

# Oxynitride Glass Formation from Gels

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Porous, multicomponent silicate gels were heated in flowing and pressurized ammonia. These treatments resulted in dense, homogeneous oxynitride (O-N) glasses which were synthesized at low temperature ( $\leq 1000^\circ\text{C}$ ) without melting. The O-N glasses exhibited increased microhardness and glass-transition temperature and altered thermal expansion characteristics compared to the respective oxide glasses prepared by densifying gels in air or by conventional melting of oxide powders. Spectroscopic evidence indicates that ammonia reacts with all of the network-formers investigated, Si, Al, and B, but from nitrogen content measurements, it appears that B and/or Al are required for significant nitridation below  $1000^\circ\text{C}$ .

## I. Introduction

RECENT investigations of oxynitride (O-N) glasses showed that replacement of oxygen with nitrogen results in improvements of such physical properties as fracture toughness, microhardness, refractoriness, and chemical durability.<sup>1-5</sup> There is mounting evidence that these improvements occur because nitrogen enters into the glass network in 3-fold coordination with network-forming cations, and thus replacement of 2-fold coordinated oxygen with nitrogen serves to more effectively crosslink the glass network.<sup>6</sup>

The usual method of O-N glass preparation is melting of mixtures of oxide and nitride powders under highly reducing conditions. The disadvantage of this method is that high temperatures (often exceeding  $1700^\circ\text{C}$ ) are required for melting and homogenizing the glass.<sup>5</sup> An alternate method was reported by Elmer and Nordberg,<sup>2,3</sup> in which a porous borosilicate glass\* is nitrided by treatments with ammonia at  $500^\circ$  to  $1050^\circ\text{C}$ . This method has the advantage that homogeneous glass can be produced at lower temperatures without melting. However, to date this method has been limited to a single high-silicate composition which, when nitrided, requires rather high temperatures for consolidation (typically  $>1200^\circ\text{C}$ ). This paper describes a new method, based in part on Elmer's original work, to prepare a wider variety of O-N glasses at low temperatures by ammonia treatments of porous gels.<sup>7</sup> In this paper physical and spectroscopic measurements will be used to compare the ammonolysis of gels to the conventional thermal conversion of gels to oxide glasses (i.e. heat treatments in air). These comparisons will be used to demonstrate the modified physical properties of nitrided gels as well as to elucidate the important reactions responsible for gel nitridation.

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\*Vycor, Corning Glass Works, Corning, NY; typical composition 96%  $\text{SiO}_2$  + 3%  $\text{B}_2\text{O}_3$  + 0.5%  $\text{M}_2\text{O}_3$  +  $\text{MO}_2$  (chiefly  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ ) and traces of  $\text{Na}_2\text{O}$  and  $\text{As}_2\text{O}_3$ .

Table I. Compositions Investigated

Composition	Constituents (wt%)				
	$\text{SiO}_2$	$\text{B}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{Na}_2\text{O}$	BaO
1	66.6	17.1	6.6	6.3	3.4
2	67.7	17.4	6.7	4.8	3.4
3	68.8	17.7	6.8	3.2	3.5
4	69.9	18.0	6.9	1.6	3.5
5	71.1	18.3	7.1	0	3.6
6	100	0	0	0	0

## II. Experimental Procedure

### (1) Sample Preparation

Silica and borosilicate gels of the compositions listed in Table I were prepared by sol-gel processes which were reported previously (process I in Ref. 8 and A3 in Ref. 9). Monolithic samples were obtained by casting concentrated solutions ( $\approx 12$  wt% equivalent oxides) in cylindrical polypropylene molds, followed by slow drying at room temperature. Individual samples  $\approx 2.5$ -mm thick were sliced from the castings with a diamond wafering saw. It should be noted that the physical and chemical structure of a desiccated gel is a result of the sequential gelation, aging, and drying conditions under which it was prepared.<sup>10,11</sup> Thus, it is expected that the results presented here depend not only on the oxide composition but also on the polymeric nature (e.g. degree of crosslinking) of the investigated gels.

Ammonia heat treatments were performed in flowing anhydrous ammonia (90 mL/min) at ambient pressure and in pressurized ammonia (0.7 to 2.8 MPa). Prior to heating, all samples were evacuated to  $\approx 1.3 \times 10^{-5}$  Pa. Heat treatments were also performed in either flowing dry air or dry nitrogen. Heating rates were  $1^\circ\text{C}/\text{min}$  unless otherwise indicated.

### (2) Characterization

H, C, and N analyses were performed by combustion analysis<sup>†</sup> in oxygen at high temperatures ( $\approx 2200^\circ\text{C}$ ), obtained by the exothermic reaction of aluminum with vanadium pentoxide. Additional nitrogen content measurements were obtained by inert gas fusion analysis. Infrared spectra of bulk samples (prepared as thin wafers or in KBr pellets) and thin films (applied to silicon or silver chloride substrates) were collected using a Fourier transform infrared spectrometer.<sup>‡</sup> Fractional shrinkage of the bulk samples was measured in flowing air and ammonia using a dual pushrod quartz dilatometer. Microhardness was measured on a standard Vicker's indenter using loads ranging from 50 to 200 g applied for 15 s.

## III. Gel-to-Glass Conversion

### (1) Oxidizing Conditions

When desiccated, metal alkoxide-derived gels result in porous xerogels of extremely high surface area (typically 400 to  $900 \text{ m}^2 \text{ g}^{-1}$ ).<sup>8,9</sup> Normally these gels are converted to dense glasses by heating under oxidizing conditions to temperatures slightly greater than  $T_g$ . During this gel-to-glass conversion, both chemical and structural transformations take place which can be summarized as follows: (1) physical desorption of water and solvents from micropore walls, (2) condensation polymerization, (3) pyrolysis of residual organics, (4) formation and collapse of micropores, and (5) viscous sintering.<sup>12</sup> Evidence of these changes is shown in Figs. 1 and 2, where infrared spectra, specific surface area, and a typical differential thermal analysis (DTA) trace are shown for a multicomponent silicate gel (composition 1) heated in air.

