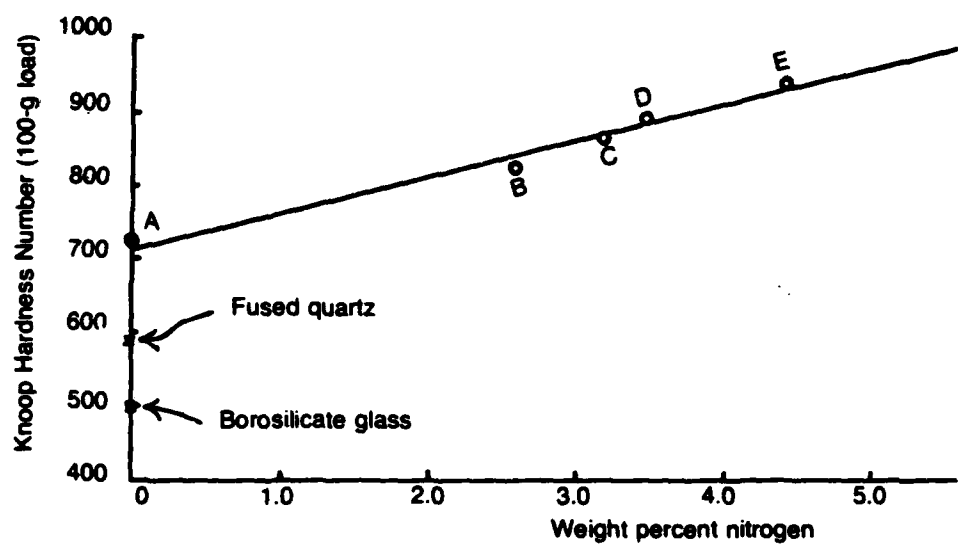
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FIGURE 8   VARIATION IN HARDNESS OF Y-Si-Al-O-N GLASSES
WITH NITROGEN CONTENT (Reference 8)

the nitrogen content increases from 0 to 4.4 wt%. Figure 9 (9) illustrates
the variation in expansion coefficient, Tg, microhardness, and fracture
toughness with nitrogen content for a similar group of Y-Si-Al-O-N glasses
whose specific compositions are given in Table 1. The scatter in some of
the data of Figure 9 has been attributed to a second-order effect resulting
from differences in Y, Si, and Al contents in samples with similar nitrogen
concentrations.

Table 1

COMPOSITIONS OF Y-Si-Al-O-N GLASSES
(Sample Numbers Correspond to those given in Figure 6) (9)

Sample	Glass Composition (at%)[*]				
Number	Y	Si	Al	O	N
6	10.3	17.6	11.7	54.0	6.5
7	6.4	19.0	9.9	57.6	7.0
8	5.6	20.3	8.1	60.3	5.7
9	9.8	19.9	5.4	60.4	4.5
10	8.9	20.9	2.8	65.8	1.6
11	16.6	15.0	3.2	63.6	1.5
12	12.7	18.6	6.7	57.6	4.4
13	15.2	14.3	7.9	57.6	5.1
14	9.6	18.8	7.5	57.8	6.3
15	16.6	15.0	3.2	65.1	0

[*]As analyzed (Reference 9).

Messier (25) prepared Y-Si-Al-O-N glasses with high nitrogen con-
tents. Microhardness measurements gave results similar to those of
Shillito et al. (8) and Loehman (9). The elastic modulus, measured by an
ultrasonic technique, showed a trend toward increasing modulus with higher
nitrogen contents. Those data are summarized in Table 2.
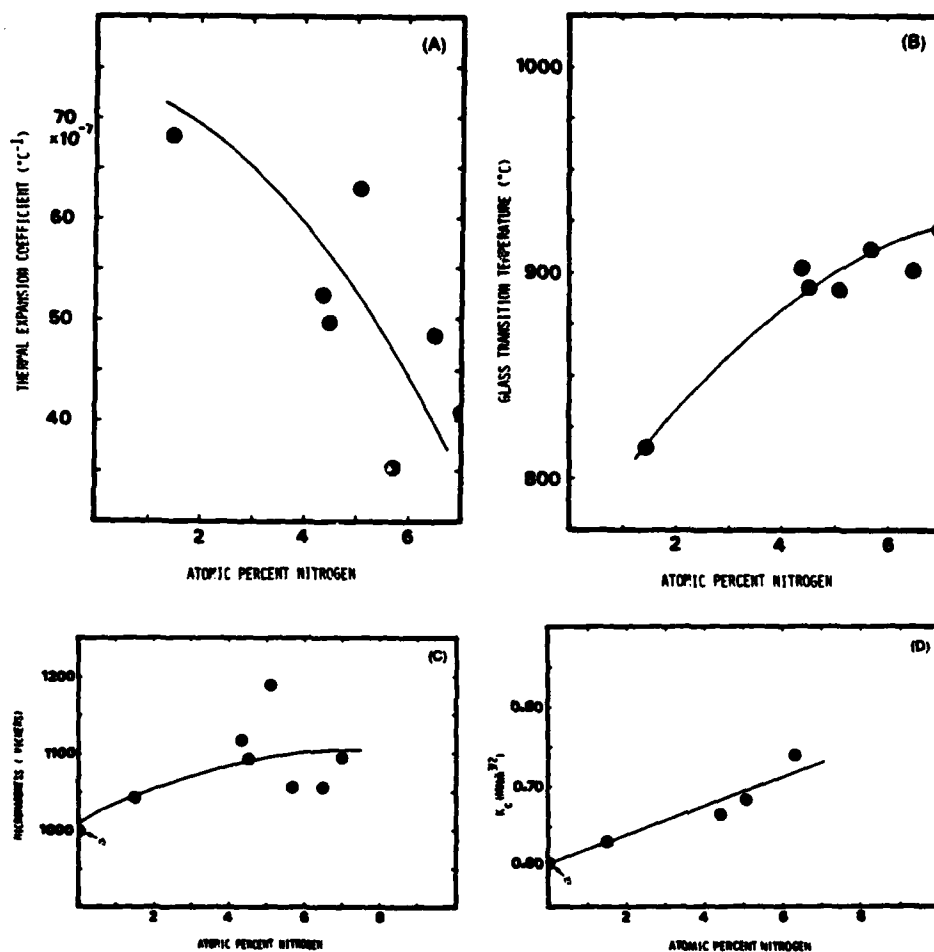
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FIGURE 9   VARIATION IN PHYSICAL PROPERTIES OF Y-Si-Al-O-N
GLASSES WITH NITROGEN CONTENT (Reference 9)

