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Influence of temperature on the physical properties of TEOS silica xerogels

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Abstract

In the present paper, the experimental results on the influence of temperature on the physical properties such as bulk density, percentage of porosity, percentage of volume shrinkage and weight loss of silica xerogels, are reported. The xerogels have been prepared by hydrolysis and polycondensation of tetraethoxysilane (TEOS) using a new catalyst (citric acid) followed by drying at ambient temperatures ($<90°$C) and atmospheric pressure. The lowest density silica xerogels obtained were of the order of $0.22 \times 10^3\,\mathrm{kg\,m^{-3}}$. The xerogels were then heated in air at different temperatures ranging from room temperature (25°C) to 1200°C with a controlled heating rate of $1.5°\mathrm{C\,min^{-1}}$. It has been found that highly transparent ($\approx 90\,\%$), monolithic, pure and densified ($2.2 \times 10^3\,\mathrm{kg\,m^{-3}}$) silica glasses were obtained at a temperature as low as 980°C when compared to conventional melting of silica glasses ($\approx 2000°$C). The experimental results have been discussed by taking into account the processing conditions and related chemical changes. Besides the porosity and density measurements, the gels and glasses were also characterised by infrared (IR) spectroscopy and scanning electron microscopy (SEM). © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved

1. Introduction

Sol–gel processing of glasses and ceramics has attracted enormous research interest during the past several years due in part to apparent advantages, over the conventional processing in special area of glass formation [1].

A controlled densification of silica xerogels is a prerequisite for some technical applications of these highly porous, sol–gel derived and conventionally dried materials. Densification is usually carried out in the temperature range from 600 to 1200°C. In this range we get partially densified porous silica glasses. These glasses are very useful for impregnation with second phases as required for many multifunctional optical devices. Recently, this process has been extrapolated to multicomponent glasses such as SiO_2–B_2O_3 and SiO_2–P_2O_5 [2] or doped glasses with lanthanides [3]. The use of open porosity of a glass to modify the nature of material has been previously applied to "Vycor glass" [4]. Xerogels are another matrix which allows the nanocomposites [5], polymer glass composites [6], materials or clays [7] and luminescence effect [8], to be obtained. For many applications silica glasses with required percentage of porosity and transparency are needed. Although Prassas et al. [9] and Henning et al. [10] described the preparation of silica glasses using tetramethoxysilane (TMOS) as a precursor and NH_4OH as a catalyst, there is no report on the physical properties such as bulk density, percentage of porosity, weight-loss and volume shrinkage of citric acid catalysed tetraethoxysilane (TEOS) silica xerogels. Moreover TEOS precursor is less toxic and much lower in price as compared to TMOS precursor. Also, the sintering temperature of TEOS xerogel is lower ($\sim 980°$C) than TMOS aerogel ($\sim 1200°$C). Therefore, we present and discuss the results on the influence of temperature on the physical properties of TEOS silica xerogels.

2. Experimental procedure

Silica alcogels (the dispersed phase is SiO_2 skeleton and the dispersing medium is alcohol) were prepared by hydrolysis and polycondensation of solvent (ethanol (EtOH)) diluted TEOS in the presence of citric acid catalyst using the following chemical reactions:
Hydrolysis:

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$$Si(OC_2H_5)_4 + 4H_2O \overset{K}{\rightarrow} Si(OH)_4 + 4C_2H_5OH \qquad (1)$$

where, K is a catalyst (citric acid).

Condensation:

$$Si(OH)_4 + Si(OH)_4 \rightarrow \equiv Si-O-Si \equiv + 4H_2O \qquad (2)$$

$$Si(OH)_4 + Si(OC_2H_5)_4 \rightarrow \equiv Si-O-Si \equiv + 4C_2H_5OH \qquad (3)$$

The chemicals used in the present work were of "pursis" grade except TEOS which is of "puram" grade, from Fluka Company (Switzerland). Triple distilled water was used for the preparation of 0.001 M citric acid solution. The TEOS was diluted with its respective alcohol (EtOH) in order to avoid transesterification [11]. In order to obtain transparent and homogeneous silica xerogels, the molar ratio of TEOS:EtOH:H_2O was kept constant at 1:5:7, respectively. Alcogels were washed in ethanol 4 times with an interval of 24 h at room temperature before aging in 70 vol% percent TEOS/EtOH for 2 days at 60°C before drying. Aging leads to improve strength and stiffness of the silica network.

