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POROUS MATERIALS

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PREPARATION OF POROUS GLASSES FOR PHOTONIC MATERIALS

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INTRODUCTION

Porous glasses prepared by phase separation and subsequent acid leaching of separated glasses have been applied in various fields of engineering as filters, supports for catalysts or enzymes, adsorbents for chemicals, etc. [1-3]. For these applications, it is desirable that the porous glasses have a high mechanical strength, a high chemical durability, a high thermal stability, in addition to the specific pore structure desired for the purpose.

Besides applications in these fields, porous glasses have recently been used as starting materials to make high-performance glasses for optical and photonic devices. These include Gradient-Index (GRIN) lenses obtained by a molecular stuffing technique [4], quantum dots materials containing nanometer-scale semiconductor particles [5], optically-integrated circuits fabricated by a photo-patterning technique [6]. In these applications, a porous glass is impregnated with a solution containing a metal salt or photosensitive organometallic compound. Then, the glass is subjected to various heat-treatments to precipitate microcrystallites of the dopant on the micropore walls, followed by drying and sintering into a fully dense glass.

The desirable properties of the porous glasses for these applications are, therefore, entirely different from those for filters, supports, etc.. It is desirable for the pores to collapse at low temperatures rather than to remain stable up to high temperatures, in order to embed the doped microcrystallites before they

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decompose. The pores of the glasses for photo-patterning must be small enough to minimize the scattering loss of the UV light irradiated for photolitic decomposition of impregnated organometallic compounds. To hinder the growth of incorporated particles before densification, a small pore size is also important for the fabrication of quantum dots materials.

Among the porous glasses developed to date, the high-silica porous glass of the Vycor-type (HSG) with pores 2-50 nm in diameter which is appropriate for the desired applications. The pores of HSG, however, did not collapse up to temperatures above 900 °C [7], which is too high. Controlled-pore glass (CPG), a product of Electro-Nucleonic, Inc., has pores of about 10 nm in diameter and is densifiable at temperatures near 800°C. However, CPG is supplied in particulate form. Porous glasses based on the Shirasu composition (SPG) are densifiable at lower temperatures than HSG, considering from its mother composition [8]. However, the pore sizes of SPG ranging from 30 nm to several microns are generally too large to be applied to optical materials.

Nakashima and Kuroki [9] investigated the effects of CaO and Al₂O₃ additions on the phase separation behavior of Shirasu-type glasses and obtained porous glasses with pores of about 10 nm in radius in the pulverized sample. However, no reference was made to the integrity of their porous glass. From the crudely estimated porosity of 50%, the fabrication of porous plates with such a pore structure will be difficult, because the skeleton of such a glass is generally thin and weak. Since integrity is essential for glasses used in optical and photonic devices, some modifications must be made on this porous glass in order to obtain a material suitable for application.

In the present study, preparation of a new porous glass was accomplished using the Shirasu-type glass reported by Nakashima and Kuroki for developing a glass with pore structure similar to HSG but densifiable at lower temperatures.

EXPERIMENTAL

Preparation of Mother Glass, Heat-Treatment for Phase Separation, and Acid Leaching

Chemical composition of the mother glass was determined and shown in Table 1 along with that of the reference glass, SPG. Taken into consideration were the following:

(1) The densification of a porous glass is accomplished by viscous sintering. Therefore, the skeletal glass should have a much lower viscosity than the HSG

glass in order to densify at lower temperatures.

(2) The Heat-treatment for phase separation must be stopped before the pores begin to coalesce in order to retain the small pores. In such a case, the porosity of the glass should not be too large in order to maintain the integrity of the glass during acid leaching.

(3) The main components of the dissolved phase of the Shirasu-type glass are B_2O_3 and CaO [9]. Higher SiO_2 content and lower B_2O_3 and CaO contents were used to increase the volume fraction of the skeletal glass part and to suppress the rapid development of phase separation. This is in order to obtain the formation of large pores.

A batch composition of reagent grade SiO_2 , H_3BO_3 , Al_2O_3 , $CaCO_3$, MgO , Na_2CO_3 and KNO_3 was melted in a platinum crucible at $1400^\circ C$ and kept for 2 hrs. The melt was quenched and pulverized to about 0.5 mm or smaller. Then the pulverized glass was remelted at $1550^\circ C$ and kept for 2 hrs in order to improve homogeneity.

Heat-treatments for phase separation were made at various temperatures in the range of $20-40^\circ C$ above T_g i.e., at 670, 680 and $690^\circ C$ for 6-96 hrs. The phase separated glasses were sliced into 0.3-0.4 mm thick samples and polished until they had lustrous surfaces. Then, the glasses were subjected to leaching in 0.1N or 1N H_2SO_4 aqueous solution at room temperature for 2 days. Leaching was repeated again with a fresh solution, followed by drying at $60^\circ C$.

