

## **Porous and Reconstructed Glasses**

Thomas H. Elmer  
Corning, Incorporated (Retired)

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# Porous and Reconstructed Glasses

Thomas H. Elmer, Corning, Incorporated (Retired)

GLASSES WITH HIGHER HEAT SHOCK RESISTANCE AND GREATER RESISTANCE TO DEFORMATION than that found in ordinary commercial glasses have been sought for decades by glass technologists. Fused quartz is an ideal glass in many ways, but fused quartz is difficult to produce in clear bubble-free form. Even at high temperatures, the glass is viscous, and the release of bubbles is slow. After melting, the glass presents difficulties in forming shapes other than tubing or sheet because the temperature required for blowing or pressing is beyond the range of known materials used for molds and plungers.

## Porous and Reconstructed Glass Processing

Glasses having the desirable properties of fused silica have been on the market for nearly a half century under the trademark Vycor. These glasses are almost pure vitreous silica. They are prepared by a unique process discovered by Hood and Nordberg (Ref 1) that circumvents the need for high temperatures in melting and forming. A relatively soft alkali-borosilicate glass is melted in a conventional manner and is then pressed, drawn, or blown into the desired but oversized shape by standard processes used in glass production. The resultant workpiece, which occasionally is given additional finishing operations, is subjected to a heat treatment above the annealing point but below the temperature that would produce deformation. During this heat treatment, two continuous closely intermingled glassy phases are produced. One phase is rich in alkali and boric oxide and is readily soluble in acids. The other phase is rich in silica and is insoluble.

After heat treatment, the workpiece is immersed in a hot dilute acid solution. The soluble phase is slowly dissolved, leaving behind a porous high-silica skeleton. The resulting porous article is commonly known as thirsty or porous glass.

In the final step of the process, the workpiece is slowly heated to  $>1200^{\circ}\text{C}$

( $>2190^{\circ}\text{F}$ ) whereby the porous structure is consolidated into a clear impervious glass known as Vycor brand 96%  $\text{SiO}_2$  glass or reconstructed glass. A flow chart of the process for making reconstructed glass is shown in Fig 1.

## Composition of Leachable Alkali-Borosilicate Glasses

The starting glasses used for the production of reconstructed glasses generally contain small amounts of alumina. A portion of the alumina is retained in the porous high-silica glass that is obtained after leaching, rendering the final sintered glass more stable against devitrification and deformation than alumina-free glass. A typical composition of a starting glass is Glass A shown in Table 1 (Ref 2). The optimum starting glasses contain up to 4%  $\text{Al}_2\text{O}_3$  for the quaternary system  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}$ .

Glass compositions in the ternary system  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$  also have been evaluated for making shaped glass components. However, these glasses generally contain a substantially higher percentage of  $\text{B}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  after leaching than glasses prepared from quaternary compositions. A typical composition that has been used extensively by numerous workers in connection with phase separation studies and the preparation and characterization of porous glass is Glass B in Table 1.

## Phase Separation

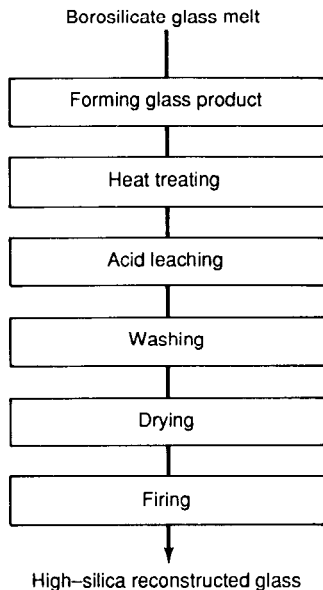
Since the discovery by Hood and Nordberg that 96%  $\text{SiO}_2$  glasses can be made from heat-treated alkali-borosilicate glasses, considerable attention has been given to the study of glasses that can be phase separated. Skatulla, Vogel, and Wessel (Ref 4) used electron microscopy to show that phase separation in the  $\text{Na}_2\text{O-B}_2\text{O}_3$  system is caused by a boron anomaly that is also responsible for phase separation in the  $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$  system and that leachable glasses are not homogeneous (this can be deduced from light scattering

measurements and the observation of opalescence of glasses that had been subjected to heat treatments). Growth of microphases with temperature was shown or discussed by Watanabe, Noake, and Aiba (Ref 5), Kühne and Skatulla (Ref 6), and others (Ref 7–10) in electron micrographs obtained by replica and transmission methods.

