

# Oxynitride glasses prepared by densification of nitrided silica aerogels

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Silica aerogels were nitrided by ammonia treatment at temperatures ranging from 700 °C to 1300 °C. It was found that the amount of nitrogen incorporated in silica aerogel depends on the final temperature of ammonolysis and on the time of heat treatment. The specific surface area of nitrided aerogels remains large and decreases with the temperature of ammonolysis and with nitrogen content. Nitrided aerogels can be converted into dense homogeneous oxynitride glasses containing 8.4–13.0 wt.% of nitrogen by heat treatment at 1600 °C in vacuum or in nitrogen atmosphere. The spectra of the Fourier transform infrared spectroscopy (FTIR) reveal that Si–N bonds exist in nitrided aerogels as well as in oxynitride glasses.

## 1. Introduction

The sol-gel method for glass preparation is a powerful and alternative technique to conventional glass melting. There are basically two ways of obtaining silica glass using this process. The first is hydrolysis and polycondensation of silica alkoxides, followed by a densification process [1], [2]. The xerogels prepared in this way can be densified at low temperature ( $\sim 1100$  °C) but large monolithic pieces are difficult to obtain since shrinkage and cracking caused by capillary forces usually develop during densification process. The second method is the aerogel route, involving hypercritical drying in autoclave. If the wet gel is placed in an autoclave and dried under hypercritical conditions, above the critical temperature  $T_c$  and critical pressure  $P_c$  of the liquid there is no longer any distinction between the liquid and vapour phases: the densities become equal, there is no liquid-vapour interface and no capillary pressure. The resulting gel, called aerogel, has a volume similar to that of the original sol. This process makes it possible to produce monolithic gels as large as the volume of the autoclave. Aerogels can be densified to monolithic glass without cracking and foaming at temperature  $\sim 1100$  °C.

An important problem in glass science is the preparation of nitrogen containing silica glass. It has been found that the ammonolysis of porous silica gels is an effective way to introduce a large amount of nitrogen in silica network. For example,

PANTANO and co-workers [3] reported that 40 mol% nitrogen was successfully incorporated by ammonolysis of sol-gel derived porous silica films. Silicon oxynitride glass fibers with high nitrogen content (up to 32.1 wt%) were prepared by ammonolysis of porous silica gel fibers [4].

These results show that ammonolysis of pure silica gels was affected by the geometric shapes of the gels. This suggests that the highest nitrogen content can be obtained in porous gels with large specific surface area. It is well known that the aerogels have very high porosity exceeding 95% and should exhibit good properties for nitridation. This paper presents the results of ammonolysis of SiO<sub>2</sub> aerogels. It will also be shown that the densification of nitrided aerogels leads to the formation of monolithic oxynitride glass.

## 2. Experiment

Homogeneous SiO<sub>2</sub> aerogels were prepared by hydrolysis and polycondensation of tetraethoxysilane (TEOS) in alcohol solution. A two-step hydrolysis process was performed. Initially the TEOS dissolved in ethanol was partly hydrolysed with 0.01 M HCl, then the polymerization was completed by an addition of 0.06 M NH<sub>4</sub>OH. The volume ratio of HCl:NH<sub>4</sub>OH was 3:13, and the molar ratio of TEOS:EtOH:H<sub>2</sub>O was as follows 1:2:2. The drying of the gels was performed under supercritical conditions for ethanol (243 °C, 65 bar) by applying an inert gas (N<sub>2</sub>) pressure in an autoclave. The initial pressure was 80 bar of N<sub>2</sub>, samples were heated at 50 °C/h and upon reaching 300 °C the pressure reached 240 bar. The vessel was then decompressed at 80 bar/h and cooled down.

The silica aerogels were exposed to reaction with ammonia in a silica glass tube furnace under NH<sub>3</sub> gas flow (100 ml/min.), heated at 10 °C/min. up to 1200 °C–1300 °C. The samples were kept at this temperature and then cooled down, also under NH<sub>3</sub> flux. Nitrided aerogels were sintered at 1600 °C in vacuum. The heating rate was 17 °C/min. up to 1100 °C and then 5 °C/min. to the final temperature (1600 °C). The final temperature was kept unchanged for 1 h and, after that, the furnace was cooled down rapidly. That process produced fully dense and transparent glasses.