The infrared spectra indicate that at low temperatures residual alkoxy groups ( $1160$  and  $950 \text{ cm}^{-1}$ ), physically adsorbed water ( $3400$  to  $3450$  and  $1635 \text{ cm}^{-1}$ ), and hydroxyl groups ( $\text{Si-OH}$  at  $\approx 3600 \text{ cm}^{-1}$  and  $\text{B-OH}$  at  $\approx 3250 \text{ cm}^{-1}$ ) are present. Heating in air results in loss of water, carbonization and oxidation of residual organic groups, and sintering, as shown by the DTA trace and the plot for specific surface area. From calculations based on the pore size ( $3.4 \text{ nm}$  pore diameters) and surface area ( $\approx 500 \text{ m}^2 \text{ g}^{-1}$ ), it

<sup>†</sup>Model 240B elemental analyzer, Perkin-Elmer Co., Norwalk, CT.

<sup>‡</sup>Model 7199, Nicolet Instrument Corp., Madison, WI.

was concluded that prior to sintering the spacing between adjacent pores is small (1.5 to 4.5 nm) so that hydroxyl and alkoxy groups are more likely located on the surfaces of the continuous micropores along with physically adsorbed water and solvents.<sup>8</sup> The reaction mechanisms which occur during heating may then be represented as occurring at the pore surface as shown schematically below:

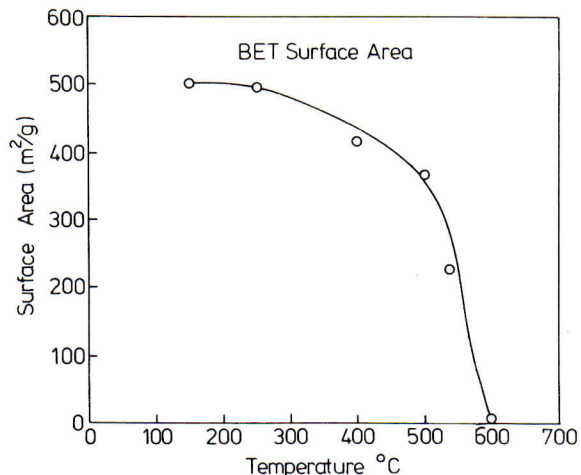
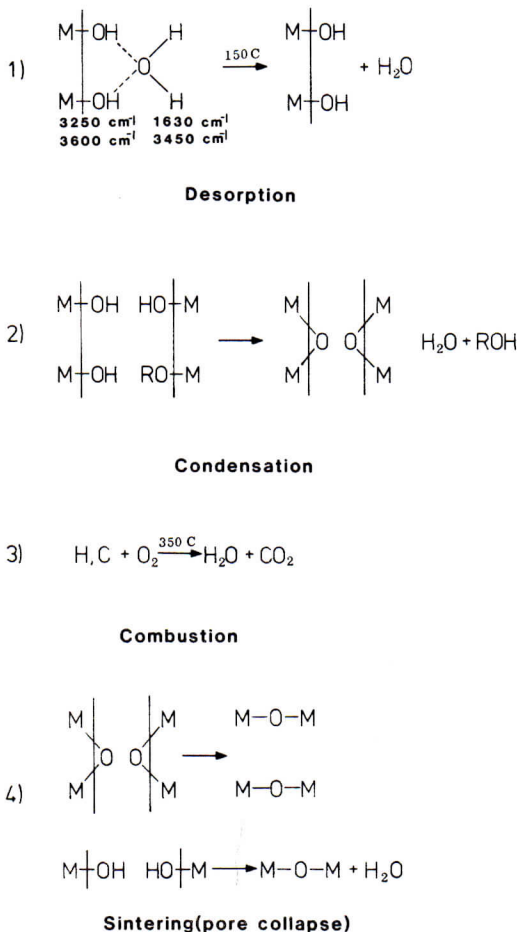


Fig. 2. Specific surface area vs treatment temperature for gel 1 heated in air.

These reaction mechanisms have received general acceptance in both sintering<sup>13</sup> and spectroscopy literature<sup>14</sup> and account for the spectral changes observed in numerous investigations of the gel-to-glass conversion.<sup>15,16</sup>

**(2) Ammonia Atmosphere**

The conversion of a porous, nitrogen-free gel to an O-N glass by heat treatments in a reactive gas such as NH<sub>3</sub> requires that reactions occur to replace oxygen with nitrogen. Thus, in addition to the chemical and structural transformations which occur during heating in a relatively nonreactive gas (with respect to the network, i.e. air), it is necessary to consider the numerous reactions which can occur between ammonia and a porous gel surface. These reactions can be summarized as follows: (1) physical and chemical adsorption of ammonia, (2) condensation of OH and OR groups, (3) dissociative chemisorption of ammonia, (4) network reduction, and (5) condensation of amines. The contribution of each of these mechanisms to the gel to O-N glass conversion will be discussed.

The introduction of ammonia at room temperature to a gel previously desiccated at 40°C results in immediate adsorption. As shown for colloidal silica,<sup>8,17</sup> and porous 96% SiO<sub>2</sub> glass,<sup>18</sup> the

<sup>8</sup>Cabosil, Godfrey L. Cabot, Inc., Boston, MA.