Some investigators proposed that the inhomogeneity in leachable glasses was caused by the formation of clusters of ions or of molecular groups similar to chemical compounds. Nordberg (Ref 11) suggested that the mutual compatibility of oxide constituents for certain glasses, particularly for alkali-borosilicate glasses, decreases on cooling from the melt and thereby leads to submicroscopic phase separation. Roy and Ruiz-Menacho (Ref 12) suggested that the phase separation in such glasses is related to the well-known phenomena of a liquid mixture separating into immiscible phases, but because of the high viscosities of glass melts which prevail at subliquidus temperatures, the liquid phases remain finely dispersed causing no light scattering. However, on subsequent heating of these glasses the submicroscopic phases start to grow, increasing in size with temperature and time (Fig 2).

## Leaching

Leaching involves the removal of the soluble constituents from the heat-treated glasses. The glasses are totally immersed in hot dilute acid solutions containing  $\text{HCl}$ ,  $\text{HNO}_3$ , or  $\text{H}_2\text{SO}_4$ . These solutions are characterized by the presence of  $\text{H}^+$  or  $\text{H}_3\text{O}^+$  ions that react with the alkali-rich phase. In glasses prepared in the  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$  system, the sodium oxide is converted to  $\text{NaCl}$ ,  $\text{NaNO}_3$ , or  $\text{Na}_2\text{SO}_4$ , depending on the type of acid used, and the boric oxide is hydrolyzed to  $\text{H}_3\text{BO}_3$ . These reaction products diffuse into the leach solution. Electroneutrality is retained even in the smallest spaces in the glass structure as the pores are filled with acid. The interaction of the acid solution with the glass leads to the gradual removal of the soluble constituents,



**Fig 1** Flow chart showing production process for reconstructed glass

leaving behind a porous high-silica structure commonly known as porous glass. This glass is generally slightly opalescent.

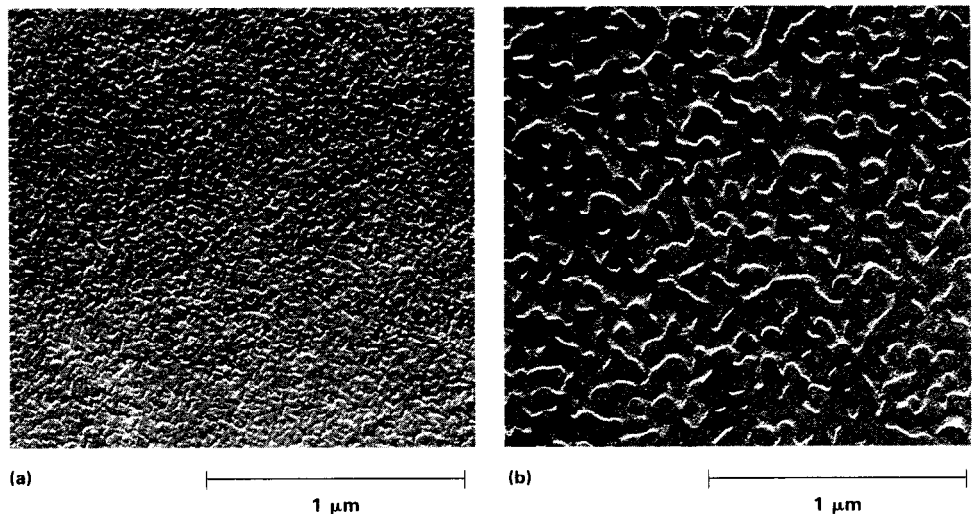
Strain develops in the leached layer as leaching progresses and it can be observed under a polarizing microscope. Swelling of the leached layer develops tensile stresses in the yet undisturbed glass while shrinkage develops tensile stresses in the porous leached layer. Excessive strain can lead to fracture following leaching. However, the strain can be controlled by the proper selection of the starting glass and by heat treatment of this glass. The patents by Hood and Nordberg that were mentioned in the section "Composition of Leachable Alkali-Borosilicate Glasses" in this article focus on this leaching problem.