Aerogels and glassy samples were investigated by FTIR. The FTIR spectra were recorded with KBr disk method using Bruker spectrophotometer type IFS66. The specific surface area and pore size distribution of aerogels were measured by nitrogen adsorption-desorption (BET) technique. The X-ray diffraction patterns of aerogels and glasses show that all the samples were amorphous. The nitrogen content of nitrided aerogels and glasses was determined chemically using the method of GUYADER *et al.* [5].

## 3. Results and discussion

### 3.1. Nitridation of aerogels

Different kinds of aerogels of different porosity were nitrided. The best results were obtained for aerogels of the surface area larger than 400 m<sup>2</sup>/g. Pore size distribu-

tion measured by nitrogen adsorption-desorption technique for aerogel of the surface area of  $430 \text{ m}^2/\text{g}$  is shown in Fig. 1. It can be estimated that 90% of the pore volume is in pores with diameters between 10 and 120 nm. We have found that the amount of nitrogen that was incorporated in the silica aerogel depends on the final temperature of ammonolysis and on the time of heat treatment.

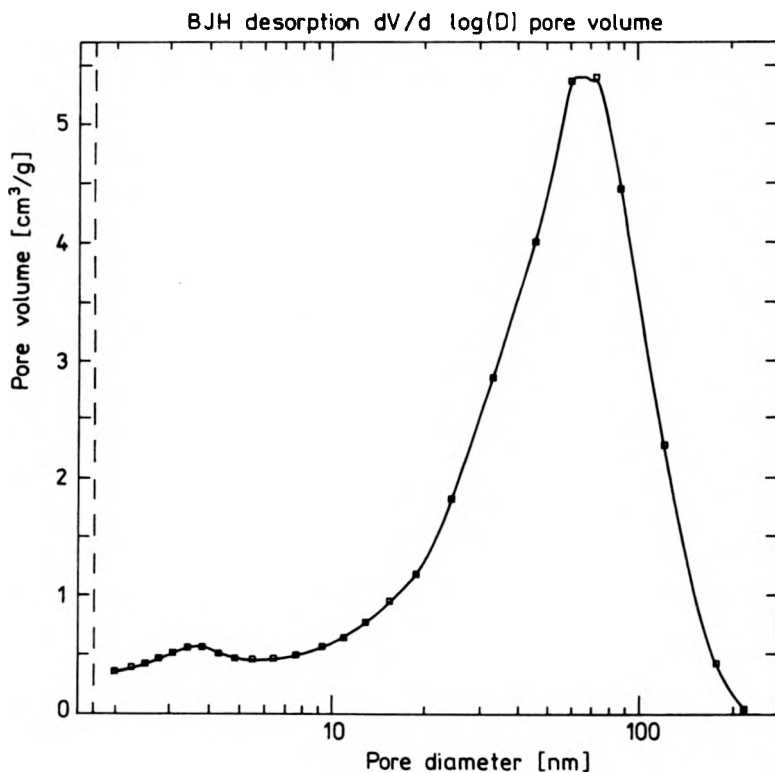


Fig. 1. Pore sizes distribution for aerogel with the surface area of  $430 \text{ m}^2/\text{g}$ . The solid line is a guide for eye.

The results of ammonolysis for different times at  $1200 \text{ }^\circ\text{C}$  for aerogel with BET surface area  $430 \text{ m}^2/\text{g}$  are shown in Fig. 2. Extensive nitridation occurs when the ammonia treatment is longer than 3 h as the nitrogen content increases to over 19 wt%. However, a longer treatment causes some saturation in the uptake of nitrogen and after 54 h of ammonolysis, the nitrogen concentration increases to 28.6 wt% only. It should be mentioned that maximum amount of nitrogen which we introduced into aerogel was 33.1 wt% but this result was achieved after 36 hours heating in ammonia at  $1300 \text{ }^\circ\text{C}$ . Figure 3 presents the results of 6 hours of ammonolysis at different temperatures (from  $700 \text{ }^\circ\text{C}$  to  $1300 \text{ }^\circ\text{C}$ ) for the same silica aerogel. It can be seen that, in this range of temperatures, the nitrogen content increases from 0.31 wt% to 23 wt%. The heating of a dry silica aerogel in air leads to gel-glass transition at  $1150 \text{ }^\circ\text{C}$ . During heating in flowing ammonia the specific surface area of the nitrated aerogels decreases slowly and remains large even at