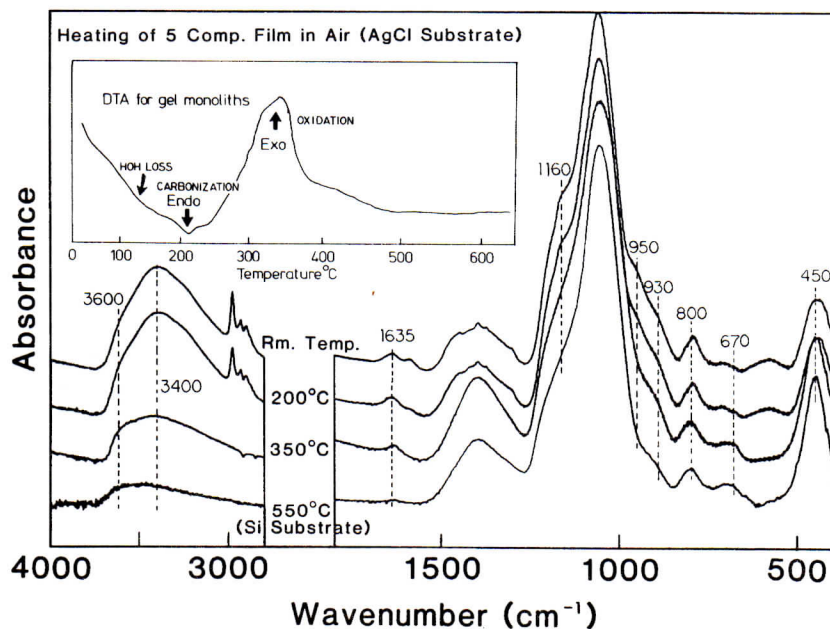
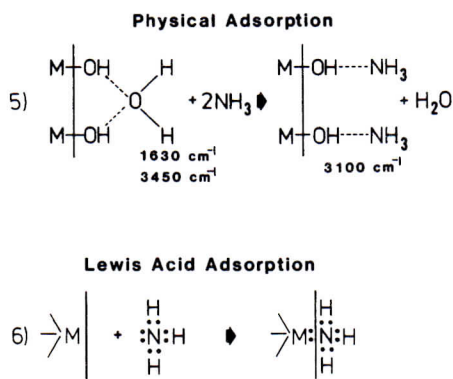
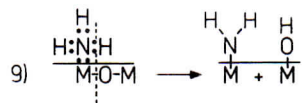
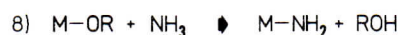
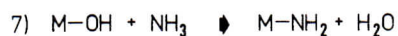


Fig. 1. Infrared spectra and DTA trace (inset) for gel 1 heated in air. Spectra were collected at room temperature from thin films deposited on AgCl or Si.

adsorption processes which occur at room temperature may be physical or chemical as illustrated below:

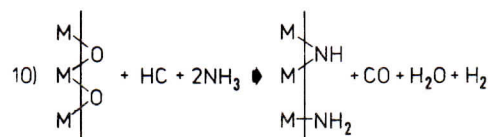


As the temperature is increased, ammonia is expected to react with the gel surface according to the following reactions:



Mulfinger<sup>19</sup> proposed reaction 7 to account for dehydroxylation of silicate glass melts. Morrow *et al.*<sup>20</sup> proposed this reaction involving the normal isolated silanols to account for the reaction of  $NH_3$  with silica at 650°C. Reaction 8 is known to occur for organosilicon compounds<sup>21</sup> and is known to occur in general for reactions of metal alkoxides with amino groups (e.g. the reaction of dibutyltin diethoxide with ethanolamine).<sup>22</sup> Repeated twice more, both reactions 7 and 8 result in chemically dissolved nitrides (N in three-fold coordination with M) with a corresponding removal of water or alcohol. Reaction 9, dissociative chemisorption of ammonia, occurs by Lewis acid adsorption followed by dissociation. This reaction is expected to be important for systems containing strong Lewis acids, i.e. boron or aluminum. Reaction 9 is not expected for  $SiO_2$  or the silica component of the glass unless the surface has been dehydroxylated at  $T > 400^\circ C$  or unless the silicate network is subjected to mechanical strain. Both these conditions result in the generation of a highly reactive site presumed to be an asymmetrical siloxane bridge containing an electron-deficient silicon atom which can act as a Lewis acid center.<sup>23</sup> Mulfinger proposed reaction 9 to account for nitridation of borate melts because, according to Bruckner<sup>24</sup> and Franz,<sup>25</sup> the hydroxyl groups in borate glasses are more tightly bound than in silicate glasses and, thus, are less likely to react with  $NH_3$  according to reaction 7. Correspondingly, Mulfinger found that, when bubbled with ammonia under similar experimental conditions, soda-lime silicate melts were completely dehydroxylated while only 60% of the OH groups were removed from borate melts. This suggests that nitridation of silica may occur predominantly by reaction 7, whereas the nitridation of boric oxide may occur predominantly by reaction 9.

In gels containing residual carbon resulting from acetates or unhydrolyzed alkoxy groups, another reaction is likely to occur which can be represented generally as:



Reaction 10 might be described as network reduction. This reaction would be especially favored at higher temperatures where: (1) ammonia is likely to be dissociated, creating a very reducing atmosphere and (2) M-O-M linkages are more easily broken. According to Low and Ramasubramanian,<sup>26</sup> the bridge bonds B-O-B are more easily broken than the bonds Si-O-Si or Si-O-B; therefore, it is expected that B-O-B linkages will preferentially react according to reactions 9 and 10. As discussed for reaction 9, strained M-O-M linkages formed by dehydration and dealcoholization (e.g. reaction 2) should allow reaction 10 to occur at lower temperatures.<sup>23</sup>

From the previous discussion, it is apparent that multicomponent silicate gels can undergo numerous reactions with ammonia, resulting in nitridation with, in some cases, a corresponding removal of water and organics. According to the law of mass action, at constant temperature the extent of these reactions depends on the difference in partial pressures of the reactants and reaction products. Thus, if the reaction products, e.g.  $H_2O$ ,  $ROH$ , or  $CO$  are continually removed or if a large excess of ammonia is supplied, the equilibria will shift to the right side of the equations. Nitridation of gels should then be promoted generally by working in flowing atmospheres or at high  $P_{NH_3}$ . However, the individual contributions of each of the proposed mechanisms to the nitridation process cannot as yet be predicted.