The diffusion of salts and acid through the porous glass determines the rate of leaching. The rate of leaching decreases with increasing thickness and is essentially a function of the square root of the leaching time. The process is therefore best adapted to relatively thin ware with a maximum thickness of 10 mm (0.4 in.) being recommended for general purposes. However, plates  $\approx 25$  mm ( $\approx 1$  in.) in thickness have been prepared, demonstrating that it is possible to make heavier ware for

**Table 1** Typical compositions for leachable alkali-borosilicate glasses

Material	System	Composition, wt%			
		SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>
Glass A	Quaternary	62.7	26.9	6.6	3.5
Glass B	Ternary	65.0	26.0	9.0	...

Source: Ref 2, 3



**Fig 2** Photomicrographs of phase separation in 67.4 SiO<sub>2</sub>-25.7 B<sub>2</sub>O<sub>3</sub>-6.9 Na<sub>2</sub>O alkali-borosilicate glass. (a) Sufficiently resolved microstructure indicates phase separation has occurred after being heat treated at 580 °C (1075 °F) for 3 h. (b) Raised and smooth surface, which indicates silica-rich phase, has markedly coarsened after being heat treated at 650 °C (1200 °F) for 3 h. Coarsening is attributed to further coalescence of silica-rich phase into an interconnecting network caused by heating.

certain applications when the additional cost of slow leaching can be justified.

After leaching, the porous glass is washed in dilute acid and distilled water to remove the leachant in the pores. This washing procedure can take from an hour in duration to as long as overnight depending on the thickness of the porous glass being leached.

The washed porous glass can be safely dried at room temperature. During the initial stages of drying, which involves the removal of capillary water, the glass turns briefly opaque (white) and eventually becomes slightly opalescent as drying continues. The white opaque appearance is due to the temporary formation of a myriad of H<sub>2</sub>O-menisci inside the partially-dried porous glass. These menisci serve as centers for the scattering of light that is responsible for the opaque appearance of the glass.

### Properties of Porous Glass

Commercially available porous glass, the properties of which are given in Table 2, is an intermediate glass prepared by heat treating and leaching a special alkali-borosilicate glass. It has a surface area of 150 to 200 m<sup>2</sup>/g as determined by the Brunauer-Emmett-Teller (BET) method (Ref 13) using nitrogen as the adsorbate and an internal pore volume of 28%. Its pore size distribution is generally very narrow (Fig 3), with about 96% of the pores in the glass being  $\pm 0.3$  nm from the average radius that for commercial porous glass is about 4 to 6 nm (40 to 60 Å).

### Enlarging Pores in Porous Glass

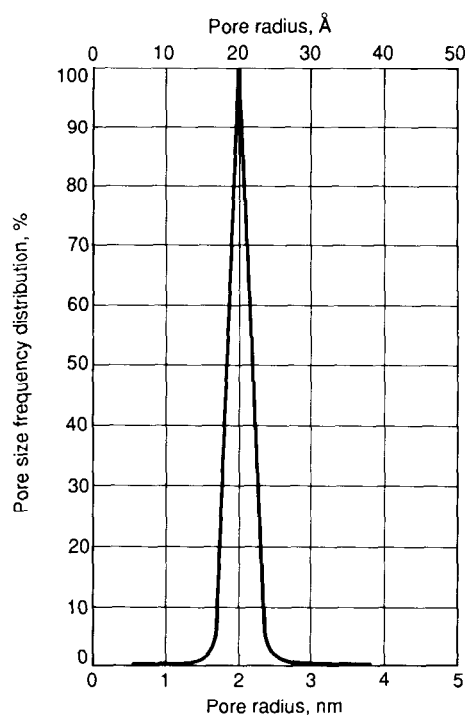
In making porous glass articles in which the pores are subsequently closed, the pore

size is generally unimportant. However, for certain applications it is desirable to have larger pore diameters. This can be accomplished by impregnating porous glass with an aqueous solution of a weakly reactive fluorine-containing compound such as 10% aqueous solution of ammonium bifluoride (NH<sub>4</sub>F·HF), reacting the compound *in situ* with a mineral acid to release hydrofluoric acid at temperatures sufficient to dissolve a portion of the glass body, and washing the treated glass to remove the soluble constituents (Ref 14). Discs and tubing with  $\approx 20$  nm (200 Å) pore size have been made from commercial glass by using such treatment or multiple treatments.

