# OXYNITRIDE GLASSES PREPARED FROM GELS AND MELTS

C. J. Brinker, D. M. Haaland and R. E. Loehman

Sandia National Laboratories
Albuquerque, New Mexico 87185

The structures of glasses prepared by melting mixtures of alkali
borosilicate glass and silicon nitride powders and by ammonolysis
of porous borosilicate gels were studied using Fourier transform
infrared spectroscopy and combustion analysis. Whereas there
was little evidence of nitride bond formation in the melt prepared
glasses, Si-N and B-N bonding were observed in the gel-derived
glasses. It is proposed that these differences occur because Na_2O
and B_2O_3 are reduced by Si_3N_4 in the melt to form $SiO_2 + N_2$ + metal.
In comparison, ammonolysis of gels is a low temperature process
(<1000°C) which occurs by Lewis acid adsorption and Lewis base
attack on bridging oxygen bonds.

INTRODUCTION

Oxynitride (O-N) glasses are normally formed by melting mixtures of oxide and
nitride (typically Si_3N_4 or AlN) powders. However, both practical and fundamental
limitations are often encountered with this procedure. An obvious practical limi-
tation is that high temperatures ($\geq$1900 K)[1] are often required for nitride dissolu-
tion and melt homogenizaton. Fundamental limitations arise because thermodynamic
equilibria are quickly established at these temperatures. Consequently, oxynitride
melt stability is ultimately determined by both the melt composition and the fur-
nace atmosphere. For example, thermodynamic calculations show that many network-
forming oxides (SiO_2, B_2O_3, and P_2O_5) are reduced by Si_3N_4 to form $SiO_2 + N_2$+
metal, which causes frothing, extensive depletion of nitrogen, and metallic inclu-
sions. This is, of course, why many melted O-N glasses are gray to black in color
and optically opaque or translucent. Additionally, because the overall reaction

$$Si_3N_4 + SiO_2(\ell) + O_2(g) \rightarrow 4SiO(g) + 2N_2(g) \qquad \Delta G°_{(1980K)} = -80.3 \text{ Kcal} \qquad (1)$$
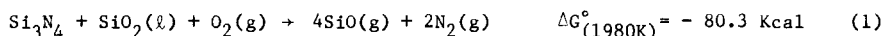
is exothermic, decomposition of Si-O-N melts is promoted by increasing both the
concentrations of Si_3N_4 and SiO_2 and by increased oxygen partial pressure[2].

From the above discussion, it is apparent that melt formation of O-N glasses limits
both the extent of nitridation and the compositional range of glass formation
(because oxides are reduced by nitrides and because of the refractory quality of
most melts). According to Eq. 1, stability of a particular melt is promoted by
working in highly reducing conditions and under high pressures of N_2, but for any
melt atmosphere there is a limit of Si_3N_4 which is stable in the melt. Thus, the
limit of nitridation in O-N glasses prepared by melting seems to be determined more
by melt conditions than by structural limitations. This provokes the following
question: Can a wider compositional range of O-N glasses (with perhaps increased
nitridation) be prepared metastably by low temperature processing where kinetic
limitations prevent thermodynamic equilibria from being established? Prompted by
this fundamental question, we have recently prepared O-N glasses at temperatures
far below the liquidus by ammonolysis of porous gels[3,4]. In this method, ammonia
is reacted with the gel surface at low temperature ($<T_g$) and the ammoniated gel is
sintered at temperatures above T_g to form a nitrided glass.

This is a low temperature process which does not rely on melting and, therefore, is not constrained by slow melt kinetics nor is it subject to the thermodynamic limitations which preclude stable melt formation. Therefore, this process can potentially broaden the compositional range of O–N glass formation. The purpose of the present study was to demonstrate this concept by comparing nitrided gels to melt-formed O–N glasses.
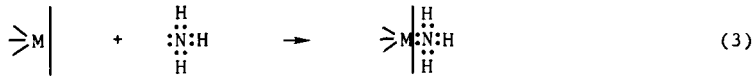
M–B–O–N GLASSES

Practically, all melt-formed O–N glass syntheses have used Si as the network forming cation. Silicate-based melts are typically quite refractory and the extent of nitridation may be limited structurally because incorporation of trivalent N requires that 3 SiO_3N^{5-} tetrahedra share a common vertex. By comparison M–B–O–N glasses, where M is metal, have lower melting temperatures and may allow more extensive nitridation because 3 BO_2N^{4-} trigonal units might more easily share a common vertex.

