Formation of Oxynitride Glasses by Ammonolysis of Gels

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Porous borosilicate gels were heated in ammonia at 460°C. The ammonia treatments reduced the carbon and hydrogen content and increased the gel sintering temperature. The increased sintering temperature was attributed to an increase in T_g due to chemically dissolved nitrogen.

Oxynitride Glass Formation

THERE are two usual methods of preparing oxynitride glasses: (1) dissolving nitrides such as Si_3N_4, AlN, or Li_3N in silicate melts,[1-3] and (2) treating melts with gases (e.g. N_2 or NH_3).[4,5] The first method requires high temperatures (1750°C) for melting and homogenizing the glass. The second incorporates only small amounts of nitrogen into the melt (<1 wt% dissolved in soda-lime-silica melts).[4] Elmer[6,7] found that treatment of a porous borosilicate glass (98% SiO_2, 2% B_2O_3) in ammonia from 500° to 1050°C caused dehydroxylation as well as the incorporation of nitrogen. In comparison with treating melts with N_2, his method resulted in higher levels of nitrogen addition (3 to 7 wt%); however, to date, studies have been limited to high-silica glasses.* This report describes a method, based on Elmer's original work, to prepare a wider variety of oxynitride glasses at low temperatures by ammonia treatments of porous gels.
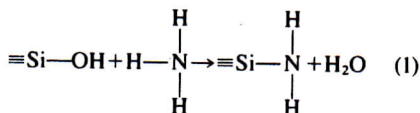
Gel structure

Recently, the physical and chemical properties of alkali borosilicate gels were investigated as a function of temperature.[8-10] These investigations showed that, below the sintering temperature, gels have extremely high-surface area (300 to 500 $m^2 \cdot g^{-1}$). Pore volumes range from 0.39 to 0.32 $cm^3 \cdot g^{-1}$ with very narrow pore size distributions averaging 3 to 4 nm in diam. Chemically, the gels are quite hydroxylated, and below ≈400°C contain up to 5 wt% carbon due to unreacted alkoxy groups, solvents, and acetates (added as

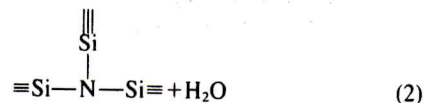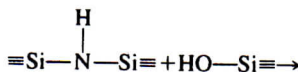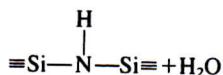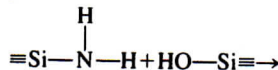salts of network-modifying cations, i.e. Na and Ba).

These physical and chemical properties were incorporated in a microstructural model of porous gels consisting of two phases: (1) cylindrical pores of uniform diameter, and (2) a low-density (high-free volume) borosilicate chain-like network.[11] Below the sintering temperature these phases occupy ≈36 and 64 vol% respectively. The spacing between pores was calculated to be ≈1.5 nm. The borosilicate network is considered to be chain-like; therefore, each network former is, on average, bonded to only 2 or 3 bridging oxygens. The remaining bonds connect to alkoxy groups (OR), where $R = (C_xH_{2x+1})^{-1}$, or hydroxyl groups. Since the spacing between pores is small, a high concentration of reactive OR and OH groups is anticipated at or near the pore surface.

Reaction with ammonia

Mulfinger[4] proposed the following reaction of ammonia with silicate melts:

$$\equiv Si-OH + H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}} \rightarrow \equiv Si-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}} + H_2O \quad (1)$$

This reaction, which causes dehydroxylation by condensation of the OH groups, can be repeated two more times to obtain N in three-fold coordination with Si (chemically dissolved or fully cross-linked nitrogen) plus two additional molecules of water:

$$\equiv Si-\underset{}{\overset{\overset{H}{|}}{N}}-H + HO-Si\equiv \rightarrow$$

$$\equiv Si-\underset{}{\overset{\overset{H}{|}}{N}}-Si\equiv + H_2O$$

$$\equiv Si-\underset{}{\overset{\overset{H}{|}}{N}}-Si\equiv + HO-Si\equiv \rightarrow$$

$$\equiv Si-\overset{\overset{\overset{|||}{Si}}{|}}{N}-Si\equiv + H_2O \quad (2)$$