**Table 2** Composition and properties of commercially available porous glass

Composition on basis of its ignited weight:	
SiO <sub>2</sub>	96.3
B <sub>2</sub> O <sub>3</sub>	2.95
Na <sub>2</sub> O	0.04
R <sub>2</sub> O <sub>3</sub> + RO <sub>2</sub>	0.72(a)
Appearance	Opalescent
Refractive index	1.33(b)
Apparent density (dry), g/cm <sup>3</sup> (lb/in. <sup>3</sup> )	1.5 (0.054)(c)
Internal pore volume, %	28
Average pore diameter, nm (Å)	5 (50)
Internal surface area, m <sup>2</sup> /g	200
Water adsorption at saturation, %	25
Modulus of rupture, MPa (ksi)	42 (6.0)(d)
Young's modulus at 22 °C (72 °F), GPa (psi)	17.6 (2.5 × 10 <sup>6</sup> )
Loss tangent at 22 °C (72 °F), 100 Hz	0.007(e)
Dielectric constant at 22 °C (72 °F), 100 Hz	3.1(e)

(a) Chiefly Al<sub>2</sub>O<sub>3</sub> + ZrO<sub>2</sub>. (b) Depends on amount of moisture in pores. (c) Depends on relative humidity. (d) Abraded 6.4 mm (1/4 in.) rods at 22 °C (72 °F). (e) Appreciably affected by moisture; values are for specimens activated at 400 °C (750 °F), cooled in a desiccator, and then immediately tested



**Fig 3** Pore size distribution of a porous glass having an average pore diameter of 4.1 nm (41 Å)

Still larger pores can be obtained by starting with glass compositions that have been especially modified to promote the formation of coarse rather than fine interconnecting phases with heat treatment (Ref 15).

### Adsorption of Water Vapor by Porous Glass

Porous glass has been referred to as "thirsty glass" because of its affinity for moisture. Its primary advantage over other adsorbents is that it can be fabricated into relatively strong, nondusting shapes including tubing, rods (cane), disks, squares, various hollow shapes, fibers, and granules. In such forms, it lends itself particularly well for use as a nondusting drying agent or moisture getter in scientific instruments. Small disks and thin rods of this material activated at 180 °C (360 °F) in an electric oven will adsorb appreciable moisture (Fig 4).

The adsorption capacity for water at high relative humidities is not impaired by heating porous glass from room temperature to 800 °C (1470 °F). Such heating results in partial loss of hydroxyl groups [water of constitution in the form of silanols ( $\equiv\text{SiOH}$ ) and boranols ( $\equiv\text{BOH}$ )] but no appreciable loss in internal surface area of the glass (Ref 16, 17). However, to ensure maximum adsorption of water vapor at low relative humidities, it is important to heat the porous glass to <200 °C (<390 °F), a temperature at which the loss of  $\text{OH}^-$  groups and the loss in surface area of colloidal deposits in the pores of leached glass

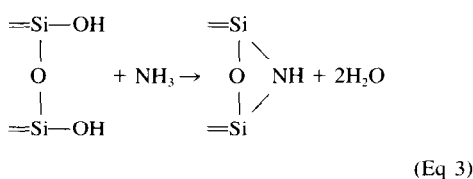
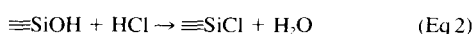
(Ref 16), resulting from acid leaching of the heat-treated starting glass, are minimal.

### Removal of $\text{OH}^-$ Groups from Porous Glass

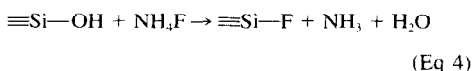
The thermal removal of hydroxyl groups from porous glass is a function of both temperature and time. The temperature for maximum removal of water decreases as the hold time increases. The optimum temperatures result from a balance in the rates of water diffusion and glass sintering that retards diffusion. A thorough discussion of thermal dehydration of porous glass is given in a paper by Elmer and Nordberg (Ref 18).