There have been few attempts to prepare M–B–O–N glasses by melting. The Gibbs energy of formation of B_2O_3 is considerably less negative than the ΔG°_R for the oxidation of Si_3N_4 and thus, we expect B_2O_3 to be reduced in the presence of Si_3N_4 to form SiO_2, N_2 and B. However, because the net reaction

$$2B_2O_3 + Si_3N_4 \rightarrow 4BN + 3SiO_2 \qquad \Delta G^\circ_{R(1900K)} = -68 \text{ Kcal} \qquad (2)$$
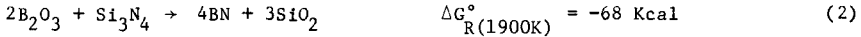
is moderately exothermic, nitrogen might still be incorporated into the melt in the form of BN. Jankowski and Risbud inductively melted mixtures of B_2O_3, SiO_2, and Si_3N_4 with and without additions of Na_2O. Despite attempts to optimize the melting procedure, they always observed considerable outgassing presumably due to the evolution of nitrogen and possibly metallic sodium and boron. Estimates of nitridation for the Si–Na–B–O–N glass ranged from 0.265 to 2.13 wt.% N compared to the calculated value of 4.66 wt.%, and the synthesized glass was translucent gray-black, evidence of melt reduction and bubble formation.

Ammonolysis of porous alumino-borosilicate gels has resulted in colorless, optically transparent O–N glasses[4]. In contrast to melt-formed M–B–O–N glasses, it appears that B promotes nitridation in gels. For example, pure silica gels heated at 1°C/min in flowing NH_3 contained low nitrogen contents, 0.1 to 0.5 wt.%, compared to alumino-borosilicate gels, 1.0 to 2.0 wt.%, for heat treatments up to 1090°C. Because B^{3+} and Al^{3+} are stronger Lewis acids than Si^{4+}, this suggests that the Lewis acid strength of the network-forming cations determines the extent and speciation of gel nitridation. We have proposed Lewis acid adsorption:

$$\ce{>M|} + \underset{\underset{H}{|}}{:\!N\!:\!H} \longrightarrow \ce{>M\!:\!N\!:\!H} \qquad (3)$$

and Lewis base attack on M–O–M linkages:

$$\underset{\overline{\text{M-O-M}}}{\underset{H}{|}{H:N:H}} \longrightarrow \underset{\overline{\quad M \quad\ M\quad}}{\overset{H\quad H\ H}{N'\quad O}} \qquad (4)$$
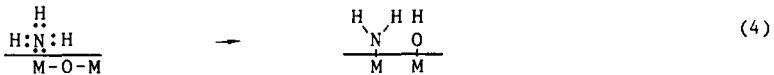
to account for low temperature nitridation .

M–B–O–N glasses, therefore, represent a potentially interesting family of oxynitride glasses which are difficult to prepare by melting, but which are readily synthesized by ammonolysis of gels. In the remainder of this paper, we compare the amount and speciation of nitrogen in M–B–O–N melts to that in M–B–O–N gels to determine whether the gel route results in N species which are unobtainable in the melt due to both thermodynamic and kinetic limitations.

EXPERIMENTAL

Monolithic gels (Comp. 1 in Table 1) were prepared according to the method outlined in reference 6. Gels were heated at 1°C/min in flowing (90 ml/min) anhydrous ammonia to temperatures ranging from 400 to 750°C. Oxide glasses, prepared by conventional melting, were ground and mixed with 3 to 10 wt.% of powdered amorphous Si_3N_4*. This mixture was added to a Mo crucible and melted at 1400 to 1475°C in flowing, anhydrous nitrogen.

Nitrogen contents were measured by combustion analysis** in oxygen at 2200°C. Infrared spectra of samples (prepared as thin films on Si or in KBr pellets) were collected using a Nicolet 7199 Fourier transform infrared spectrometer (FT-IR).