#### IV. Physical and Spectroscopic Measurements

##### (1) Nitrogen Content

Figure 3 shows the removal of carbon and the uptake of nitrogen for two samples of composition 1 heated to the indicated temperatures at 1°C/min in flowing  $NH_3$  or in flowing air. Also plotted are nitrogen contents for this composition after various heat treatments in ammonia at higher pressures (0.7 to 1.3 MPa). These data show that reactions causing removal of carbon, e.g. reactions 8 and 10, occur gradually over a wide temperature range for ammonia treatments, whereas combustion in air causes rapid carbon removal at  $\approx 350^\circ C$ . These data also indicate a strong dependence of ni-

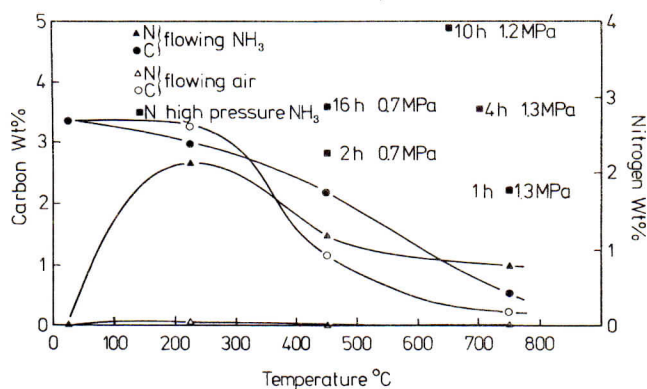
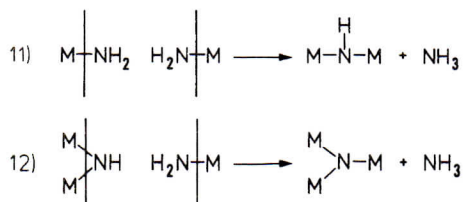


Fig. 3. Measured carbon and nitrogen contents for gel 1 heated in flowing air or  $NH_3$  and in high-pressure  $NH_3$ .

tridation on both  $P_{\text{NH}_3}$  and treatment time, i.e. at any temperature, longer treatment times and/or higher  $P_{\text{NH}_3}$  resulted in increased nitridation. Measured nitrogen contents for air-fired gels were very low (0.2 wt%). Heat treatments of gels in pure nitrogen (6.5 h at 500°C) at higher pressure (2.0 MPa) resulted in gels of only slightly higher nitrogen contents compared to air (0.10 to 0.23 wt%). In addition, nitrogen-fired gels were dark brown due to residual carbon.

Compositionally, no obvious trend in nitridation was observed for the multicomponent silicate gels (compositions 1 to 4); however, pure silica gels heated at 1°C/min in flowing  $\text{NH}_3$  contained low nitrogen contents, 0.07 to 0.49 wt%, for treatment temperatures up to 1090°C. Thus, the extent of nitridation appears to be strongly influenced by the Lewis acidity of the metal atoms. This suggests that Lewis acid adsorption and/or dissociative chemisorption involving boron and/or aluminum are primarily responsible for low-temperature (<1000°C) nitridation. Although it is reported that dehydroxylation of silica surfaces at  $T > 400^\circ\text{C}$  in vacuum forms Lewis acid centers which were found to be highly reactive to ammonia<sup>23</sup> at room temperature; apparently the heat treatments in the presence of ammonia result in only a limited formation of these sites.

The results represented in Fig. 3 suggest a third trend which has not been reported in previous studies of porous glass, i.e. the reduction of nitrogen content at higher temperatures during densification. This reduction may be a consequence of the polymerization process which accompanies sintering (pore collapse) as shown below:



If ammonia is initially only singly bonded to network-forming cations, M, then a 3-fold reduction in nitrogen content might be expected during sintering to produce N in 3-fold coordination with M. In practice, the reduction was a factor of approximately 2, which might indicate that either reaction 12 predominates or that some amine groups are retained in the final glass (as in reaction 11). The practical consequence of having reactions such as 11 and 12 accompany sintering is that, whereas nitridation reactions are promoted by high  $P_{\text{NH}_3}$ , polymerization reactions are promoted by low  $P_{\text{NH}_3}$ . Therefore, the optimum O-N synthesis conditions are predicted to be long isothermal treatments in flowing or pressurized ammonia at intermediate temperatures, where the porous structure is stable, followed by sintering in an ammonia-free atmosphere, i.e. vacuum or gas of high molecular diffusivity and solubility such as He. For example, the glass prepared by heating composition 3 in flowing  $\text{NH}_3$  at 750°C for 16 h followed by vacuum sintering at 900°C was dense, colorless, and optically transparent (Fig. 4). Measured nitrogen contents of glasses prepared in this manner were between 1.5 and 2.0 wt%.

## (2) Infrared Spectroscopy

Evidence for the adsorption mechanisms suggested by reactions 5 and 6 were obtained from infrared spectra for gels of composition 1 heated in air or  $\text{NH}_3$  to 220°C. Because the samples were too optically dense to measure the transmission spectra directly, these samples were powdered and pressed into KBr pellets for the infrared studies. In accordance with reaction 5, the spectra showed that ammonia caused a reduction in intensity of bands due to physically adsorbed water (3450 and 1630  $\text{cm}^{-1}$ ) and adjacent hydrogen-bonded hydroxyl groups (3600  $\text{cm}^{-1}$ ). Two new bands