It should be pointed out that if the porous glass is rapidly heated, the capillary water (molecular water) is expelled violently causing it to break and shatter. This problem is easily avoided by equilibrating the porous glass in room air preferably at <65% relative humidity and then heating it slowly in an electric oven.

The chemistry of silanol groups in porous glass can be studied in both aqueous and non-aqueous media and in gaseous atmospheres. The hydroxyl groups in porous glass can be replaced with chloride and amide groups by treating the glass with thionyl chloride ( $\text{SOCl}_2$ ) or exposing it at elevated temperatures to atmospheres containing chlorine, hydrogen chloride, or ammonia diluted with nitrogen as shown in Eq 1 through 3:



Impregnation of porous glass with aqueous ammonium fluoride solutions followed by drying and gradual heating to 800 °C (1470 °F) also results in the removal of hydroxyl groups in such glass. This is due to a replacement of  $\text{OH}^-$  groups by fluoride ions:



There is a reduction by about a factor of 10 in the amount of water adsorbed at room temperature and low relative humidities by ammonium fluoride-treated porous glass compared to untreated porous glass under the same water vapor pressure. The substitution of fluoride ions for hydroxyl groups changes the interfacial forces between glass and water making the porous glass, which is normally hydrophilic, more hydrophobic.

### Cleaning of Porous Glass

Because porous glass adsorbs not only moisture but also organic molecules from the atmosphere, it has also been used as an organic

getter. Organic impurities in the atmosphere cause it to turn yellow or brown with time and generally necessitate the glass to be cleaned prior to use. The adsorbed organic molecules can be removed by immersing the glass in an oxidizing acid such as nitric acid to which has been added a small amount of sodium or potassium chlorate, or by treating the glass in 30%  $\text{H}_2\text{O}_2$  solution preferably at about 90 °C (195 °F). After subsequent washing in distilled water, the glass can be kept in a desiccator or stored in distilled water prior to use. Instead of wet oxidation, the organic contamination in porous glass can also be removed by gradually heating it in air or oxygen from room temperature to about 500 °C (930 °F) and holding at this temperature until all of the contamination is removed by oxidation.

Precleaned porous glass has found use in liquid chromatographic and electrophoretic separations (Ref 19).

Commercially available porous glass generally has a mean pore diameter of 4 to 6 nm (40 to 60 Å) that is much smaller than the mean free path (10 to 100 nm, or 100 to 1000 Å) of most gases at atmospheric pressure and temperature. This also makes porous glass a suitable material for porous membranes to be used at elevated pressures for the separation of gases.

By using special leaching, washing, and various post treatments, it also is possible to prepare semipermeable porous glass membranes with superfine structure capable of purifying water that has been contaminated with mineral salts and of desalinating sea water (Ref 20–22).

The above information, which is by no means complete, shows that porous glass is a versatile inorganic material. It has been and continues to be of interest to workers in diverse scientific fields chiefly because of its unique properties (Table 2). The mechanical strength of porous glass is discussed in a recent paper by Elmer, Helfinstine, and Seward III (Ref 23).

### Controlled-Pore Glass

Haller (Ref 24, 25) developed porous glasses with very sharp pore distribution that can be tailor-made for having mean pore diameters over a range from 7.5 to 300 nm (75 to 3000 Å). These glasses have become known as controlled pore glass (CPG). These glasses have found wide application for size-exclusion and adsorptive chromatography of proteins, nucleic acids, viruses, and high polymers. They have been covalently derivatized and are used as such for affinity chromatography, as solid support for bioactive molecules in bioreactors and diagnostic kits, and as substrates for sequential analysis and synthesis of deoxyribonucleic acid (DNA) and proteins.

Controlled-pore glass is generally made in the form of granules and is now offered for sale in various pore sizes by a company called

CPG, Inc. of Fairfield, New Jersey. The primary application is in permeation chromatography, where the chemical resistance and mechanical stability of porous glass significantly exceeds that of polymer materials used for the same purpose. Because of the organophilic nature of porous glass, its internal surface can be modified with organo-functional silane coupling agents. It can also be modified by using the methods of classic biochemistry. The surface-treated controlled-pore glasses have found uses for the preparation of specialized diagnostic products and for the immobilization of enzymes in fixed-bed reactors.