In order to obtain the best quality silica glasses in terms of transparency, homogeneity and monolithicity, isothermal sintering of TEOS xerogels covering a temperature range from room temperature to 1200°C was done with controlled heating rate of 1.5°C min^{-1} using microprocessor based Eurotherm Temperature Controller connected to a muffle furnace.

Thermogravimetric analysis (TGA) of the xerogel samples of 10 to 20 mg in weight were carried out in air atmosphere on a thermobalance with a heating rate of 1.5°C min^{-1} up to 1000°C . The physical and chemical changes lead to weight losses; were interpreted by TGA. In order to measure the volume shrinkage of the xerogels during sintering, the dimensions of the samples like diameter and length were measured accurately using a travelling microscope.

Percentage of porosity (P_r) was obtained from the values of bulk (ρ_b) and skeletal (ρ_s) densities using the relation

$$P_r = 1 - (\rho_b/\rho_s) \qquad (4)$$

The skeletal density (ρ_s) was measured by the pycnometer (QUANTACHROME) while the bulk density was measured from the known volumes and weights of the xerogels.

The surfaces of the xerogel and glass samples, heated at different temperatures have been carefully observed by SEM with Cambridge 250 MK3 scanning electron microscope. The xerogel samples were carefully cut into $3 \times 3 \times 2\,mm^3$ sizes at atmospheric pressure in a dust-proof clean chamber. Then the samples were coated with gold containing 20% palladium, at a pressure of 1.333 Pa, in order to avoid electric charge during the SEM observations. In the present work, different samples, each prepared under the indentical conditions have been examined and the results have been found to be very similar. The xerogels and glasses were also characterised by the Infrared Spectrophotometer (model: Perkin–Elmer).

3. Results and discussion

We have used parent solvent (EtOH) for the TEOS precursor and citric acid as the catalyst because this combination resulted in the best quality silica xerogels in terms of monolithicity and transparency. From the present studies it has been found that the temperature influences strongly the physical properties such as bulk density, percentage of porosity and volume shrinkage and weight loss of the citric acid catalysed (TEOS) silica xerogels.

3.1. Bulk density

The variation of bulk density versus temperature is shown in Fig. 1. Before any heat treatment, the bulk density of the xerogels has been found to be around 0.22×10^3 kg m^{-3}. After the heat treatment with a controlled heating rate of 1.5°C min^{-1}, the bulk density of the xerogel decreases from 0.22×10^3 to 0.19×10^3 kg m^{-3} with an increase in temperature from 25 to 250°C, which is due to the evaporation of the trapped solvent molecules while with an increase of temperature above 250°C, the bulk density of the xerogel

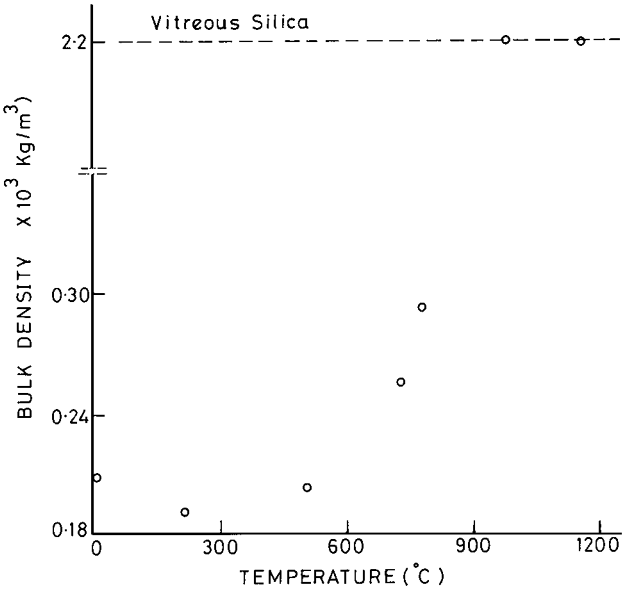

Fig. 1. Bulk density of silica xerogel vs temperature.

increases and it reaches a maximum value of 2.2×10^3 kg m^{-3} at 980°C which is equal to the density of vitreous silica. It has been found that above 980°C the bulk density remains constant. This density enhancement can also be attributed to the elimination of the steric effect of the organic species and to the smoothening of the roughness of the particles which occurs due to heat treatment [12]. During the heat treatment at higher temperatures (>950°C) the structure of the xerogels tends to change progressively towards the structure of glass. Water and unstable products are slowly eliminated and non-bridging oxygen molecules disappear. After the complete densification at 980°C, the resulted glassy structure was found to be very similar and close to the vitreous silica; and the bulk density (ρ_b) and the refractive index (n) were found to be 2.2×10^3 kg m^{-3} and 1.5, respectively.