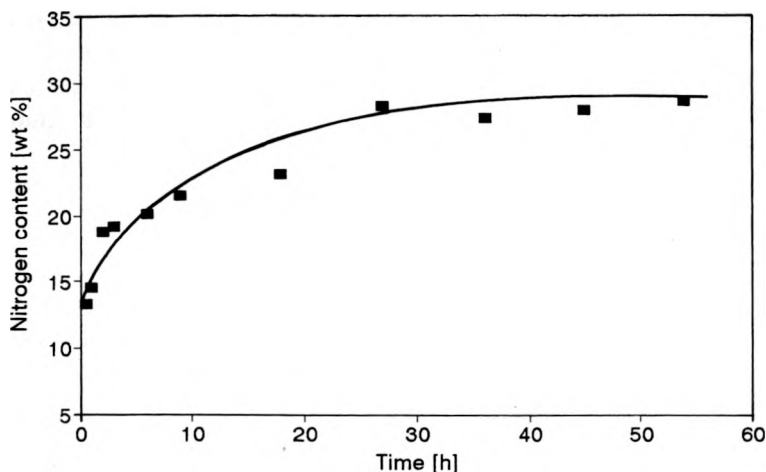


Fig. 2. Nitrogen content vs. time for aerogel heated in flowing ammonia at 1200 °C. The solid line is a guide for eye.

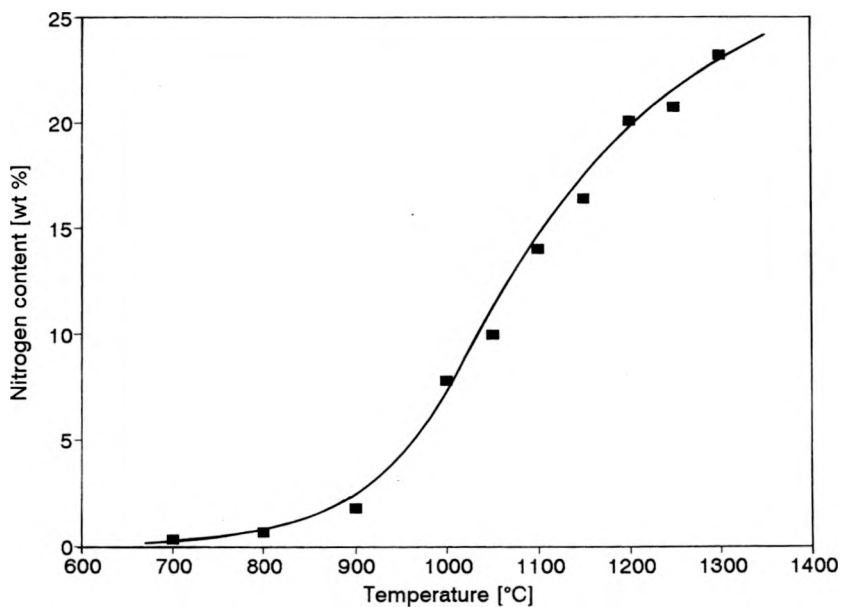


Fig. 3. Nitrogen content vs. heat treatment temperature for aerogel heated in flowing ammonia. The solid line is a guide for eye.

1300 °C (Fig. 4). The FTIR spectra of silica aerogels before and after nitridation are shown in Fig. 5. The antisymmetric Si–O stretching vibration at  $1088\text{ cm}^{-1}$  broadens and shifts towards smaller wave numbers ( $1076\text{ cm}^{-1}$ ) for nitrated aerogel. The broadening and the shift of this band can be attributed to greater disorder and bond strain caused by the introduction of nitrogen into the network. When the content of nitrogen increases, this band progressively shifts to lower wave numbers,