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Table 2

MECHANICAL PROPERTIES OF Y-Si-Al-O-N GLASSES (25)

Specimen	Composition (a/o)[*]					Density (g/cm^3)	Microhardness (Knoop, 100 g)	Elastic Modulus (GPa)	Poissons Ratio
	Al	Si	Y	O	N				
a	6.3	18.7	12.5	56.2	6.3	3.82	919 ± 66	141	0.288
b	13.3	13.3	13.3	46.7	13.3	3.94	1058 ± 56	157	0.315
h	10.0	15.0	15.0	45.0	15.0	4.00	1058 ± 48	186	0.291

[*]As batched.

Figures 10 and 11 (26) show that the properties variations in oxynitride glasses are not confined to a single compositional system. The expansion coefficient and Tg exhibit the same trends in Na-Ca-Si-O-N glasses as they do in the yttrium-based materials. The only obvious, and not surprising, difference is that the Tg values are lower and the expansion coefficients are higher in glasses made from Na-Ca-Si-O-N than they are in the more refractory Y-Si-Al-O-N glasses.

One method of assessing the effects of nitrogen additions more directly is to compare the properties of pairs of glass compositions that are nearly the same except for the nitrogen content. Table 3 gives the results for two Y-Si-Al-O-N glasses. Table 4 is another comparison of properties for a more extensive series of glass compositions in the Mg-Si-Al-O-N system. The data in both Tables 3 and 4 are consistent with the results of Figures 8 through 11; i.e., the addition of nitrogen to oxide glasses promotes an increase in Tg, density, and microhardness and causes a decrease in the thermal expansion coefficient. The only exception is that for the NGM 30/30-0 pair, the oxynitride has a lower density than the oxide glass. That reversal in the trend to increased density with nitrogen addition is explained by the observation that the oxide glass, NGM 30-0, was partly crystalline, which increased its density relative to the glass.
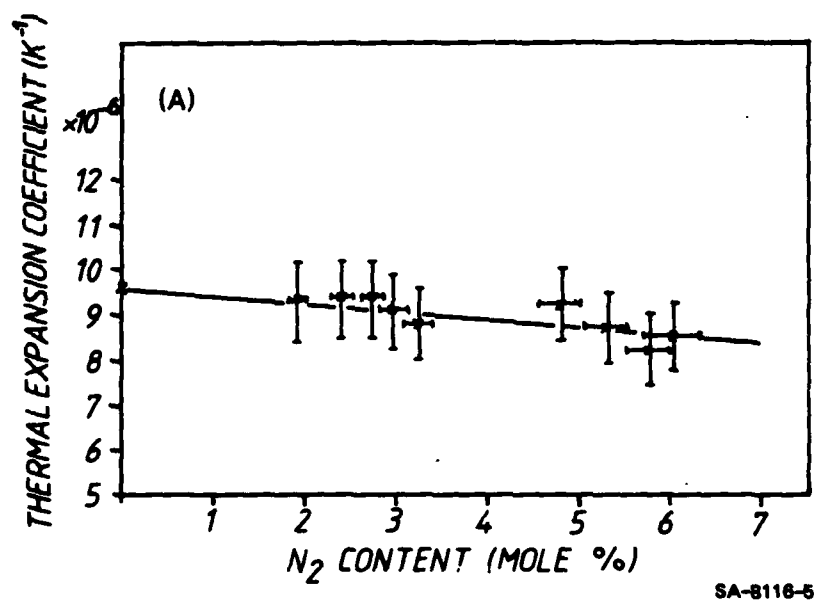
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FIGURE 10   VARIATION IN THERMAL EXPANSION COEFFICIENT
WITH NITROGEN CONTENT OF Na-Ca-Si-O-N GLASS
(Reference 26)