3.2. Weight loss and volume shrinkage

The most obvious physical change that occurs when gel is heated above room temperature is shrinkage. The variation of weight loss and volume shrinkage of the xerogels as a function of temperature is shown in Fig. 2 The shrinkage curve is divided into two regions defined by the accompanying weight loss.

In region I the weight loss is substantial. In region II both the shrinkage and weight loss are substantial and at last instant (~875°C) shrinkage occurs without weight loss. The weight loss of around 16% in region I (up to the temperature of 400°C) corresponds to the endothermic reaction which is attributed to the desorption of physically adsorbed water (or perhaps residual solvent). Here in region I the removal of EtOH and H_2O contents takes place. Hence a negligible shrinkage with a weight loss of around 16% results from an increase in surface energy caused by desorption of water and alcohol. Concurrent weight loss (≈18%) and volume shrinkage (≈90%) in region II are attributed primarily to the removal of organics (principally weight loss), polymerization (shrinkage is proportional to weight loss), structural relaxation (only shrinkage) and viscous flow [13]. Shrinkage in region II is the structural relaxation a process by which excess free volume is removed, allowing the structure to approach the configuration characteristics of the metastable liquid [14]. Structural relaxation occurs by diffusive motion of the network. It has been found that the network densifies rapidly in the last stage of the region II which can be due to viscous flow and structural relaxation, an irreversible process in which the free energy decreases through bond restructuring or rearrangements with no associated weight loss at and above the temperature of 875°C has been observed.

3.3. Porosity as a function of temperature

The percentage of porosity as a function of temperature is shown in Fig. 3 It has been found that the percentage of porosity remains constant (80%) up to a temperature of around 400°C. Fig. 4 shows the SEM picture of the xerogel which is heated up to 400°C. It is clearly seen from the figure that almost all the SiO_2 particles of the network are spherical in shape and pores are uniform. This can be due to reversible dehydroxylation which occurs with the departure of physical water and decomposition of organic residues. Further increase in temperature (from 400 to 800°C) led to a decrease in

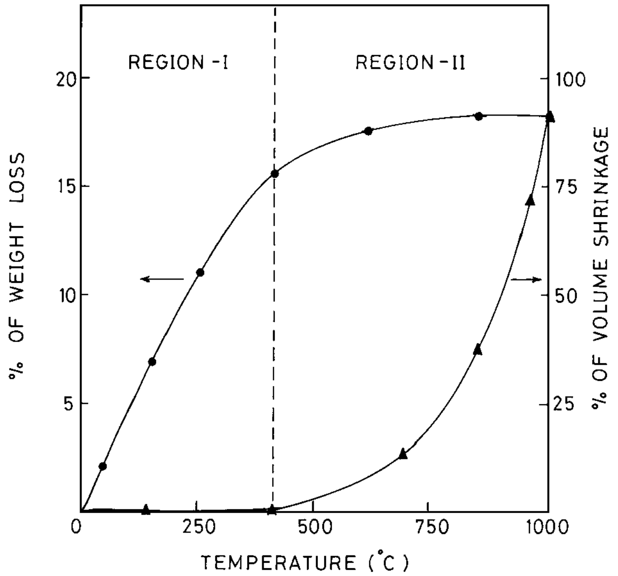

Fig. 2. Percentage of volume shinkage and weight loss of the xerogel vs temperature.

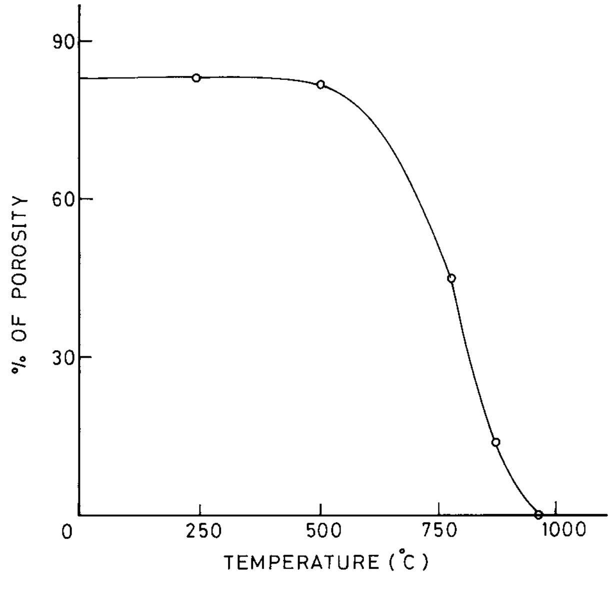

Fig. 3. Percentage of porosity of the xerogel vs temperature.