This reaction probably accounts for Elmer's observations of dehydroxylation and incorporation of nitrogen in porous borosilicate glasses.[6,7]

The following reaction occurs in the ammonolysis of esters[12]:

$$\equiv C-OR + H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}} \rightarrow \equiv C-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}} + ROH \quad (3)$$
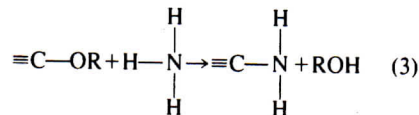
A similar reaction is proposed between $\equiv M-OR$ (where $M \equiv Si, B, Al$) and NH_3 to form $\equiv M-NH_2 + ROH$. This reaction could also be repeated to obtain chemically dissolved nitrogen with a corresponding removal of alcohol.

Because the pore phase is continuous, the bulk gel is permeable to ammonia. It follows from Reactions (1) and (2) that a high-surface area combined with large-surface concentrations of OH and OR groups could provide a large number of reaction sites for ammonolysis. Due to the high permeability and potentially large number of reaction sites, it was hypothesized that oxynitride glasses could be prepared at low temperatures by treating porous gels with ammonia.

Sample preparation method

Monolithic gels of the compositions listed in Table I were prepared by a sol-gel process similar to those developed by Dislich[13] and Thomas[14,15] in which metal alkoxides of network-forming cations (Si, Al, and B) are partially hydrolized and then polymerized to form a gel network linked by bridging oxygen atoms. Network-modifying cations, Na^{1+} and Ba^{2+}, were added as acetates in aqueous solutions.[8,9] Monolithic samples were prepared by casting concentrated solutions (12 wt% equivalent oxides) in polypropylene molds followed by slow drying.

Heat treatments were performed in anhydrous ammonia at 460±5°C. Prior to heating, the stainless steel sample chamber was evacuated to 1.3×10^{-5} Pa and backfilled with anhydrous ammonia. During the heat treatment ammonia flowed through the chamber at a rate of 160 mL/min.

Characterization methods

The carbon, hydrogen, and nitrogen contents of the gels were determined before

Table I. Glass Compositions Investigated

Composition	Constituent (wt%)				
	SiO_2	B_2O_3	Al_2O_3	Na_2O	BaO
1	71.1	18.3	7.1	0	3.6
2	69.9	18.0	6.9	1.6	3.5
3	68.8	17.7	6.8	3.2	3.5
4	66.6	17.1	6.6	6.3	3.4

Table II. HC and N Content Before and After Ammonia Treatments

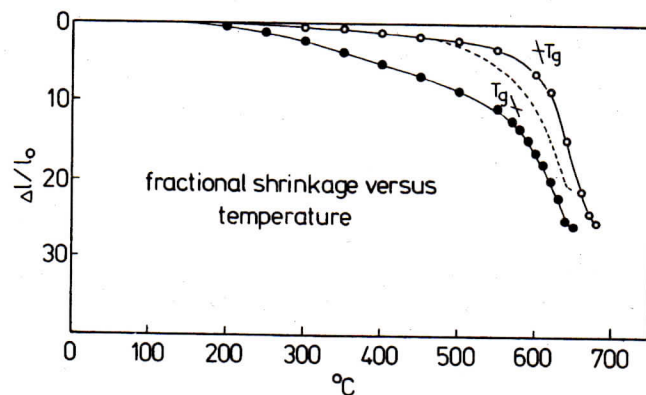| Composition	Unheated (wt%)			NH_3(460°C)			Air 460°C (interpolated)		
	C	H	N	C	H	N	C	H	N
1	5.0	2.1	0	0.3	1.1	2.9	0.6	1.2	0.1
2	4.5	1.7	0	0.5	1.0	2.0	1.1	0.7	0.1
3	4.3	1.8	0	0.1	0.5	1.3	1.1	0.6	0
4	4.6	1.6	0	0.2	0.5	1.1	0.2	0.3	0

Fig. 1. Fractional shrinkage of an ammonia-treated (○) and an untreated gel (●). Dashed line represents a vertical shift of the shrinkage curve for the untreated gel to account for shrinkage caused by low-temperature condensation reactions and volatile loss.

and after ammonia treatments by combustion analysis[†] in pure oxygen at 1000°C. Under these conditions, nitrogen which is three-fold coordinated with network-forming cations is probably not detected; therefore, the measured nitrogen contents are indicative of amine groups or unreacted ammonia entrapped within micropores.