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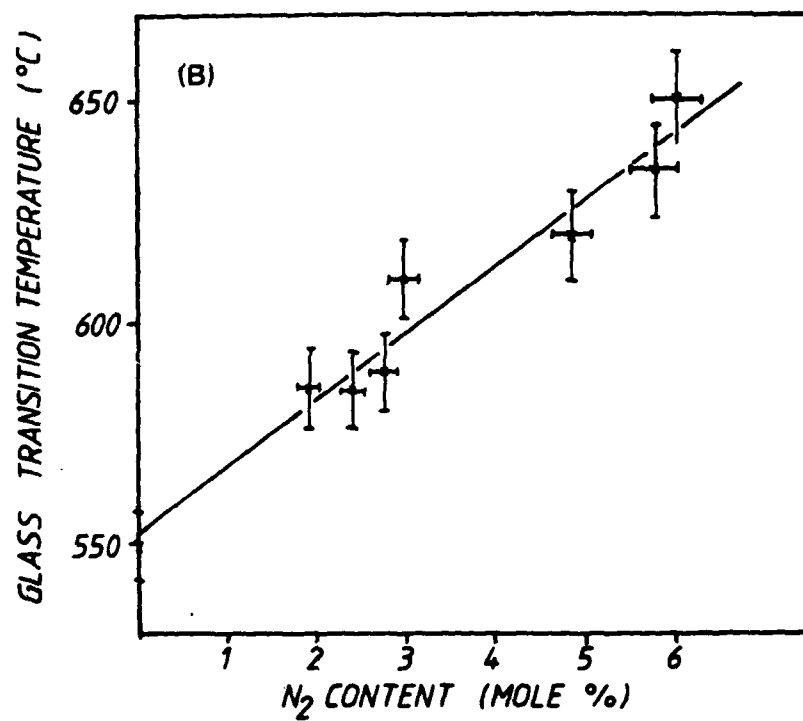
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FIGURE 11 VARIATION IN GLASS TRANSITION TEMPERATURE
WITH NITROGEN CONTENT OF Na-Ca-Si-O-N GLASS
(Reference 26)

Table 3

COMPARISON OF Y-Si-Al-O-N PROPERTIES WITH AND WITHOUT NITROGEN (9)

Compositions[*]	Tg(°C)	Expansion Coefficient (°C^{-1})	Density (g/cm^3)
11	900	68 x 10^{-7}	3.92
15	830	75 x 10^{-7}	3.83

[*]See Table 2 for elemental composition.

Table 4

COMPARISON OF Mg-Si-Al-O-N PROPERTIES WITH AND WITHOUT NITROGEN (10)

Sample Number	Composition (wt%)[*]				Density (g/cm^3)	Tg(°C)	Vicker's Hardness (kg/mm^2)
	MgO	SiO$_2$	Al$_2$O$_3$	Si$_3$N$_4$			
NGM26	14	56	20	10	2.593	865	686
NGM26-0	16	62	22	0	2.389	691	621
NGM27	23	47	20	10	2.700	839	703
NGM27-0	26	52	22	0	2.621	785	676
NGM28	18	56	16	10	2.533	864	773
NGM28-0	21	62	17	0	2.509	805	604
NGM30	20	42	28	10	2.657	845	731
NGM30-0	22	47	31	0	2.665	781	641

[*]Before melting.

There is evidence that nitrogen increases the chemical durability of oxynitride glasses. Three specimens of Y-Si-Al-O-N glass were continuously exposed to 95°C distilled water for 350 h in a Soxhlet apparatus. The sample weight losses after that time were 0.111% (Sample 7, Table 1), 0.016% (Sample 11), and 0.011% (Sample (9). These values compare with a weight loss of 0.04 wt% found for fused silica under comparable conditions

(31). The relatively high weight loss for Sample 7 was attributed to increased solubility resulting from partial crystallinity.

The Na-Ba-Al-P-O-N glass prepared by Wilder (27) exhibited a greater than two order of magnitude increase in leach resistance compared with similar compositions without the AlN. Weight loss in 20°C deionized water was reduced from 6.0×10^{-8} g/cm^2 sec to 8.3×10^{-10} g/cm^2 sec when the Na-Ba-P-O glass was prepared with at least 1.5 wt% AlN. By contrast, addition of 5 wt% Al_2O_3 was required to reduce the dissolution rate of the Na-Ba-P-O parent glass into the same 10^{-10} g/cm^2 sec range (32).

The 18 at% La-Si-O-N glass prepared under high N_2 pressure (23) was reported to have been highly resistant to attack by alkali solutions when soaked for 18 hours at 95°C.

There have been several investigations of the electrical properties of oxynitride glasses. Elmer and Nordberg (2) reported an increase in resistivity by about a factor of 40 at 350°C in a glass to which 3 wt% nitrogen had been added. The specimen was prepared by heating a 98% SiO_2, 2% B_2O_3, porous glass in ammonia before it was consolidated into a dense glass. The authors hypothesized that nitriding increases the resistivity because nitrogen ties up part of the sodium ions present as an impurity and thereby lowers the effective charge carrier concentration. No direct evidence for such Na^+ immobilization was presented, however.