TABLE 1. Compositions Investigated (wt%)

	SiO_2	B_2O_3	Al_2O_3	Na_2O	BaO	Si_3N_4
Comp 1	68.8	17.7	6.8	3.2	3.5	--
Comp 2	64.6	16.7	6.4	6.1	3.3	3.0
Comp 3	59.9	15.4	5.9	5.6	3.1	10.0

RESULTS AND DISCUSSION

The melted O-N glass compositions (Comps. 2 and 3) showed extensive frothing and were a translucent gray in color. This is qualitative evidence of the formation of gaseous nitrogen (and possibly silicon monoxide or sodium) and of the reduction of cations to metallic form. The measured nitrogen analyses were 0.9 and 2.9 wt.%, respectively, for Comps. 2 and 3 (in which 1.2 and 4.0 wt.% nitrogen were added to the melt as Si_3N_4). However, as discussed below much, if not all, of this measured nitrogen may have been present as undissolved Si_3N_4.
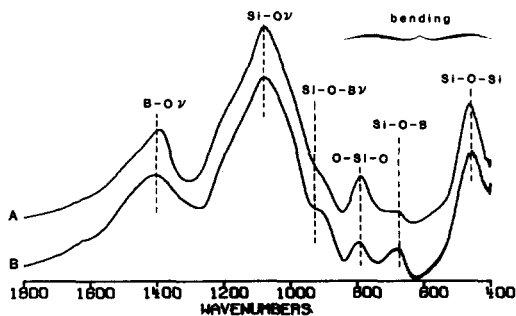

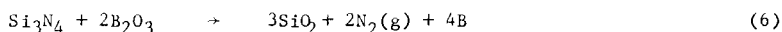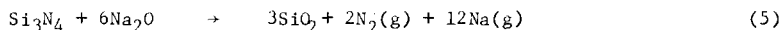Figure 1. Infrared spectra (in KBr) of A) Comp. 3 and B) the parent oxide glass

Infrared spectra of Comp. 3 and of the parent oxide glass are shown in Figure 1. It is clear from these spectra that there is a narrowing of the B-O ($\sim$1400 cm^{-1}) and Si-O ($\sim$1080 cm^{-1}) stretching vibrations relative to the parent oxide glass. The integrated intensity of the B-O stretching vibration of the melted nitride glass has decreased relative to the Si-O stretching vibration. In addition, we observe a decrease in the relative intensities of the Si-O-B vibrations at $\sim$915 and 675 cm^{-1} and an increase in the intensity of the O-Si-O and Si-O-Si bending vibrations at $\sim$800 cm^{-1} and $\sim$465 cm^{-1}, respectively. In oxynitride glasses,

*GTE Sylvania SN402
**Perkin Elmer Model 240B elemental analyzer

B-N and Si-N result in rather broad bands centered at 1510^4 and 970^7 cm^{-1}, respectively. Subtraction of spectrum B from spectrum A in Fig. 1 showed no evidence of B-N bond formation, however, this subtraction showed a band at $\sim$950 cm^{-1} which may be evidence of unreacted Si_3N_4 ($\sim$950 cm^{-1}) or limited O-N glass formation.

These infrared results may be interpreted by consideration of both the thermodynamics of the Si_3N_4-glass mixture and possible oxide glass structures. Based on the Gibbs energies of oxide and nitride formation, the stability of the oxides in the presence of Si_3N_4 in this mixture at 1400°C is (in order of increasing stability) Na_2O, B_2O_3, SiO_2, BaO, Al_2O_3. Therefore, we might expect the following reactions to occur as Si_3N_4 begins to react with the melt:

$$Si_3N_4 + 6Na_2O \quad \rightarrow \quad 3SiO_2 + 2N_2(g) + 12Na(g) \tag{5}$$

$$Si_3N_4 + 2B_2O_3 \quad \rightarrow \quad 3SiO_2 + 2N_2(g) + 4B \tag{6}$$

The parent glass, however, does not contain pure oxides. For example, Na_2O probably donates oxygen to stabilize some of the B and Al in 4-fold coordination (with O), and because of the relatively high silica content, most B (and Al) is expected to be bonded through oxygen to silicon, i.e. there is little B-O-B bonding as evidenced by the absence of a B-O-B bending band (720 cm^{-1}). The expected reactions with Si_3N_4 (Eqs. 5 and 6), can, therefore, only proceed by attack of Si-O-B bonds. According to Eqs. 5 and 6, the melt should become enriched in SiO_2 and, as determined experimentally by Jankowski and Risbud[5] for Si-Na-B-O-N glasses, depleted in Na_2O and B_2O_3. This explains the relative decrease in both B-O stretching and Si-O-B stretching and bending vibrations relative to the Si-O stretching vibration. The sharpening of the B-O stretching band may indicate that due to the vaporization of sodium (eq. 5), most of the remaining B exists in 3-fold coordination (rather than as a mixture of 3-fold and 4-fold) and,thus,we might expect a narrower range of vibrational frequencies. Because the glass has become both enriched in SiO_2 and depleted in Na_2O and B_2O_3, there will be an increase in the relative numbers of Si-O-Si bonds compared to Si-O-M. This may explain the sharpening of the Si-O stretching band. The intensities of Si-O-Si and O-Si-O bending vibrations are very sensitive to strain. Therefore, increases in the relative intensities of these bands compared to the intensity of the Si-O stretching band may reflect a slight distortion of the network due perhaps to both the changes in oxide composition and boron coordination which occur during melting. Some formation of M-N bonds (which also cause distortion) cannot be totally discounted, however.

There appears to be little evidence of Si-N and no evidence of B-N bond formation in the melt prepared glass. Therefore, the infrared and nitrogen content results obtained from those glasses can be interpreted in terms of a rapid reaction causing loss of N_2 and sodium vapor and reduction of B_2O_3. Under such conditions, the subsequent reaction of boron with nitrogen to form B-N bonds (eq. 2) apparently does not occur, perhaps due to kinetic limitations. These results suggest that the $\sim$3 wt% N contained in this glass may be predominantly in the form of undissolved Si_3N_4, because, if a homogeneous O-N glass were formed, we might also expect to see some evidence of B-N bonds.

Gel-Derived O-N Glasses

By contrast with syntheses involving melting, the formation of M-B-O-N glasses is possible by ammonolysis of gels[3,4]. Heat treatments of Comp. 1 in flowing ammonia followed by vacuum sintering at 900°C resulted in clear, bubble-free glasses containing $\sim$2 wt% N. These gel-derived O-N glasses exhibited an 80% increase in Vicker's microhardness, a 65°C increase in glass transition temperature, and altered thermal expansion characteristics compared to the parent oxide compositions.

Ammonia treatments of gels result in the formation of Si-N and B-N bonds as evidenced by the infrared spectra shown in Figure 2. Here we see a 1510 cm^{-1} shoulder

on the B–O stretching vibration, which is assigned to a B–N stretching vibration. There is a relative loss of B–O stretching intensity as expected by the attack of NH_3 on B–O bonds (Eqs. 4), and there is a broadening of the Si–O stretching vibration. The low energy broadening of this band has been assigned to the Si–N stretching vibration. An increase in the intensity of the O–Si–O and Si–O–Si bending vibrations coupled with an increase in the width of Si–O stretching vibrations suggests a distoration of the normal silicate bond angles. This would be expected upon incorporation of nitrogen into the glass structure, because, as described previously, three SiO_3N^{5-} (or combinations of SiO_3N^{5-} and BO_3N^{4-}) tetrahedra share a common vertex and thus distort the local Si–O–Si environment.
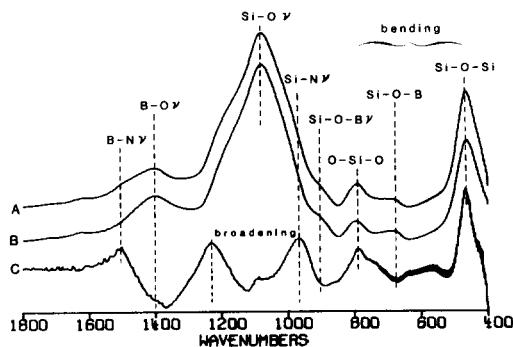

Figure 2. IR Spectra (in KBr) of Comp. 1 A) after heating to 750°C in NH_3, B) after heating to 750°C in air and C) difference spectrum scale expanded by factor of 5.