The sintering curves of an ammonia-treated and an untreated gel were compared for composition 4 (Table I). Wafers ≈2.5 mm thick were heated at 5°C/min to 750°C in a dual pushrod dilatometer under flowing nitrogen and air for the ammonia and untreated gel, respectively. The glass transition temperature was estimated from the sintering curve by the intersection of lines extended from the low and high shrinkage portion of the shrinkage curves.

Results

Table II lists the C, H, and N contents measured before and after heating for 1 h in anhydrous ammonia at 460°C. Comparable values for heat treatments in air were estimated from plots of C, H, and N contents vs heat-treatment temperature.

It is apparent that both ammonia and air are effective in removing carbon. The ammonia-treated and air-treated samples were clear and colorless and were measured to contain low carbon contents. In comparison, heating in an inert gas, such as argon, always produced a black opaque material of high carbon content. This indicates that carbon can only be removed by a reactive gas and gives evidence for the proposed reaction between ammonia and $\equiv M$—OR groups.

Ammonia treatments also reduced the hydrogen content; however, measured H values were greater than expected for air treatments. This is probably indicative of $NH_{(3-x)}$ (where $x=0$, 1, or 2) groups due to unreacted or partially reacted ammonia.

Table II also indicates the incorporation of nitrogen into the gels, most likely as $NH_{(3-x)}$ rather than chemically dissolved nitrogen as mentioned previously. The decrease in nitrogen content with increasing Na_2O content may reflect a change in the ratio of chemically dissolved nitrogen to $NH_{(3-x)}$ groups. It might also indicate a sys-

tematic change in the pore structure or number of reaction sites.

Nitrogen chemically dissolved in glass has been shown to increase T_g. Recent work on gel sintering[11] has related T_g to the temperature corresponding to the onset of viscous sintering. As T_g increases, so does the sintering temperature. The fractional shrinkage curves for an ammonia-treated gel and a previously untreated porous gel are shown in Fig. 1. Estimates of T_g made from these curves are 575° and 605°C for the untreated and ammonia-treated curves, respectively. The ammonia-treated sample showed little shrinkage below 460°C, the temperature of the ammonia treatment, indicating the prior removal of water and organics (solvents and alkoxy groups) which normally contribute to low-temperature shrinkage. The sintering curves are therefore more properly compared by shifting the curve for the untreated sample in the *y* direction to make both curves coincide at 460°C. This comparison shows that the previous ammonia treatment caused approximately a 20° shift in the sintering curve.

These sintering results indicate that ammonia treatments cause: (1) an increase in T_g, (2) removal of water and organics, and (3) a shift toward higher temperature in the sintering behavior. This suggests that by 460°C some amount of nitrogen was incorporated into the gel network by condensation Reactions 1 and 2 and that during the ammonia treatment or during the sintering treatment some of this nitrogen became chemically dissolved in the gel network. These conclusions are further supported by very recent work in which the sintering temperature for composition 3 was increased by over 200°C, when ammonia was used as the sintering atmosphere rather than just the pretreatment atmosphere (this will be the subject of a more extensive paper).

Conclusions

Heating porous borosilicate gels in ammonia at 460°C reduces their carbon and hydrogen content and causes uptake of nitrogen. The removal of carbon and hydrogen was attributed to condensation reactions of hydroxyl and alkoxy groups with ammonia to produce M—NH_2 plus water and alcohol, respectively. The samples heated in NH_3 were clear and colorless and showed little evidence of carbonization.

The increase in sintering temperature found after heating in NH_3 at 460°C was attributed to an increase in T_g due to chemically dissolved nitrogen.

The results of this investigation show that porous gels are potentially useful precursors for preparing oxynitride glasses by ammonia treatments. The advantages of using gel precursors are: (1) lower processing temperatures compared to the dissolving of nitrides in melts, and (2) potentially wider composition range compared to Elmer's method of ammonia treatments of borosilicate glass.

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[†]Model 240-B elemental analyzer, Perkin-Elmer Corp., Norwalk, Conn.