Leedecke and Loehman (33) studied the electrical behavior of some of the same Y-Si-Al-O-N glasses listed in Table 1. Table 5 presents the parameters that were calculated from their data.

It can be seen that all the glasses exhibited high resistivities. They are, in fact, one to three orders of magnitude greater than the highest resistivity glasses measured by Elmer and Nordberg (2), probably because of the lower alkali content of the Y-Si-Al-O-N glasses. By contrast with Elmer and Nordberg's results (2), the specimens listed in Table 5 showed an increase in conductivity on nitriding (compare Samples SG-11 and SG-11/0). The other electrical behavior of the Y-Si-Al-O-N glasses was complex, and there was no apparent dependence on the nitrogen contents of the various specimens.

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Table 5

ELECTRICAL PROPERTIES OF Y-Si-Al-O-N GLASSES

DC Properties

Sample	Activation Energy at $T > 450°C$ ($\times 10^{19}$ J)	Preexponent, σ_o ($\Omega \cdot cm)^{-1}$	Conductivity at $500°C$ ($\Omega \cdot cm)^{-1}$
SG-11	2.80	1.53×10^{1}	5.94×10^{-11}
SG-11/0	3.32	2.74×10^{2}	8.73×10^{-12}
SG12	2.95	5.81×10^{1}	5.85×10^{-11}
SG-13	2.48	2.12×10^{0}	1.66×10^{-10}
SG-14	3.11	1.45×10^{2}	3.26×10^{-11}

AC Properties

Sample	Activation Energy at $T < 450°C$ ($\times 10^{19}$ J)	Dielectric Constant at 10 KHz	
		20°C	365°C
SG-11		12	12
SG-11/0	0.99	11	12
SG-12	1.01	10	11
SG-13	0.93	13	13
SG-14	1.02	10	10

Thorp and Kenmuir (34) investigated the electrical properties of three specimens of Ca-Al-Si-O glasses containing 0, 4.9, and 5.8 at% N and two specimens of Mg-Al-Si-O glass containing 0 and 7.6 at% N. They found an increase in the conductivity and the dielectric constant when nitrogen was incorporated in their glass specimens, similar to the results of Leedecke and Loehman (33) on the Y-Si-Al-O-N glasses. The Ca-Si-Al-O-N and Mg-Si-Al-O-N specimens exhibited higher AC conductivities (roughly one to two orders of magnitude) and somewhat lower dielectric constants (about 10% to 20%) than the Y-Si-Al-O-N glasses. Electrical conduction in all three systems was attributed to some form of hopping of carriers over a potential barrier, with no explicit role assigned to the nitrogen. On the basis of all three studies (2, 33, 34), it seems likely that the effect of nitrogen on electrical conduction is only secondary and that other constituents such as alkali impurities (2) dominate.

If the role of nitrogen substitution in oxynitride glasses is the replacement of bivalent oxygen by trivalent anions, the resulting increased cross-linking should give rise to a higher melt viscosity. Jankowski and Risbud (35) added a small amount of Ca_3N_2 to a commercial low-melting frit and measured the melt viscosity between 800° and 1200°C. The viscosity ranged from 10^3 poise at 800°C to 30 poise at 1200°C, with the viscosity of the melt being slightly higher for the nitrided frit than for the unaltered base glass ($\sim$ 160 poise with Ca_3N_2 compared with 138 poise without, at 1000°C). The effect is very small, and the interpretation is somewhat ambiguous because the scatter in the data was large, the level of nitrogen was very low (0.042 wt%), and the compositions of the two melts differed slightly other than in the nitrogen contents. Even so, it is of interest that the trend observed in the viscosity variation is consistent with other properties measured for oxynitride glasses.

Crystallization of Oxynitride Glasses

One of the early interests in oxynitride glasses was their potential as precursors for glass-ceramics containing refractory nitride species. Wusirika and Chyung (12, 19) reported 46 compositions that were investigated for their crystallization behavior. They found that the oxynitride glasses were self-nucleating and that heating between 800° and 1400°C produced fine-grained glass ceramics. All but one of Wusirika and Chyung's compositions were based on SiO_2, Al_2O_3, and Si_3N_4, with other added ingredients, so many of the observed crystalline species were those predicted by the Si-Al-O-N behavior diagram (24). In particular, for low concentrations of Si_3N_4 ($\lesssim$ 20 wt%), they found the X-phase, a compound with the approximate formula $Si_4Al_4O_{11}N_2$ (24) (the precise composition has been subject to dispute), whereas for high Si_3N_4 levels, β-Si_3N_4 was a major crystalline phase. Other observed species varied with the particular system studied. For example, in MgO-Al_2O_3-SiO_2-Si_3N_4, the X-phase crystals formed in a β-quartz or cordierite matrix, whereas in BeO-Al_2O_3-SiO_2-Si_3N_4, beryl crystals were obtained (19). The glass-ceramic microstructures appeared to vary with composition. High aspect-ratio

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(approximately 1:10) X-phase needles crystallized in Si-Al-O-N, Li-Si-Al-O-N, and Mg-Si-Al-O-N glasses, but in Ba-Mg-Si-Al-O-N and Cs-Mg-Si-Al-O-N the crystallization was spherulitic. The authors attributed the difference to the larger cationic size of Ba^{2+} and Cs^+ compared with Mg^{2+} and Li^+. However, other factors may have been involved, and there is at least one report of spherulitic morphology in a Mg-Si-O-N glass (37) (see below). Spherulitic crystallization was suppressed and dendritic crystals formed when 3 wt% MgF_2 was added to a $BaO-MgO-Al_2O_3-SiO_2-Si_3N_4$ melt (19).