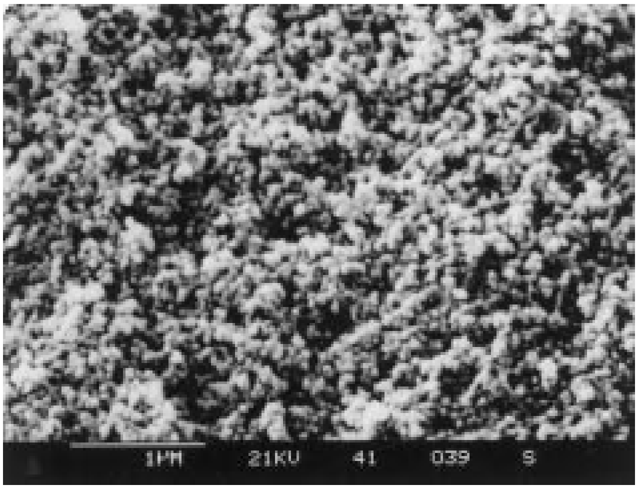

Fig. 4. SEM picture of silica xerogel heated up to 400°C.

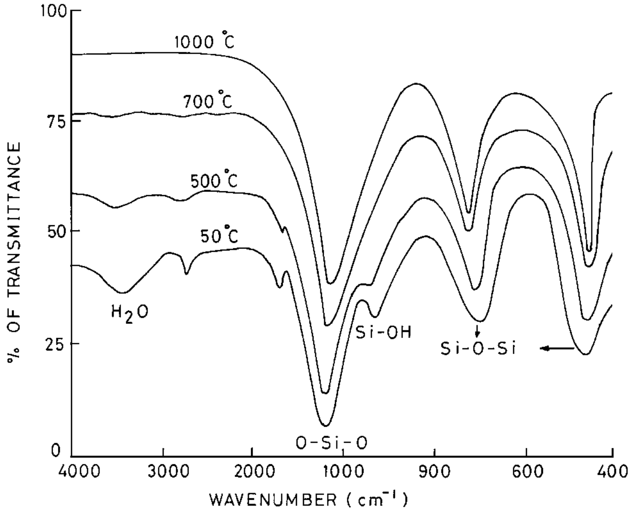

Fig. 6. IR spectra of silica xerogel heated at different temperature.

the percentage of porosity. The xerogels heated at higher temperatures of ~980°C led to the formation of continuous SiO_2 network without any porosity or negligible porosity (Fig. 3) as observed by the SEM picture (Fig. 5). This also can be due to irreversible dehydroxylation. The departure of water through condensation mainly takes place between neighbouring silica particles, on the surface, with the volume shrinkage of overall surface. Thus, the number of existing silanol groups on the gel surface is an inverse function of the densification temperature. It has been found that at ≈780°C the percentage of porosity becomes 50% to that of the initial porosity. Above 780°C, the densification process is enhanced by three mechanisms—condensation reaction, structural relaxation and viscous sintering. Due to these mechanisms the percentage of porosity was found to change drastically from 50 to 0% within the temperature range of 780 to 980°C.

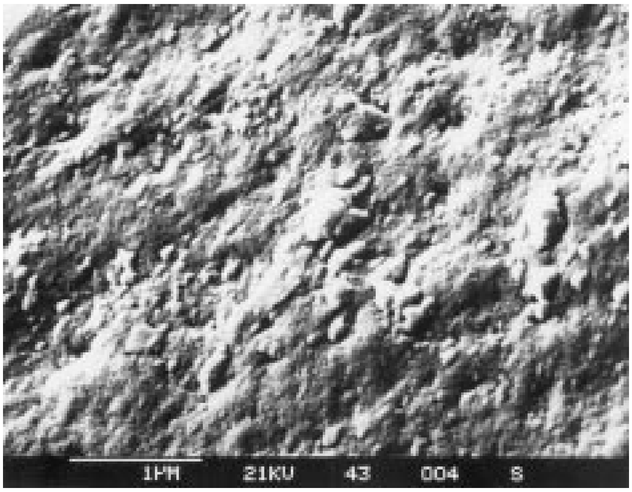

Fig. 5. SEM picture of silica xerogel heated up to 980°C.