### Reconstructed Glass Products Obtained from Consolidation of Treated and Impregnated Porous Glass

A whole family of reconstructed glasses can be made by starting with

- Alkali-borosilicate glass and varying the conditions of heat treatment, leaching, and firing
- Porous glass and subjecting the leached glass to additional processing steps (for

**Table 3 Properties of consolidated 96% silica glass**

Refractive index	1.458
Average thermal expansion coefficient (0 to 300 °C, or 32 to 572 °F), °C <sup>-1</sup> (°F <sup>-1</sup> )	$7.5 \times 10^{-7}$ ( $4.2 \times 10^{-7}$ )
Density, g/cm <sup>3</sup> (lb/in. <sup>3</sup> )	2.18 (0.0788)
Annealing point, °C (°F)	1020 (1870)(a)
Specific heat, cal/g · °C	0.18
Thermal diffusivity, cm <sup>2</sup> /s	0.009
Thermal conductivity, W/m · K (cal/cm · s · °C)	1.38 (0.0033)
Total normal emissivity, 100 °C (212 °F)	0.87
Young's modulus at 22 °C (72 °F), GPa (psi)	68 ( $9.8 \times 10^6$ )
Shear modulus at 22 °C (72 °F), GPa (psi)	28 ( $4.0 \times 10^6$ )
Poisson's ratio	0.19
Modulus of rupture at 22 °C (72 °F), abraded surface MPa (ksi)	48 (7.0)
Hardness, HK <sub>100</sub> kgf/mm <sup>2</sup>	487
Dielectric constant at 22 °C (72 °F):	
1 MHz	3.8
8.6 GHz	3.8
Electrical resistivity, Ω · cm:	
Log <sub>10</sub> ρ at 250 °C (480 °F)	9.7(b)
Log <sub>10</sub> ρ at 350 °C (660 °F)	8.1(c)
Chemical durability, weight loss, mg/cm <sup>2</sup>	0.0005(d)(e), 0.07(f), 0.90(g)

(a) 1080 °C (1975 °F) for special processed ware. (b) 11.4 for special processed ware. (c) 9.7 for special processed ware. (d) 5% HCl at 100 °C (212 °F) for 24 h. (e) Reconstructed Pyrex glass is ten times as durable in 5% HCl as Pyrex No. 7740 glass (which itself has excellent acid resistance). (f) N/50 Na<sub>2</sub>CO<sub>3</sub> at 100 °C (212 °F) for 6 h. (g) 5% NaOH at 100 °C (212 °F) for 6 h

example, impregnation with various coloring oxides prior to consolidation into an impervious glass)

Consolidation of the leached glass (porous glass) generally involves slowly heating it to >1200 °C (>2190 °F) so that the porous structure is consolidated (sintered) into an impervious clear high-silica glass. The end product undergoes shrinkage of 35% in volume or about 14% in linear dimensions. For this reason, the starting glass that is melted in a conventional manner and is blown, drawn, or pressed must be formed into oversize shapes.

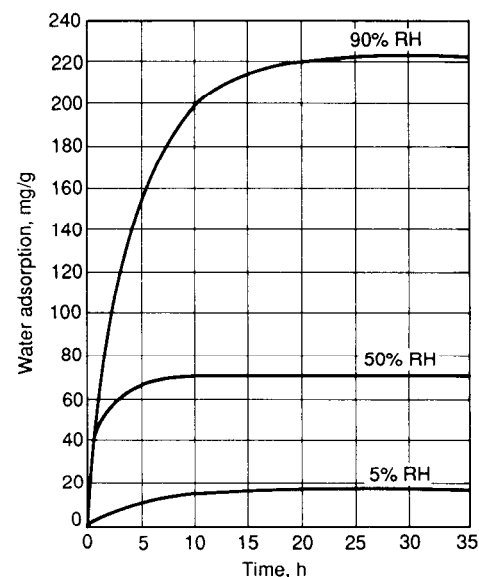
Products made from consolidated reconstructed 96% SiO<sub>2</sub> glass are comparable in performance and properties to those of fused quartz and silica. The end products have excellent heat shock resistance, allowing them to be heated repeatedly to red heat and then plunged into ice water without breakage. Special firing and outgassing *in vacuo* significantly reduce the hydroxyl content in such glass to ensure greater heat resistance. The lower water content (hydroxyl groups) in the glass workpiece reduces any tendency of the glass to deform at high operating temperatures and allows the glass to be used continuously at 900 °C (1650 °F) and intermittently at >1200 °C (>2190 °F). The consolidated glasses are mechanically strong and their strength increases at higher temperatures. Selected properties of reconstructed glass are given in Table 3.