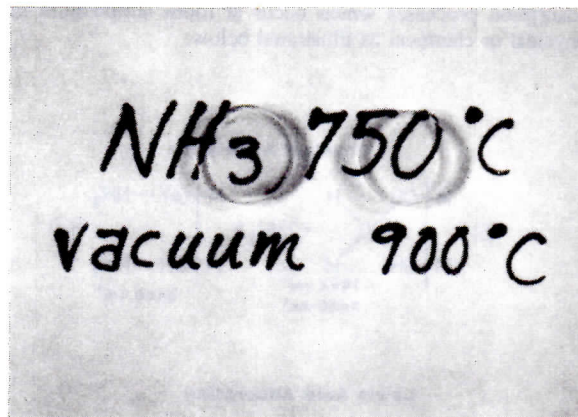


Fig. 4. Gel 3 after 16-h heat treatment in flowing  $\text{NH}_3$  at 750°C followed by vacuum sintering at 900°C for 1 h.

at 3100 and 1400  $\text{cm}^{-1}$  were present in the ammonia-treated sample, which are attributed to  $\text{NH}_4\text{Br}$  which is formed when chemisorbed ammonia is pressed at high pressure into KBr pellets.<sup>27</sup> There may also be some contribution to the 3100  $\text{cm}^{-1}$  band from the M-OH stretch vibrations perturbed by hydrogen-bonded ammonia. Unfortunately, the exchange of  $\text{NH}_4^+$  with  $\text{K}^+$  in KBr does not allow an exact determination of the adsorption site or sites for ammonia, but the exchange does prove that ammonia chemisorbs on the gels heated to 220°C, in accordance with reaction 6.

The infrared spectra of the gels heated to 750°C in flowing ammonia and air are presented in Fig. 5 along with their difference spectrum. The important features involve a decrease in the B-O stretching band at 1405  $\text{cm}^{-1}$ , the appearance of a new band (shoulder) at 1510  $\text{cm}^{-1}$ , a broadening of the Si-O stretching mode at 1088  $\text{cm}^{-1}$  coupled with a 4  $\text{cm}^{-1}$  shift to lower energy, and an increase in the intensities of the O-Si-O and Si-O-Si bending modes at 798 and 466  $\text{cm}^{-1}$ , respectively (for these assignments, see Ref. 28). A decrease in the B-O intensity is expected if nitrogen is incorporated according to reactions 9 and 10. We attribute the 1510  $\text{cm}^{-1}$  shoulder to a B-N stretching vibration. This vibration has been shifted to higher energy from its normal position of 1370  $\text{cm}^{-1}$  in boron nitride by the presence of the more electronegative oxygen. A shift to higher energy has also been observed for the Si-N stretching vibration when oxygen is introduced into silicon nitride to form a silicon oxynitride compound.<sup>29</sup> Lucovski<sup>30</sup> demonstrated that similar shifts in Si-H stretching modes can be quantitatively determined from the electronegativity of substituent groups.

The broadening of the Si-O stretching vibration in Fig. 5 may be due to greater disorder or bond strain caused by the introduction of nitrogen into the network of the  $\text{NH}_3$ -treated sample. This would also account for the greater relative intensity of the O-Si-O and Si-O-Si bending vibrations. These bending modes are dependent on bond angle distortion, and since the vibrational force constants of the O-Si-O and Si-O-Si bending vibrations are 14 and 100 times smaller than the radial Si-O stretching force constant,<sup>31</sup> the intensity of these bending vibrations is more sensitive than the stretching vibration to the local environment of the glass matrix. The subtraction scale factor used in Fig. 5 was chosen to most nearly cancel the Si-O stretching band. Therefore, the difference spectrum simply demonstrates this greater sensitivity of the bending vibrations to local perturbations. Similar observations were made previously for SiH vibrations in hydrogenated amorphous silicon.<sup>32</sup>

It should also be noted that the broadening on the low-energy side of the Si-O stretching vibration may have a contribution from the presence of Si-N stretching vibrations. The slight (4  $\text{cm}^{-1}$ ) shift in the Si-O stretching frequency to lower energy<sup>33</sup> and the observed formation of a low-energy shoulder at 970  $\text{cm}^{-1}$  (Ref. 34) is expected if a portion of the nitrogen is incorporated in

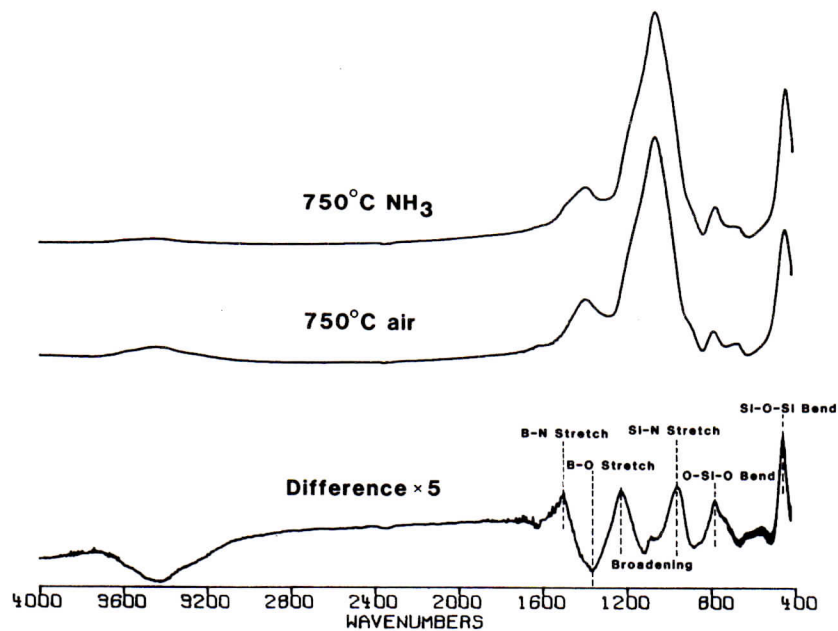


Fig. 5. Infrared absorbance spectra of gel 1 in KBr after it was heated to 750°C in flowing  $\text{NH}_3$  and in air. KBr blank spectra were subtracted from each spectrum to eliminate the small  $\text{H}_2\text{O}$  component of KBr pellet. Scale of difference spectrum has been expanded by a factor of 5.