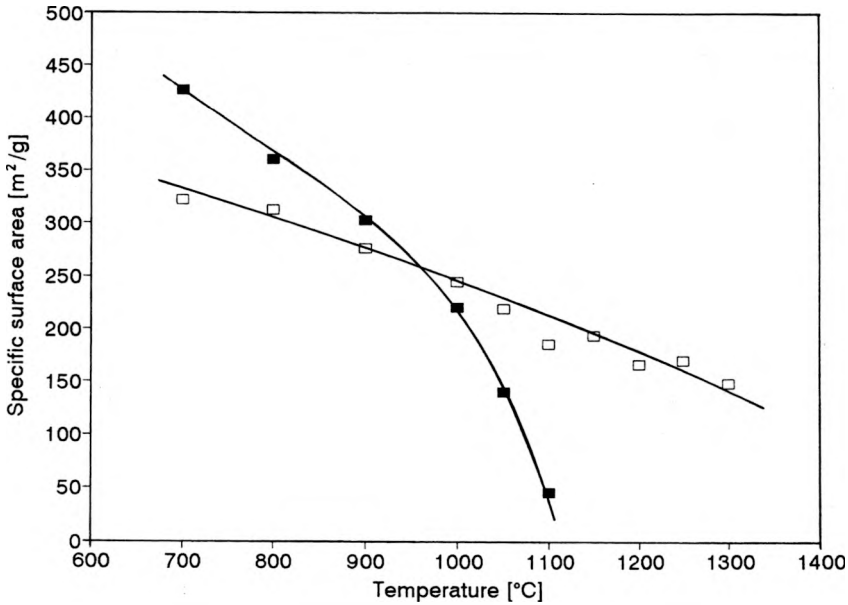


Fig. 4. Specific surface area vs. heat treatment temperature for aerogel heated in air (■) and in flowing ammonia (□). The solid lines are a guide for eye.

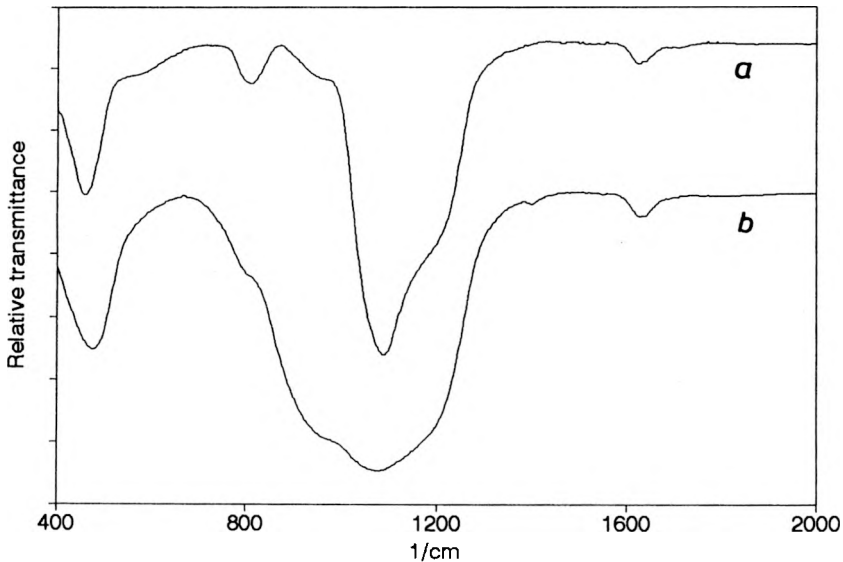


Fig. 5. FTIR spectra of silica aerogels before (a) and after nitridation (b). Nitrogen content was 15.4 wt%.

reaching a value of about  $1050\text{ cm}^{-1}$  in an aerogel with 25 wt% nitrogen. Another important feature is the disappearance of the symmetric Si–O–Si vibration at  $800\text{ cm}^{-1}$ . These changes provide evidence for the incorporation of nitrogen into the aerogel [6].

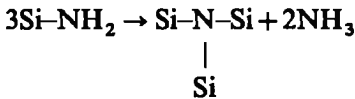
The mechanism for the incorporation of nitrogen into the silica aerogel is complicated because it is necessary to consider the numerous reactions and processes which can occur between ammonia and the porous network. Several reactions between ammonia and silica aerogel can be proposed to account for this mechanism [7], [8]. For example, at low temperatures amine species may form from interactions between ammonia and silanol groups



or with siloxane bonds



As the treatment temperature is increased, process II becomes dominant and at high temperatures (> 1000 °C) the resultant Si-NH<sub>2</sub> groups condense to form nitrides according to the reaction



According to these reactions a two-coordinated oxygen is replaced by a three-coordinated nitrogen in the aerogel structure. Consequently, the reduction in BET surface area occurs (Fig. 4). We have observed that 15 wt%–37 wt% nitrogen escaped from the aerogel during densification. This indicates that a large portion of the nitrogen is incorporated in the aerogel to form Si-N bonds.

### 3.2. Densification of nitrated aerogels

During the heating of a dry silica aerogel in air the shrinkage begins at about 800 °C, the specific surface area decreases rapidly and, at 1150 °C, the densification is fully completed (see Fig. 4). The totally densified material is transparent and exhibits the same physical properties as silica glass. However, the densification of nitrated aerogels can also be observed. We have found that the nitrated aerogels can be converted to dense oxynitride glasses by heating at 1600 °C in vacuum or in a nitrogen atmosphere. As shown in the Table, during gel to glass conversion the nitrogen content decreases to 13.0 wt%–8.4 wt% for aerogels containing 16.8 wt%–10 wt% nitrogen prior to sintering.