### Transmittance Properties of Reconstructed Glasses

The ultraviolet transmittance of 96% SiO<sub>2</sub> glass can be engineered to produce glasses with cutoffs at nearly any desired wavelength in the ultraviolet spectrum. This is accomplished by varying the leaching and firing conditions and by impregnating the porous glass with appropriate ultraviolet absorbing inorganic salts that upon firing supply network forming or modifying ions (for example, Ce<sup>4+</sup>, Sn<sup>4+</sup>, Ti<sup>4+</sup>, V<sup>4+</sup>, V<sup>3+</sup>, and Fe<sup>3+</sup> ions).

Reconstructed 96% SiO<sub>2</sub> glasses effectively transmit infrared radiation. Degassing of the porous glass in a vacuum prior to its consolidation substantially increases the infrared transmittance of the glass but does not completely eliminate the absorption band at 2.73 μm (109 μin.) (Fig 5), that is attributed to the presence of OH<sup>-</sup> groups in the structure of the glass. Impregnation of the porous glass with aqueous fluoride-containing solutions, followed by drying and firing in air or in a vacuum eliminates hydroxyl groups, thereby substantially improving the usefulness of such a glass as an infrared window (Ref 26).

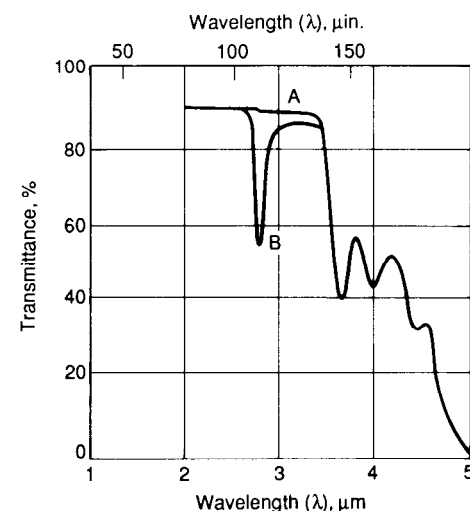
The OH<sup>-</sup> groups in porous glass can also be eliminated by subjecting the porous glass to a stream of gas containing combined or free fluorine plus a carrier gas (for example,



**Fig 4** Water adsorption at room temperature in mg/g of activated porous glass at relative humidity (RH) levels of 5, 50, and 90%. The glass was activated at 180 °C (360 °F).

nitrogen). Complete removal of OH<sup>-</sup> groups is accomplished by exposing the porous glass to a chlorine-containing atmosphere at elevated temperature prior to consolidation in a vacuum (Ref 27). The annealing point of the final glass product is markedly increased by the above treatments that result in the elimination of the OH<sup>-</sup> band in the infrared spectrum by both thermal dehydroxylation and substitution of F<sup>-</sup> or Cl<sup>-</sup> ions at OH<sup>-</sup> sites in the porous glass.

The infrared transmittance can be further increased by subjecting the porous glass to a stream of ammonia and nitrogen at elevated temperature (Ref 28, 29) and after cooling,



**Fig 5** Infrared spectra of 96% SiO<sub>2</sub> glass of 1.5 mm (0.06 in.) thickness: A, treated with ammonium fluoride; B, untreated

releaching the nitrated porous structure in hot dilute acid, drying, and then consolidating the chemically treated porous glass in a vacuum at 1350 °C (2460 °F). These glasses have annealing points in excess of 1150 °C (2100 °F), indicating that they are substantially harder than reconstructed glass prepared by conventional processing methods which have annealing points around 1025 °C (1880 °F).