Shaw (36) studied in detail the crystallization behavior of some Mg-Si-O-N glasses that had compositions simpler than those just discussed. Melts with compositions around 59 wt% SiO_2, 32 wt% MgO, and 9 wt% Si_3N_4 separated into SiO_2-rich and MgO-rich glassy phases on cooling. The microstructure, shown in Figure 12, consisted of SiO_2-rich droplets about 3 μm in diameter dispersed in a MgO-rich matrix. Heat treatments between 1000° and 1300°C crystallized the matrix phase into spherulites of enstatite without affecting the dispersed SiO_2-rich droplets. The plate-like enstatite crystallites that formed the spherulites were separated by thin films of uncrystallized glass. Heating above 1300°C caused faceted grains of enstatite to form adjacent to the SiO_2 droplets by recrystallization of the spherulites. Si_2N_2O also was produced by crystallization of the glassy regions between the enstatite crystallites. Shaw concluded from his research that the Mg-Si-O-N glasses might be useful precursors for new glass-ceramics (36).

Jankowski and Risbud (37) made a preliminary study of the crystallization of several Si-Ca-Al-O-N and Si-Ca-Al-B-O-N glasses. Scanning electron microscopy (SEM) of fracture surfaces showed phase separation in some compositions, although the morphology was apparently different from that in the analogous Mg-Si-O-N system studied by Shaw (36). A limited X-ray diffraction analysis identified Si_2N_2O, crystobalite, and sillimanite (Al_2SiO_5) as crystal species that were present in some of the Ca oxynitride glasses after heat treatment (37).

Loehman (10) studied the time-temperature-transformation behavior of the Y-Si-Al-O-N specimens listed in Table 1. Differential thermal

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FIGURE 12 PHASE SEPARATION IN Mg-Si-O-N GLASS

Light phase is SiO_2-rich, matrix is magnesium-rich (Reference 36)

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analysis (DTA) and X-ray diffraction (XRD) analysis of specimens heated
for various combinations of times and temperatures revealed extremely
complex crystallization behavior. The glasses were found to be very
stable to devitrification, withstanding 12 hours or more at 1000°C without
detectable crystallization. The DTA results for most compositions listed
in Table 1 showed multiple exotherms between 1000° and 1300°C that were
attributed to the development of different crystalline species. There was
a general trend to formation of $Y_2Si_2O_7$ in glasses exposed to higher
temperatures for longer times, as indicated by XRD analysis of specimens
heated isothermally at 1000°, 1100°, or 1200°C. Intermediate heat treat-
ments gave mixtures of as many as five crystalline species that were iden-
tified as yttrium silicates, yttrium-aluminum silicates, or nitrogen
apatite ($Y_4Si_4O_{11}N_2$). Substitution of nitrogen for oxygen in the crystal-
line yttrium silicates may have been indicated by slight shifts in their
XRD peak positions. Thus, the apparent path of crystallization in those
Y-Si-Al-O-N glasses was initial formation of a variety of metastable
phases that later transformed to $Y_2Si_2O_7$, with nitrogen ending up either
in the residual glassy phase or incorporated in the $Y_2Si_2O_7$ (10). This
compositional system was deemed promising for forming refractory glass-
ceramics.

Leedecke (38) crystallized four of the compositions listed in Table 1
by heating them in Ar for 16 h at 1250°C. He then measured the electrical
properties of the resulting glass-ceramics. Table 6 lists the crystalline
phases found in the glass ceramics using X-ray diffraction analysis. The
minimum crystallinity was an estimated 50 vol% in SG-11 and it increased
in the order SG13, SG12, SG14 in the other compositions. The electrical
properties measured for the glass-ceramics were very similar to those
found for the parent glasses. There was no apparent dependence of any of
the electrical properties on nitrogen content, a result similar to that
observed with uncrystallized material.