3.4. IR spectra

Fig. 6 illustrates the infrared spectra of the silica xerogel between 4000 and 400 cm^{-1}, heated at 50, 500, 700 and 1000°C. The IR absorption bands at 3400 and 2750 cm^{-1} are characteristics for free or absorbed water and is accompanied by another band at 1620 cm^{-1}. With the heat treatment of the xerogels, these bands become weaker at and above 500°C suggesting that the gradual evaporation of water and residual ethanol. The 1080, 800 and 460 cm^{-1} bands are attributed to different modes of Si–O or O–Si–O vibrations [12,13]. The band around 950 cm^{-1} corresponds to the streching vibrations of Si–O–H. The band disappears at 700°C because of polycondensation of Si–OH bonds into Si–O–Si bonds and the evaporation of water [14,15].

4. Conclusions

We have prepared monolithic, transparent and high purity silica glasses from citric acid catalyzed TEOS silica xerogels by heating them in air at around 980°C for 8 h with a controlled heating rate of 1.5°C min^{-1}. It was found that initially within the temperature range of 25 to 250°C, the bulk density decreased from 0.22×10^3 to $0.19\times10^3\,\text{kg}\,\text{m}^{-3}$ due to significant weight loss without any volume or porosity change of the xerogels. While above 250°C the bulk density, percentage of volume shrinkage and weight loss increased with an increase in temperature. On the other hand, the percentage of porosity was found to decrease with an increase in temperature (above 250°C). Around 980°C, due to viscous flow, the xerogels have been found to yield transparent glassy masses without any porosity.

The studies on the influence of heat treatment on the acoustical and mechanical propertis of the TEOS silica xerogels are in progress.

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References

[1] (a) C.J. Brinkman, D.E. Clark, D.R. Ulrich, (Eds.), Better ceramics through chemistry. Materials Research Society Symposia Proceedings 32 (1984); (b) S. Sakka, Am. Ceram. Soc. Bull., 64 (11) (1985) 1463, (c) D.W. Johnson, Jr. Am. Ceram. Soc. Bull; 64 (12) (1985) 1597.

[2] T. Woignier, J. Phalippou, in: Proceedings of the First International Workshopon Non-Crystalline Solids, M.D. Baro, N.L. Clavaguera, (Eds.), World Scientific, Singapore, 1986, p. 415.

[3] J. Bouaziz, T. Woignier, D. Bourret, R. Sempere, J. Non-Cryst. Solids 82 (1986) 225.

[4] M.E. Nordberg, J. Am. Ceram. Soc. 27 (1944) 299.

[5] D. Hoffman, R. Roy, S. Komarneni, Mater. Lett. 2 (1984) 245.

[6] E.J.A. Pope, J.D. Mackenzie, In Better Ceramics Through Chemistry II, Vol. 73, C.J. Brinker, D.E. Clark, D.R. Ulrich, (Eds.), Materials Research Society, Pittsburgh, PA, 1986, p. 809.

[7] D. Levy, D. Avnir, J. Phys. Chem., 92 (1988) 4734.

[8] B. Dunn, E. Knobbe, J.M. Kieman, J.C. Pooxviel, J.I. Zink, in: Better Ceramics Through Chemistry III, Vol. 121, ed C. J. Brinker, D.E. Clark, D.R. Ulrich, (Eds.), Materials Research Society, Pittsburgh, PA, 1988, p. 331.

[9] M. Prassas, J. Phalippou, J. Zarzycki, J. Mater. Sci. 19 (1984) 1656.

[10] S. Henning, L.S. Svensson, Physica Scripta 23 (1981) 697.

[11] G.M. Pajonk, A. Rao, Venkateswara, N.N. Parvathy, E. Elaloui, J. Mater. Sci. 31 (1996) 5683.

[12] R. Vacher, T. Woignier, J. Pelous, E. Courtens, Phys. Rev. B-27 (1988) 6500.

[13] C.J. Brinker, G.W. Scherer, Sol–Gel Science, Academic Press, New York, 1990, pp. 542–551.

[14] G.W. Scherer, Relaxation in Glasses and Composites, Wiley, New York, 1986.

[15] N.N. Parvathy, Preparation and characterization of silicon aerogels. Ph.D. thesis, Shivaji University, Kolhapur, India, 1994.