

## Sol–gel preparation of silica glass

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**Abstract.** This paper is a preliminary report on the preparation of silica glass containing very low amount of hydroxyl by the sol–gel processing technique. Gels were prepared from optimized amounts of tetraethyl orthosilicate, fumed silica and water. Acids and bases in small quantities were added for catalysing hydrolysis and adjusting the pH. Dried gels were heated up to 1400°C in various atmospheres to obtain transparent silica glass of the required density and very low (< 5 ppm) hydroxyl content.

**Keywords.** Silica glass; sol–gel.

### 1. Introduction

High purity silica glass finds applications in semiconductor technology, optical communication and other areas of electronic and related interest (Fanderlik 1991). The sol–gel process of preparing high purity materials has become a potential route because of inherent advantages compared to conventional processing. The high surface area of dried gels results in very high reactivity which, in turn, permits low temperature processing. Thus, unique advantages are offered by this process for the preparation of high-melting special glasses in that the glasses are obtained without melting the starting materials, at temperatures several hundred degrees below the respective melting temperatures. Global efforts (Clasen 1987; Mori *et al* 1988; Rabinovich 1989; Hensch and West 1990) are therefore in progress to develop cost-effective sol–gel technologies for the manufacture of silica glass, which is normally prepared via the melting route at high temperatures.

The present work is a preliminary report of the developments in an on-going project aimed at the preparation of silica glass containing very low amounts of hydroxyl and other impurities by the non-melting, sol–gel technique.

### 2. Experimental

Silica sols were prepared by mixing tetraethyl orthosilicate (TEOS), fumed silica (surface area  $180\text{ m}^2\text{ g}^{-1}$ ), double-distilled water and catalytic amounts of HCl. The molar composition of a standard sol was  $\text{SiO}_2$  from TEOS:  $\text{SiO}_2$  from fumed silica:  $\text{HCl}:\text{H}_2\text{O} = 1:0.75:0.01:14$ . The pH of the sol was adjusted to 4.2–4.7 by addition of  $\text{NH}_4\text{OH}$  before casting. The sol and gel preparation processes are shown in the flow diagram (figure 1).

Glasses were prepared from dried gels via heat-treatment at around 1400°C in an atmosphere control furnace. During heating, different atmospheres, i.e. vacuum, carbon tetrachloride (with nitrogen as carrier gas), oxygen and helium, were used sequentially at different stages. The physical properties of the gel monoliths were examined by mercury porosimetry (Autoscan 60, Quantachrome) and BET surface area measurement (Sorpty 1750, Carlo Erba). Hydroxyl contents of the glasses were measured by FTIR spectrometry (5 PC, Nicolet).

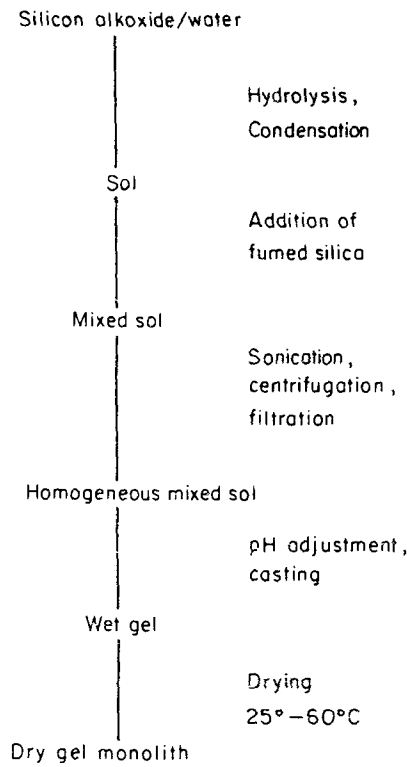


Figure 1. Flow chart for the preparation of monolithic silica gels.