Complex crystallization behavior was observed by Messier (25) for the
Y-Si-Al-O-N glasses listed in Table 2. The heat treatment, which was more
extensive than that used by either Loehman (10) or Leedecke (38),

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Table 6

PHASES IN Y-Si-Al-O-N GLASSES HEATED 16 h AT 1250°C

Sample Number[*]	Phase Content
SG-11	$Y_2Si_2O_7$; Y_2SiO_5; glass
SG-12	$Y_2Si_2O_7$; Si_2N_2O; glass
SG-13	$Y_2Si_2O_7$; Si_2N_2O; $Al_6Si_2O_{13}$; glass
SG-14	$Y_2Si_2O_7$; $Y_3Al_5O_{12}$(YAG); Y_2SiO_5; Si_2N_2O; glass

[*]For compositions see Table 1.

consisted of 4 h at 1000°C to nucleate the glass, followed by 16 h at
1400°C to crystallize it. The phases revealed by X-ray diffraction
analysis are presented in Table 7. The density and microhardness values
are similar to those for the uncrystallized specimens presented in Table
2. Because they were heated more extensively, Messier's glasses were
more highly crystalline than those studied by Leedecke (38). Furthermore,
as Table 7 shows, both compositions developed Si_3N_4 phases on crystalli-
zation. That result probably stems from the higher nitrogen content in
Messier's glasses (25) relative to those studied by other workers.

Thomas et al. (39) also studied the crystallization of Y-Si-Al-O-N
glasses, primarily using transmission electron microscopy for micro-
analysis and for revealing crystal morphologies. They found that glass
formation was enhanced by nitrogen additions, which is consistent with
observations in other systems (10,37), and that crystallization on
quenching the melt occurred only when ZrO_2 was added. The main crystal-
line species was identified as $Y_2Si_2O_7$, as was also the case in Loehman's
(10) and Messier's (25) studies. Analytical electron microscopy revealed
that all the Zr and most of the Al was in the residual glassy phase after
crystallization, that the Si concentrations were about equal in the
crystals and the glass, and that the Y content of the crystals was about
1.5 times greater than of the glass.

Table 7

CRYSTALLIZATION OF Y-Si-Al-O-N GLASS HEATED FOR 4 h AT 1000°C
PLUS 16 h AT 1400°C (25)

Specimen[*]	Phase Content	Density (g/cm^3)	Microhardness (Knoop, 100 g)
a	β-$Y_2Si_2O_7$, δ-$Y_2Si_2O_7$, α-Si_3N_4	3.82	950 ± 107
b	β-Si_3N_4, $Y_3Al_5O_{12}$, Y_2SiO_5 (2 forms)	3.92	1192 ± 227

[*]See Table 2 for glass compositions.

Structure of Oxynitride Glasses

Very little direct evidence of oxynitride glass structure has been
reported. Most structural models, which are only very rudimentary at
present, are plausibility arguments based on analogous crystalline
structures and on glass properties data. The existence of (SiN_4) and
($SiON_3$) tetrahedral structural units in crystalline Si_3N_4 and Si_2N_2O (40)
leads one to postulate that oxynitride glasses containing silicon are
built up of $Si(O,N)_4$ tetrahedra. As already discussed, the variation of
glass properties with nitrogen content shows an increase in Tg, a decrease
in thermal expansion coefficient, and an increase in hardness and fracture
toughness as the nitrogen content increases (Figures 8 and 11). Those
changes in properties are consistent with a glass structure in which the
degree of linkage has increased because of substitution of trivalent
nitrogen for bivalent oxygen.

Infrared spectroscopic measurements of several Y-Si-Al-O-N glasses
(9) showed only a broad peak around 850-900 cm^{-1}, which is in the region
of the major Si-N and Si-O absorption in crystalline Si_3N_4 and SiO_2,
respectively. Thus the absorption spectra indicate that most of the
nitrogen was bonded to silicon. The nitrogen source in those glasses was
AlN, and little infrared activity was observed in the 700 cm^{-1} region

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where the major AlN absorption occurs, which is evidence for reforming of nitrogen bonds on dissolution of AlN.

Risbud (41) adapted the approach of Stevels (42) to characterize the network structure of oxynitride glasses by calculating several parameters related to the degree of linkage in the network. The parameters are:

$$R' = \text{average number of anions per network forming ion} = \frac{(\text{at\% O} + \text{at\% N})}{(\text{at\% Si} + 2/3 \text{ at\% Al})}$$

$$X' = \text{average number of nonbridging anions per polyhedron} = 2R' - 4$$

$$Y' = \text{average number of bridging anions per polyhedron} = 8 - 2R'$$

Risbud assumed that nitrogen forms only Si-N bonds and that two-thirds of the Al atoms are network formers in fourfold coordination, with the remaining one-third present as modifiers in sixfold coordination. For a series of ten actual oxynitride glass compositions, the calculated R' falls between 2.16 and 2.96, which compares with the 2.25 to 2.75 value found for many oxide glasses (43). Y', the average number of bridging anions per tetrahedron, was calculated to lie between 2.08 and 3.68 for the oxynitride glasses. Obviously, the R' and Y' values depend on what fraction of the Al is assumed to be in network-forming sites. However, under the stated assumptions, the analysis shows Y' increases sharply with nitrogen content in the 1 to 8 at% N range common for oxynitride glasses, which is in accord with observed trends in physical properties.