We have proposed Lewis acid adsorption (Eq. 3) and Lewis base attack on bridging oxygen bonds (Eq. 4) to account for ammonolysis. To examine the effects of Lewis acid sites on ammonolysis in more detail, we used in situ FT-IR. Thin (∿1000Å) borosilicate films (∿20 wt.% B_2O_3, 80 wt.% SiO_2) were deposited on Si substrates, mounted in an infrared cell, and heated to temperatures up to 700°C in flowing anhydrous NH_3. Spectra were collected at ∿100°C intervals during the NH_3 treatment (because Si is quite IR absorbing above 300°C, higher temperature spectra were collected after cooling the substrate to 300°C). Figure 3 shows the spectra collected
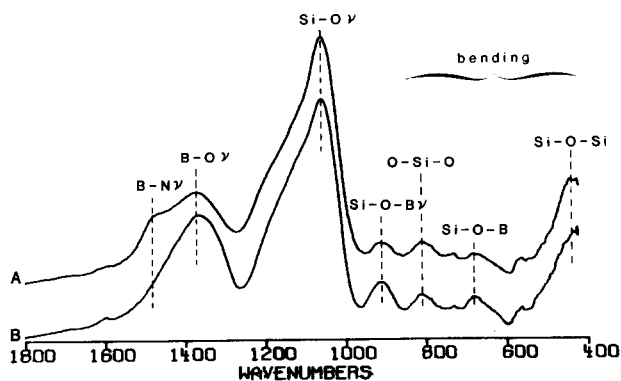

Figure 3. Thin Film Spectra A) after 600°C in NH_3 and B) after 400°C in NH_3 (after subtraction of the Si substrate spectrum)

after the 400°C treatment and after the subsequent 600°C treatment. The difference between these spectra indicates that, between 400 and 600°C, B-N bonds form (as evidenced by the 1510 cm^{-1} shoulder) at the expense of Si-O-B (reduced relative intensities of B-O stretch, Si-O-B stretch and Si-O-B bend). These observations are consistent with results obtained from the more complex multicomponent gels and are expected if Lewis base attack by NH_3 is directed at the Lewis acid sites of Si-O-B linkages (Eq. 4). Unlike the multicomponent gels, there is no evidence of Si-N bond formation. This may indicate that a critical modifier content is required to obtain Si-N bonds at these low temperatures. This result is qualitatively consistent with the finding that for Ca-Al-Si-O-N glasses, Si_3N_4 solubility was negligible until a critical level of CaO was exceeded[8].

Unfortunately, we were unable to synthesize the corresponding Si-B-O-N glass by melting, and thus we cannot compare ammonolysis to the reaction of Si_3N_4 with this binary composition. This result, however, is a practical example of how gel-processing extends the compositional limits of O-N glass formation.

CONCLUSIONS

The results of these experiments show that, due to both thermodynamic and kinetic limitations, it is difficult to synthesize M-B-O-N glasses by melting powdered mixtures of oxides and nitrides. The reduction of B_2O_3 and Na_2O by Si_3N_4 caused frothing, loss of nitrogen, and apparent reduction of Na_2O and B_2O_3. This is predicted to be a general problem of melt synthesis of O-N glasses involving oxides, e.g. SiO_2, P_2O_5, Na_2O, and B_2O_3, that are reduced by Si_3N_4.

M-B-O-N synthesis is possible by ammonolysis of porous gels. In this process, nitridation occurs by reactions such as Lewis acid adsorption and Lewis base attack on bridging oxygen bonds. Because these are low temperature reactions which do not involve Si_3N_4, thermodynamic limitations (which are encountered in the melt) can be avoided. Infrared spectroscopy shows that both B-N and Si-N bonds are formed during ammonolysis of Si-Al-B-Na-Ba-O gels with Si-O-B bonds being preferentially attacked. In situ FT-IR of NH_3-treated Si-B-O films shows only formation of B-N bonds with a corresponding reduction of Si-O-B bonds.

The most important conclusion of this study is that the gel-route not only provides a low-temperature method of O-N glass synthesis, but, more significantly, expands the compositional range of O-N glass synthesis.

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