### 3. Results and discussion

For obtaining an optimum workability of the sol (time at hand before gelation), an accurate control of the gelling time of a sol composition is very important. The gelling time is a joint effect of several parameters in sol preparation, e.g.  $\text{H}_2\text{O}/\text{TEOS}$  ratio, fumed silica/TEOS ratio, pH of the sol etc. In the present case, an optimum ratio of the major components of the sol was maintained (as under § 2), and the gelling time was controlled by a control of the sol pH before casting. As expected, a monotonic decrease in gelling time was observed with increasing pH (figure 2).

The range of pH selected in this work gave good workability, i.e. 15 to 40 min; lower values of pH caused unnecessary prolongation of gelling time, while higher values led to almost instantaneous gelation. A pH value of 4.7 was found suitable for most castings.

Figure 3 shows the axial shrinkage behaviour of gel rods during transition from wet to dry condition. Note that the drying time depended upon the size and shape of the wet gel. Bulk density and surface area of the dry gel bodies prepared at  $\text{pH} = 4.7$  were around  $0.8 \text{ g cm}^{-3}$  and  $360 \text{ m}^2 \text{ g}^{-1}$  respectively. The average pore diameter exhibited two modes at around 60 and 90 Å.

In the sol-gel processing route, the conversion of dried gel bodies to the corresponding transparent glass bypassing the phenomenon of melting, has been explained by the process of viscous sintering (Brinker and Scherer 1990). The

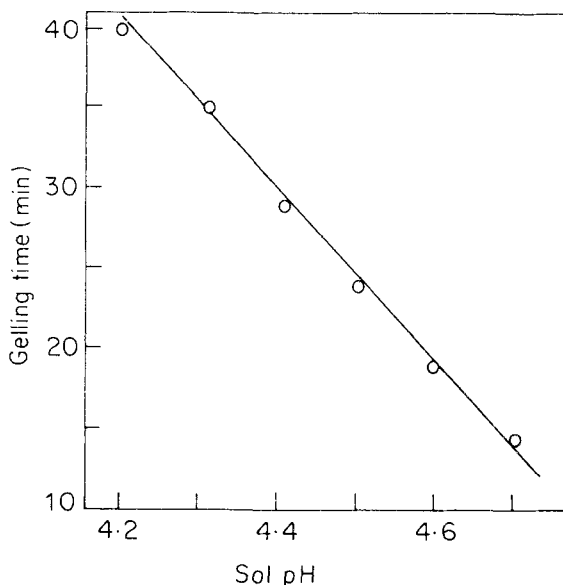


Figure 2. Effect of sol pH on gelling time.

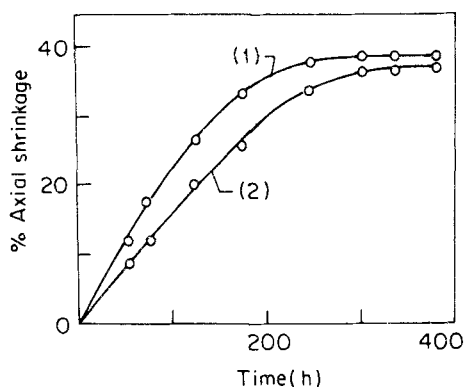
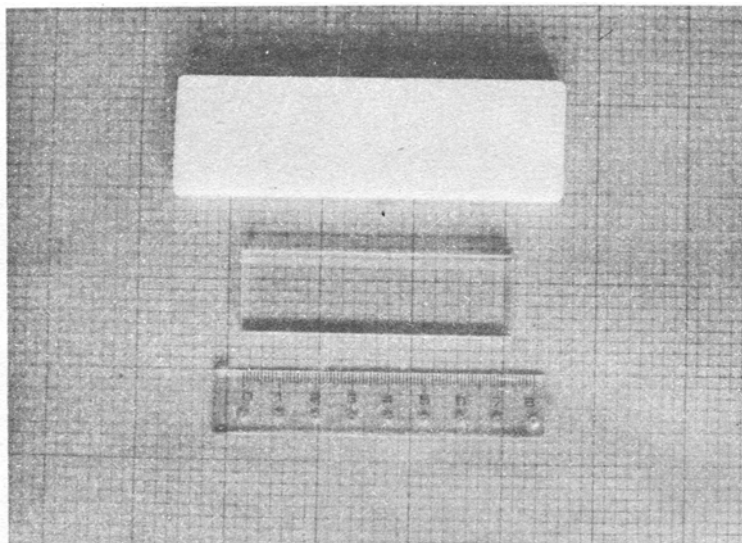