Applications of Oxynitride Glasses

Because widespread interest in oxynitride glasses is a relatively recent phenomenon, few commercial applications have been developed. The increase in hardness effected by nitrogen additions has been exploited by

researchers from the Japanese National Institute for Research in Inorganic Materials to produce scratch-resistant glass for watch crystals. The possibility of making oxynitride glass-ceramics has been investigated by several groups, as discussed earlier, but no material of obvious commercial promise has been described to date. Incorporation of nitrogen has potential for increasing the strength, hardness, and modulus of silicate-based glass fibers (44), a use that would be very important commerically. A significant increase in leach resistance has been found to result from nitrogen incorporation in several compositional systems (9,27). Thus, it may be possible to improve the chemical durability of currently unusable glasses so that their other desirable properties can be exploited. Another obvious use of this particular properties improvement is to increase the leach resistance of glasses for nuclear waste encapsulation by adding Si_3N_4 or AlN.

One final application makes use of the chemical compatibility of oxynitride glasses and Si_3N_4 to give a method for joining Si_3N_4 parts (45). Complex shapes of Si_3N_4 can be built up from simpler parts by reactive joining using oxynitride glasses. The glass is compatible with the ceramics because its composition is chosen to match that of the grain boundary phase already present in the Si_3N_4. Fourpoint bend strengths in excess of 60,000 psi have been obtained (46) for joined test bars of Si_3N_4, a value more than twice as great as any reported previously for other joining methods.

Additional applications for oxynitride glasses will undoubtedly be developed as their properties become more thoroughly understood and as more researchers and technologists become familiar with them. It is clear from what is known already that oxynitride glasses have considerable potential that will ultimately be exploited.

REFERENCES

1. H. O. Mulfinger, "Physical and Chemical Solubility of Nitrogen in Glass Melts," J. Amer. Ceram. Soc. 49, 462-67 (1966).

2. T. H. Elmer and M. E. Nordberg, "Effect of Nitriding on Electrolysis and Devitrification of High-Silica Glass," J. Amer. Ceram. Soc. 50, 175-79 (1967).

3. F. L. Harding and R. J. Ryder, "Effects of Silicon Nitride Additions to a Container Glass Batch," Glass Technology 11 [2], 54-58 (1970).

4. K. H. Jack, "Review: Sialons and Related Nitrogen Ceramics," J. Mater. Sci. 11 [6], 1135-58 (1976).

5. R. E. Loehman, "Oxynitride Glasses and Silicon Nitride Processing," Ceramic Engineering and Science Proceedings, 3 [1-2], 35-49 (1982).

6. P. Drew and M. H. Lewis, "The Microstructure of Silicon Nitride Ceramics During Hot-Pressing Transformations," J. Mater. Sci. 9 [2], 261-69 (1974).

7. R. Kossowsky, "The Microstructure of Hot-Pressed Silicon Nitride," J. Mater. Sci. 8 [11], 1603-15 (1973).

8. K. R. Shillito, R. R. Wills, and R. B. Bennett, "Silicon Metal Oxynitride Glasses," J. Amer. Ceram. Soc. 61 [11-12], 537 (1978).

9. R. E. Loehman, "Preparation and Properties of Yttrium-Silicon Aluminum Oxynitride Glasses," J. Amer. Ceram. Soc. 62 [9], 491-94 (1979).

10. Ronald E. Loehman, "Oxynitride Glasses," J. Noncryst. Solids 42, 433-46 (1980).

11. C. J. Brinker, "Formation of Oxynitride Glasses by Ammonolysis of Gels," J. Amer. Ceram. Soc. 65, C4-5 (1982).

12. K. Chyung and R. R. Wusirika, U.S. Patent No. 4,070,198, January 24, 1978.

13. E. A. Dancy and D. Janssen "The Dissolution of Nitrogen in Metallurgical Slags" Can. Met. Quart. 15 [2], 103-110 (1976).

14. R. L. Tsai and R. Raj, "Dissolution Kinetics of β-Si_3N_4 in an Mg-Si-O-N Glass," J. Amer. Ceram. Soc. 65, 270-74 (1982).

15. R. Raj and P.E.D. Morgan, "Activation Energies for Densification, Creep, and Grain-Boundary Sliding in Nitrogen Ceramics," J. Amer. Ceram. Soc [64], C143-C145 (1981).

16 D. R. Stull and H. Prophet JANAF Thermochemical Tables, 2nd ed NSRDS-NBS Pub. 37 (U.S. Govt. Printing Office, Washington, DC, 1971).

17. R. A. Swalin, Thermodynamics of Solids, 2nd ed. (John Wiley, New York, 1972), p. 116.

18. Ronald E. Loehman, unpublished research.

19. R. R. Wusirika and C. K. Chyung, "Oxynitride Glasses and Glass-Ceramics," J. Noncryst. Solids $\underline{38}$, 39-44 (1980).

20. K. K. Naik, L. J. Gauckler, and T. Y. Tien, "Solid-Liquid Equilibria in the System Si_3N_4-AlN-SiO_2-Al_2O_3," J. Amer. Ceram. Soc. $\underline{7}$ [7-8], 332-35 (1978).

21. K. H. Jack, "The Crystal Chemistry of the Sialons and Related Nitrogen Ceramics," in Nitrogen Ceramics, F. L. Riley, Ed. (Noordhoff, Leyden, 1977) pp. 109-128.