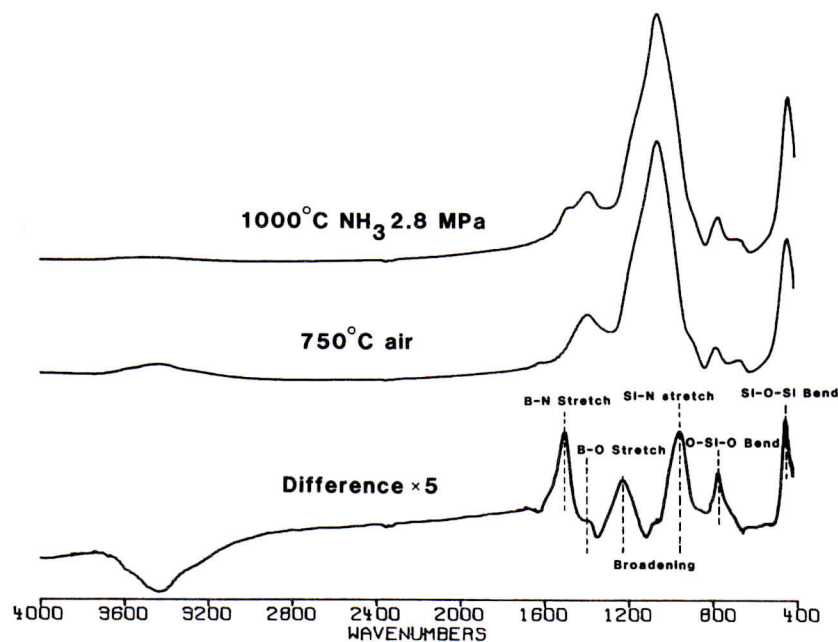


Fig. 6. Infrared absorbance spectra of gel 1 in KBr after it was heated 1000°C in pressurized  $\text{NH}_3$  (2.8 MPa) and to 750°C in flowing air. KBr blank spectra were subtracted from each to eliminate the small  $\text{H}_2\text{O}$  component of KBr pellet. Scale of difference spectrum has been expanded by a factor of 5.

the glass in the form of Si–N bonds. Habraken *et al.*<sup>34</sup> recently observed a band at  $980\text{ cm}^{-1}$  in nitrated  $\text{SiO}_2$  films. They assigned this band to the Si–N stretching vibration of a silicon oxynitride, and they found that the frequency of this band is somewhat dependent on the O/N atom ratio. Thus, it is most likely that the development of the  $\approx 970\text{ cm}^{-1}$  shoulder in this study is due, at least in part, to the formation of a silicon oxynitride. The B–N and Si–N bands become even more pronounced in the high-pressure  $\text{NH}_3$ -treated samples, as demonstrated in Fig. 6. The greater formation of B–N and Si–N bonds with increased  $\text{NH}_3$  pressure is expected from reactions 5 to 10.

Transmission spectra of the densified bulk gels, along with the difference spectrum, are presented in Fig. 7 for gels of composition 2 treated in air to 750°C and in  $\text{NH}_3$  to 750°C followed by vacuum sintering for 1 h at 900°C. Because the spectra represent that of the bulk gels, the spectra are optically too dense to obtain meaningful information below  $\approx 2000\text{ cm}^{-1}$ . The spectra in Fig. 7 have been scaled for their relative thicknesses. The difference spectrum was obtained by zeroing the  $3596\text{ cm}^{-1}$  band followed by

a 5-fold scale expansion. Both air- and ammonia-treated samples have a band at  $3596\text{ cm}^{-1}$  due to the presence of OH in the bulk glass. The reduced intensity of this band in the ammonia-treated sample is presumably a result of dehydroxylation by ammonia (reaction 7). In addition, the dense ammonia-heated glass shows considerable evidence of N–H stretching modes. The new bands introduced during  $\text{NH}_3$  treatment are located at 3531, 3430, 3336, 3273, and  $3196\text{ cm}^{-1}$  with a shoulder at  $3400\text{ cm}^{-1}$ . Although the full interpretation of these bands awaits studies with single- and binary-composition glasses, the observed bands have been reported previously in the literature (e.g. see Ref. 35) and have been variously assigned to N–H stretching vibrations for groups attached to Si, Al, and B. The  $3200\text{ cm}^{-1}$  band, however, may be due to the presence of  $\text{B}(\text{OH})_3$ . Further information is obtained from the transmission spectra by comparing the relative intensities of the  $2748\text{ cm}^{-1}$  B–O band in the  $\text{NH}_3$  and air-treated samples.<sup>3</sup> The absorption coefficient for this band is less in the  $\text{NH}_3$ -treated sample ( $4.2$  vs  $3.2\text{ cm}^{-1}$ ), indicating a decrease in B–O bonds with the increase in the number of B–N bonds. This is expected from

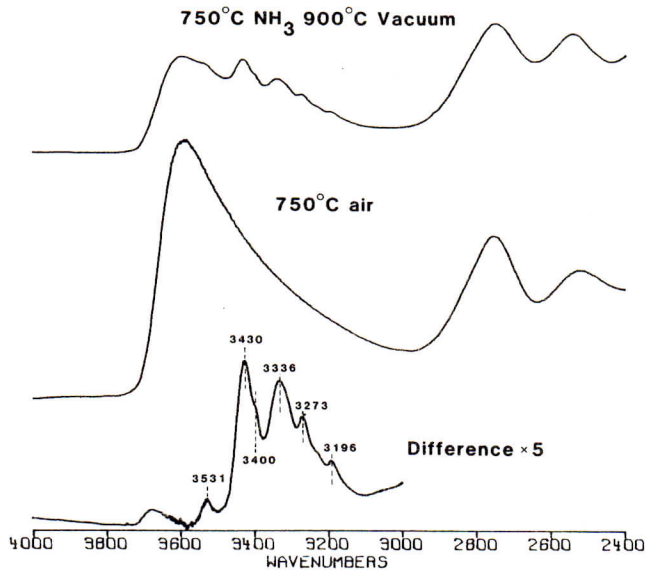


Fig. 7. Infrared absorbance spectra of bulk gel after it was heated to 750°C in NH<sub>3</sub> followed by 900°C in vacuum and to 750°C in air. Scale of difference spectrum has been expanded by a factor of 5.

the proposed reactions with ammonia in which B–O–B linkages are preferentially broken to form B–N (reaction 9) and as indicated from KBr pellet studies (Fig. 5).