Figure 3. Time dependent axial shrinkage behaviour of gels during drying at 60°C. Curves 1 and 2 represent the axial shrinkage of gels obtained from 12 and 20 ml sols (taken in polypropylene tubes of height 18 cm and diameter 1.7 cm) respectively.

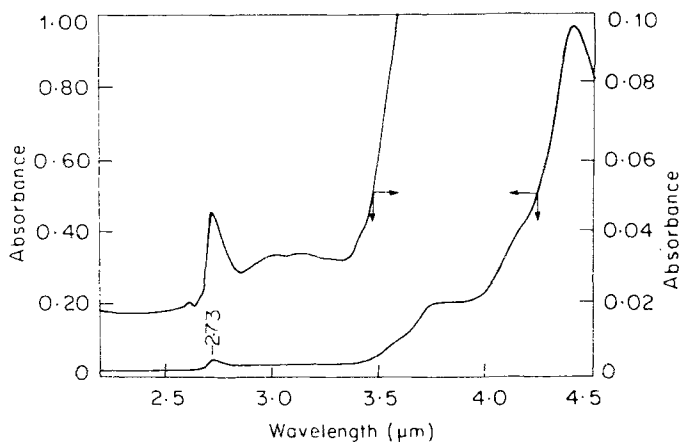
transformation thus depends on effective elimination of the pores in the gel body and consequent densification via viscous flow of material. One important factor which profoundly influenced densification in the present case was the quantum of tightly bound hydroxyl groups on the surfaces of the pores (Hench and West 1990). Hydroxyl ions on the surface of the gel/glass pores undergo dehydroxylation via OH-OH condensation leading to the formation of  $H_2O$  within the temperature range 200–1300°C, while densification via sintering takes place within 1200–1400°C. Therefore, densification and dehydroxylation (and formation of  $H_2O$  vapour) occur simultaneously in the temperature range 1200–1300°C. Thus, if densification is attempted without the removal of a substantial amount of OH groups from the gel, foaming, bloating and bubble formation will result due to the expansion of  $H_2O$  and other vapours formed and trapped in the closed pores.

To remove the OH prior to densification, the gel samples were heat-treated in  $\text{CCl}_4$  when  $\text{OH}^-$  groups were replaced by  $\text{Cl}^-$  ions. These low-OH gels, when heated in the temperature range  $1300\text{--}1400^\circ\text{C}$  in helium atmosphere, transformed into transparent silica glass. Figure 4 shows a gel body and the corresponding glass after densification. The glass samples were found to have a density very close to  $2.2\text{ g cm}^{-3}$ .

The OH content of the glasses was measured by FTIR spectrometry, following Beer-Lambert law and using an  $\epsilon$  value of  $1811\text{ mol}^{-1}\text{ cm}^{-1}$  (Shelby *et al* 1982). Figure 5 shows a typical FTIR spectrum of Si-OH at  $2.73\text{ }\mu\text{m}$ , on which the quantitative measurement was based, for a fully densified silica glass. The OH content of such glasses was found to be around 5 ppm.



**Figure 4.** An opaque gel (top) and the corresponding polished glass (bottom) after densification at  $1400^\circ\text{C}$ .



**Figure 5.** FTIR spectrum of silica glass prepared at  $1400^\circ\text{C}$  (thickness  $2.525\text{ mm}$ ); Si-OH peak at  $2.73\text{ }\mu\text{m}$  was used for quantitative measurement.

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