Table. Nitrogen content (wt%) in nitrated aerogel and oxynitride glasses.

Aerogel	16.8	15.4	12.7	10.0
Glass	13.0	9.6	9.5	8.4

The FTIR spectra for oxynitride glass and silica glass obtained by densification of silica aerogel in air are shown in Fig. 6. The antisymmetric Si-O stretching vibration observed for silica glass at 1088 cm<sup>-1</sup> broadens and shifts to 1103.5 cm<sup>-1</sup> in oxynitride glass. This shift involves a strengthening of the network and can be interpreted as sintering produced by interparticle bonding formation. In oxynitride

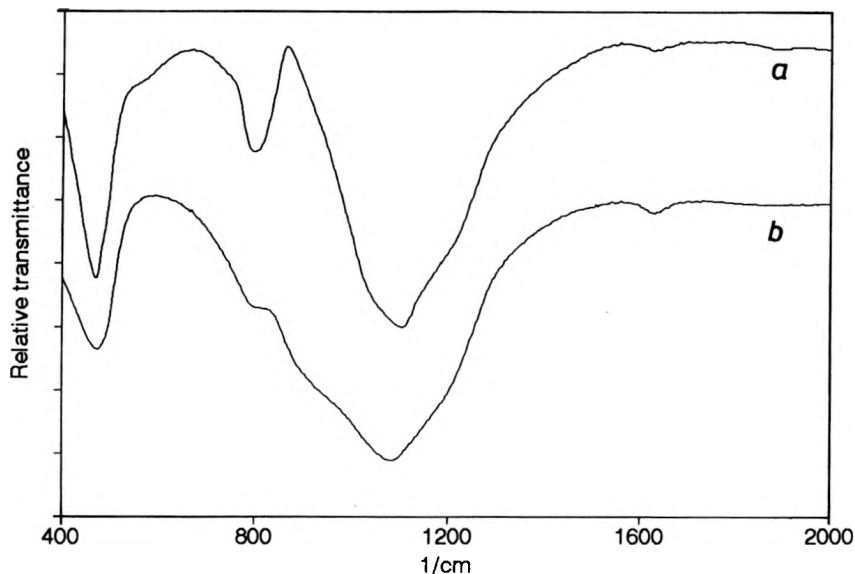


Fig. 6. FTIR spectrum of silica glass obtained after densification of silica aerogel in air (a). FTIR spectrum of oxynitride glass containing 9.6 wt% of nitrogen (b).

glass the position of this band remains at the same wavelength as in the nitrated aerogel containing a similar amount of nitrogen. Therefore, we can conclude that nitrogen is incorporated into the glass network.

Some differences are observed when the densification processes of aerogels in air and in ammonia are compared (Fig. 4). There are at least three mechanisms responsible for the shrinkage and densification of gel during the gel-glass conversion by heat treatment in air: condensation reactions, structural relaxation and viscous sintering [9]. In nitrated aerogel during densification in an ammonia atmosphere, the first reaction can be attributed to the condensation of amines. At higher temperatures, ammonia is likely to be dissociated, creating a strongly reducing atmosphere which promotes the nitridation process. Therefore, it is difficult to obtain fully densified glass during heat treatment in ammonia. In addition, nitrogen in three fold coordination serves as a crosslinking agent which should raise the glass-transition temperature and therefore the required sintering temperature of a nitrated aerogel. The important result is that the aerogel-glass conversion of nitrated aerogels proceeds in the same way as in silica aerogels and the same processes should be observed during densification, namely structural relaxation and viscous sintering.

#### 4. Conclusions

Silica aerogels were nitrated by ammonia treatment in the range of temperatures from 700 °C to 1300 °C. The amount of nitrogen incorporated in silica aerogels depends upon the final temperature of ammonolysis and upon the time of heat

treatment. The maximum amount of nitrogen introduced into an aerogel was 33.1 wt%. The specific surface area of nitrated aerogels remains large and decreases with the temperature of ammonolysis and with the nitrogen content. The FTIR spectra of nitrated aerogels indicate that the ammonia reacts with silica aerogels to form Si-N bonds. We have found that the nitrated aerogels can be converted to dense homogeneous oxynitride glasses by heat treatment at 1600 °C in vacuum or in a nitrogen atmosphere. After the gel-to-glass conversion the nitrogen contents were 13.0 wt%–8.4 wt% for aerogels containing 16.8 wt%–10 wt% nitrogen before sintering.

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