The nitrogen content and ir results indicate that ammonia reacts with multicomponent gels to form M–N linkages with all of the network-forming cations Si, Al, and B. However, nitridation at  $T < 1000^\circ\text{C}$  is obviously promoted by substitution of B and Al for Si and is accompanied by reduction of B–O bonds. This suggests that the more important nitridation reaction mechanisms are: (1) Lewis acid adsorption (reaction 6), (2) dissociative chemisorption of ammonia (reaction 9), and (3) preferential breakage of B–O–M linkages during network reduction (reaction 10). Because the Lewis acid properties of B would be greatly influenced by its coordination with oxygen prior to the introduction of ammonia, investigation of the system SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O (where Na:B varied from 0 to 1) would greatly help to provide an understanding of the contribution of each of the proposed mechanisms to nitridation.

### (3) Physical Properties of Ammonia-Treated Gels

From studies of the conversion of silicate and borosilicate gels to glass by heat treatments in air, it was concluded that densification can occur by at least three mechanisms: condensation reactions (e.g. reaction 2), structural relaxation, and viscous sintering.<sup>8</sup> Chemisorption of ammonia necessarily changes the possible condensation reactions which can contribute to densification at low temperatures. In addition, nitrogen in three-fold coordination with M serves as a crosslinking agent which should increase the glass-transition temperature and, therefore, the required sintering temperature (e.g. Ref. 1).

Figure 8 shows fractional shrinkage as a function of temperature for two gel samples (composition 3 which differs from compositions 1 and 2 only by a slight reduction in Na<sub>2</sub>O). One sample was heated at 2°C/min in dry air while the other was heated at 2°C/min in ammonia to 650°C, followed by heating in vacuum at 2°C/min to 850°C. It is apparent from this figure that the ammonia treatment affects both the low- and high-temperature portions of the shrinkage curves, presumably due to the presence of chemisorbed ammonia as evidenced by the ir results. Estimates of  $T_g$  made from these curves were 725° and 790°C for the air- and ammonia-treated samples, respectively. Above  $T_g$ , the shrinkage curve for the ammonia-treated sample has a steeper slope and shows a greater total shrinkage than the air-fired sample.

These results are consistent with those reported previously, in which the shrinkage of an air-fired gel was compared to the shrinkage of a gel which had been previously heated to 450°C in am-

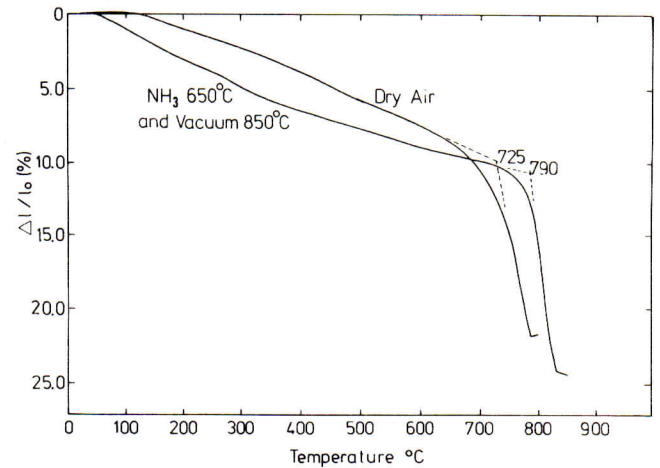


Fig. 8. Fractional shrinkage vs temperature for gel 3 heated at 2°C/min in flowing air or in flowing NH<sub>3</sub> (to 650°C) followed by vacuum (to 850°C).

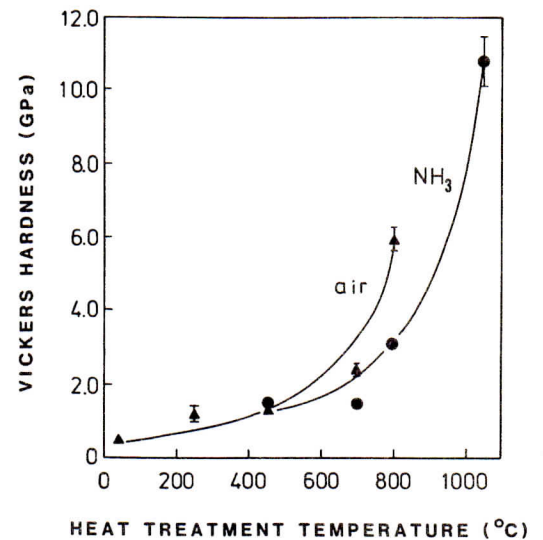


Fig. 9. Vickers microhardness vs treatment temperature for gel 3 heated in flowing air and in flowing NH<sub>3</sub>.

monia.<sup>7</sup> In that study, the 450°C treatment resulted in only a 30°C increase in  $T_g$ ; however, as in the present study the shrinkage curve of the ammonia-treated sample was steeper and showed greater total shrinkage. The steepness of the curve might imply a greater activation energy for viscous flow,<sup>36</sup> whereas the greater total shrinkage might reflect the higher density of O–N glasses compared to their oxide counterparts.