### Colored Reconstructed Glasses

Porous glass is well suited for producing a wide variety of reconstructed colored glasses, including white, opaque, and black glasses. This is accomplished by simply impregnating the porous glass in aqueous solutions containing the desired coloring ions, which are generally selected from nitrate or chloride salts. The impregnated glass is rinsed in distilled water to remove excess salt solution from its surface. The impregnated glass is then dried and consolidated in air or oxygen at 1225 °C (2240 °F). In contrast to porous glasses that are colored by dipping in organic coloring solutions and then used in the air-dried state, the color of consolidated glasses is not degraded by heat.

**Red reconstructed glass** is made by impregnating porous glass in an aqueous solution containing nitrate salts (that is, of Fe, Ni, and Al), drying, and subsequently slowly heating in a stream of air to 1225 °C (2240 °F). X-ray diffraction studies (Ref 30) show that spinel crystallites, which are present in colloidal sizes, are responsible for the red color. The glass absorbs most of the visible light from a tungsten filament heated to 2425 °C (4395 °F) but effectively transmits infrared radiation and consequently is used in the form of tubing and sheet in heating applications.

**Black Reconstructed Glass.** By impregnating porous glass with furfuryl alcohol ( $C_5H_6O_2$ ) solutions, polymerizing the alcohol in the glass to a resin, pyrolyzing, and then firing to consolidate the porous structure to an impervious glass, it is possible to make a black glass. By varying the concentration of furfuryl alcohol in the impregnating solution, it also is possible to prepare glasses with resistivities ( $\log_{10} \rho$ ) at 22 °C (72 °F) ranging from 0.1 to 8.5 (Ref 31). The carbon phase in the fired glasses is amorphous. Carbon is an excellent dehydroxylating agent, removing silanols and boranols ( $OH^-$  groups) in porous glass that, if left in the structure, soften the end-product glass. Consequently, the annealing point of reconstructed glass can be markedly increased by incorporating carbon in porous glass and firing in a dry nonoxidizing atmosphere (Ref 32). The carbon-containing glasses are not only black but totally opaque to radiation in the ultraviolet, visible, and part of the infrared spectra. Furthermore, the carbon-containing glasses have excellent chemical durability and superior devitrification resistance at high temperatures compared to that of carbon-free glass, which is com-

parable to that of fused quartz and silica glasses.

**Specialized Applications.** For special heating lamp applications, porous glass tubing may be unilaterally impregnated by introducing the solution containing the inorganic glass-coloring agents in the porous glass from the external surface only. By controlling the depth of penetration of the impregnating solution, it is possible to retain a layer of clear glass along the inner wall of the tubing, indicating no colorant additives. Consolidated glass tubes prepared by this method avoid the possibility of the coloring additives reacting with other lamp components (for example, tungsten from the filament in an infrared heating lamp that could produce an adverse effect on lamp operation and/or light transmission) (Ref 33).

### Graded Seals

Thermal seals with expansion matched to fused quartz or silica and glass of higher expansion can be made by starting with short pieces of porous glass tubing (Ref 34). One end of each tube to be converted to a graded seal is impregnated with an aqueous solution composed of alkali borates and then washed to remove a part of the alkali borates from the pores near the surface of the impregnated glass. The tube is then consolidated to an impervious clear glass to prepare it for use in sealing glasses of different expansion characteristics.

### Product Applications

The above information gives some insight into how reconstructed high-silica glass products are prepared. Porous glass is not only a unique material with interesting properties but a marvelous starting material for making a whole family of reconstructed glasses that have many applications in both research laboratory and commercial industrial applications.

Reconstructed glass has favorable optical characteristics, high electrical resistivity, and excellent chemical durability and heat resistance properties that make it applicable for a wide range of applications:

- Laboratory ware
- Lamps (germicidal, photochemical, halogen-cycle, and radiant types)
- Heat sheath tubing
- Thermocouple protection tubing
- Welding torch tips
- High-temperature trays and jars
- Sight glasses
- Photomultiplier tubes
- Camera and space windows
- Exhaust tubing
- Radiant heaters
- Precision pore tubing
- Fritted glassware
- Special coatings for space vehicles

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