22. P. L. Jankowski and S. H. Risbud, "Synthesis and Characterization of an Si-Na-B-O-N Glass," J. Amer. Ceram. Soc. $\underline{63}$ [5-6], 350-52 (1980).

23. A. Makishima, M. Mitomo, H. Tanaka, N. Ii, and M. Tsutsumi, "Preparation of La-Si-O-N Oxynitride Glass of High Nitrogen Content," Yogyo-Kyokai-shi $\underline{88}$ 701-2 (1980).

24. L. J. Gauckler, H. L. Lukas, and G. Petzow, "Contribution to the Phase Diagram Si_3N_4-AlN-Al_2O_3-SiO_2," J. Amer. Ceram. Soc. $\underline{58}$, 346 (1975).

25. D. R. Messier, "Preparation and Crystallization of Si-Y-Al-O-N Glasses," to be published.

26. G. H. Frischat and C. Schrimpf, "Preparation of Nitrogen-Containing Na_2O-CaO-SiO_2 Glasses," J. Amer. Ceram. Soc. $\underline{63}$ [11-12], 714-15 (1980).

27. J. A. Wilder, personal communication.

28. R. H. Doremus, Glass Science (John Wiley, New York, 1973), pp. 34-35.

29. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th ed. (John Wiley, New York, 1980), pp. 460-65.

30. H. N Ng and C. Calva, "X-Ray Study of the α-β Transformation of Berlinite ($AlPO_4$)," Can. J. Phys. $\underline{54}$ 638-47 (1976).

31 G. B. Alexander, W. M. Heston, and R. K. Iler, "Solubility of Amophous Silica in Water," J. Phys. Chem. 59, 453-55 (1954).

32. J. A. Wilder, Jr., "Glasses and Glass-Ceramics for Sealing to Aluminum Alloys," J. Noncryst. Solids 38-39, 879-54 (1980).

33. C. J. Leedecke and R. E. Loehman, "Electrical Properties of Yttrium-Aluminum-Silicon-Oxynitride Glasses," J. Amer. Ceram. Soc. 63, 190-93 (1980).

34. J. S. Thorp and S.V.J. Kenmuir, "Dielectric Properties of Some Oxynitride Glasses," J. Mater. Sci. 16, 1407-09 (1981).

35. P. E. Jankowski and S. H. Risbud, "Comparative Experimental Measurements of Viscosity-Temperature Relations of an Oxide and Slightly Nitrided Glass," submitted to the J. Amer. Ceram. Soc.

36. T. C. Shaw, "Crystallization of Glasses in the Mg-Si-O-N System, Ph.D. Thesis, University of California (Berkeley), LBL Report 11759 (Oct. 1980).

37. P. E. Jankowski and S. H. Risbud, "Formation and Characterization of Oxynitride Glasses in the Si-Ca-Al-O-N and Si-Ca-Al,B-O-N Systems," submitted to the J. Amer. Ceram. Soc.

38. C. J. Leedecke, "Electrical Properties of Some Y-Si-Al Oxynitride Glass Ceramics," J. Am. Cer. Soc. 63 (7-8), 479-480 (1980).

39. G. Thomas, C. Ahn, and J. Weiss, "Characterization of Y-Si-Al-O-N Glass and Glass-Ceramics," to be published.

40. K. H. Jack, "Electrical Properties of Some Sialons," in Nitrogen Ceramics F. L Riley, Ed. (Noordhoff, Leyden, 1977), p. 597.

41. S. H. Risbud, "Analysis of Bulk Amorphous Oxynitride Structures Using the Network Theory of Glasses," Phys. Chem. Glasses 22 [6], 168-70 (1981).

42. J. M. Stevels, Handbook of Physics XIII, 510 (1962).

43. W. D. Kingery, H. K. Bowen, and D. R. Uhlmann Introduction to Ceramics, 2nd ed. (John Wiley, New York, 1976), pp. 104-108.

44. J. Homeny, personal communication.

45. R. E. Loehman, "Transient Liquid-Phase Bonding of Silicon Nitride Ceramics," in Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems J. A. Pask and A. G.Evans, Eds. (Plenum, New York, 1981), pp. 701-711.

46. R. E. Loehman, M. L. Mecartney, and D. J. Rowcliffe, unpublished work.

PUBLICATIONS AND TECHNICAL REPORTS

1. Ronald E. Loehman, "Oxynitride Glasses," J. Noncryst. Solids 42, 433–446 (1980).

2. T. C. Shaw, "Crystallization of Glasses in the Mg-Si-O-N System, Ph.D. Thesis, University of California (Berkeley), LBL Report 11759 (Oct. 1980) (Collaboration between SRI and U.C. Berkeley).

3. R. E. Loehman, "Transient Liquid-Phase Bonding of Silicon Nitride Ceramics," in Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems, J. Pask and A. Evans, eds. (Plenum, New York, 1981), pp. 701-711.

4. R. E. Loehman, "Oxynitride Glasses and Silicon Nitride Processing," Ceramic Engineering and Science Proceedings 3 [1-2] 35-49 (1982).

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