Numerous reports have indicated that O–N glasses exhibit increased microhardness and decreased thermal expansion coefficients compared to oxide glasses. These comparisons are made in Figs. 9 and 10 for microhardness and thermal expansion, respectively. Figure 9 shows the values of Vicker's microhardness measured after heat treatments at 1°C/min to the indicated temperatures in air or ammonia. Both samples exhibited very low microhardness at low temperature due to extensive microporosity. Sintering above 700°C caused a sharp increase in microhardness for the air-fired sample. The value for microhardness obtained for the dense air-fired gel equals that generally measured for melted aluminoborosilicate glasses  $\approx 5.8$  GPa. The ammonia treatment increased the sintering temperature and caused a significant increase in the value of microhardness measured for the dense gel, presumably due to the formation of a more highly crosslinked network.

Figure 10 compares the thermal expansion (measured in flowing

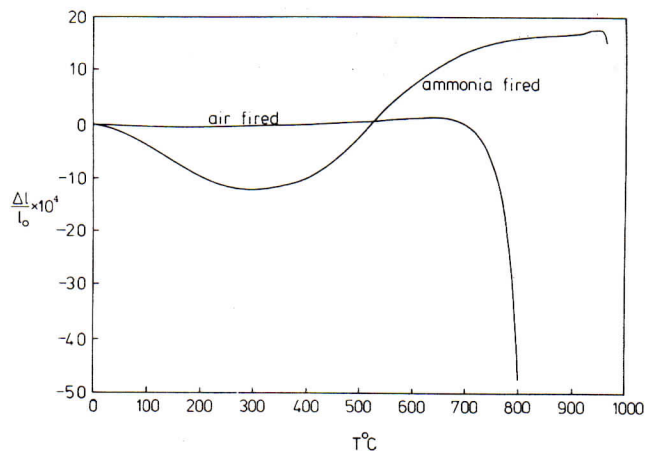


Fig. 10. Fractional change in length for gel 3 after densification in flowing air and in flowing  $\text{NH}_3$  (16 h at 650°C followed by vacuum to 900°C).

air) of a dense air-fired gel to that of a dense ammonia-treated gel (composition 3 prepared as indicated in Fig. 4). The air-fired sample exhibits a very low positive expansion up to its softening point,  $\approx 750^\circ\text{C}$ . The ammonia-fired sample, however, exhibits a net negative thermal expansion from room temperature to  $\approx 500^\circ\text{C}$ . Above  $500^\circ\text{C}$ , the net expansion is positive up to the softening point,  $950^\circ\text{C}$ . The magnitude of the negative thermal expansion coefficient is extremely large for an isotropic material ( $\alpha_{(RT \text{ to } 500^\circ\text{C})} = -44 \times 10^{-7}/^\circ\text{C}$ ). At present, because it is very difficult to prepare the oxide and the O-N glasses corresponding to composition 3 from the oxide and nitride powders, it is not understood whether the measured expansions are due simply to compositional effects or the fact that these glasses were prepared from gels.

## V. Conclusions

Four reactions were proposed to explain the observed results of ammonolysis of porous multicomponent silicate gels. These reactions are: (1) Lewis acid adsorption of ammonia, (2) condensation of ammonia with OH and OR groups, (3) dissociative chemisorption of ammonia, and (4) network reduction. The specific contributions of each of these reactions to nitridation have not yet been determined, but it was demonstrated that boron and possibly aluminum content,  $P_{\text{NH}_3}$ , and treatment time all are important to the nitridation process. It was also shown that molecular nitrogen does not react significantly with multicomponent silicate gels at temperatures up to  $500^\circ\text{C}$  and pressures up to 2.0 MPa, thus supporting the proposed mechanisms of nitridation.

Comparisons of infrared spectra obtained from air-treated and ammonia-treated gels indicated that by  $220^\circ\text{C}$  ammonia had displaced adsorbed water and had adsorbed onto Lewis acid sites. By  $750^\circ\text{C}$  more nitrogen had been incorporated into the gels, primarily as B-N, with a corresponding reduction of B-O. Spectra collected from dense gels (after sintering at  $900^\circ\text{C}$ ) showed evidence of  $\text{NH}_2$  and  $\text{NH}$  attached to Si, Al, and B, which indicates that  $\text{NH}_3$  does not react exclusively with boron and that even after heating to  $900^\circ\text{C}$  not all nitrogen is in three-fold coordination with network-forming cations.

The optimum processing conditions for O-N synthesis are predicted to be long isothermal treatments in flowing or pressurized ammonia at intermediate temperatures (slightly below  $T_g$ ) followed by vacuum or He sintering at temperatures slightly above  $T_g$ . Glasses prepared under these conditions were dense, colorless, and homogeneous, and contained 1.5 to 2.0 wt% nitrogen. Nitrided gels exhibited improved physical properties such as increased microhardness and glass-transition temperature. Nitridation also significantly affected thermal expansion characteristics of dense gels.

Ammonia treatments of porous multicomponent gels were

shown to result in O-N glasses at relatively low temperatures ( $< 1000^\circ\text{C}$ ) without melting. The nitrogen contents measured for nitrided gels were in the same range as those measured for conventional melt-formed oxynitride glasses and, thus, the gel route provides a useful low-temperature alternative to melting of oxide and nitride powders. It is also interesting to note that in gel-derived O-N glasses there was strong evidence for B-N bonding, whereas B-N bonding is difficult to achieve in a melt. This is due to the apparent low solubility of BN in most O-N melts (BN, in fact, is often used as crucible material) and to the fact that  $\text{B}_2\text{O}_3$  is unstable with respect to  $\text{Si}_3\text{N}_4$ .<sup>36</sup> (It is reduced to form  $\text{SiO}_2 + \text{N}_2$  causing vigorous frothing). Therefore, in addition to low-temperature formation, the gel route also expands the compositional range of O-N glass formation.

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