Characterization

Specific surface area, S_g , pore size distribution, and pore volume were measured by a nitrogen adsorption technique. The composition of the skeletal glass was estimated from porosity and the composition of the dissolved phase in the H_2SO_4 solution, which was analyzed by inductively coupled plasma emission spectroscopy (ICP).

Table 1. Chemical composition of the mother glass.
(in mol%)

	Present Study	Shirasu-Type Glass [8]
SiO_2	64.0	51.99
Al_2O_3	6.2	2.81
B_2O_3	9.5	21.81
Na_2O	4.1	5.46
K_2O	1.7	0.67
CaO	14.2	16.84
MgO	0.3	0.19
Fe_2O_3	-	0.24

Changes in pore structure at elevated temperatures were monitored after isothermal heat-treatment of the glasses at 700, 750 and 800°C. S_g and the pore size distribution were measured with a Quantachrome AUTOSORB1 on samples collected during heat-treatment at intervals of 2-3 hrs. Ultraviolet-visible (UV-Vis) transmission spectra of the porous glass and fully-densified glass were measured from 200 to 800 nm with JASCO UVIDECE- 610C Spectrophotometer.

RESULTS

Pore Structure

The dependence of the integrity of the porous glass after the leaching with 0.1N H_2SO_4 solution on heat-treatment temperature and time for phase separation is depicted in Fig. 1. All the glasses soaked at 670°C did not maintain integrity during the leaching process. Heat-treatment at 680°C for longer than 40 hrs was necessary to develop a skeletal structure of glass which maintained its integrity, while 10 hrs was enough to maintain integrity for the sample heat-treated at 690°C. These relations were also found by the leaching with 1N H_2SO_4 solution.

The relationships between pore structure and conditions of heat-treatment are shown in Figs. 2 and 3. The average

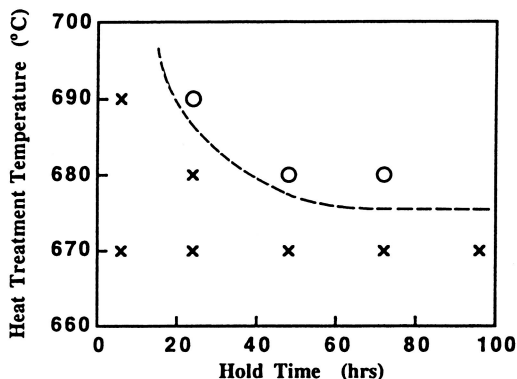


Figure 1 Dependence of the integrity of porous glass on heat-treatment temperature and time.

O : maintain integrity.
x : disintegrated.

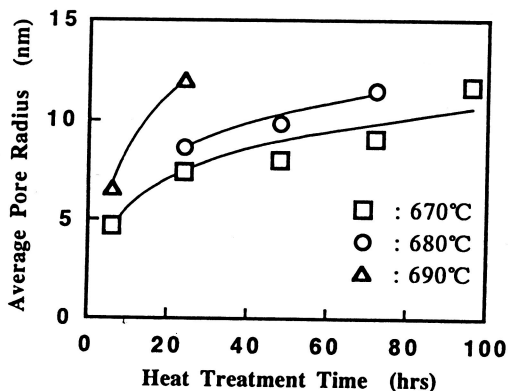


Figure 2 Changes in average pore radius of porous glass with the temperature and time of heat-treatment.

pore radius, R_{ave} , increased from 5 to 9-10 nm on the samples obtained by leaching with 0.1N H_2SO_4 solution, and S_g decreased from 50 to 30-40 m^2/g when the skeleton of the glass was well-developed. The porosity of the glass with a well-developed skeleton was estimated to be 40%.

A typical pore size distribution is shown in Fig. 4 for samples heat-treated at 680°C for 48 hrs and leached with 0.1N H_2SO_4 solution. In principle, the distribution is unimodal, although it looks bimodal with one mode at 10-20 nm and the other mode below 3 nm in radius. This effect is due to residual silica gel which precipitated during leaching and remained in the larger pores. The pore size distribution is more clear in the glass leached with 1N H_2SO_4 solution than that leached with 0.1N H_2SO_4 solution.

Table 2 shows the estimated composition of the skeletal glass along with those of SPG and the composition of the leached phase. The SiO_2 content in the new porous glass is comparable to or slightly higher than that of SPG. The glass contains an unexpectedly large amount of CaO, despite that it was obtained from a mother glass of smaller CaO content than SPG.

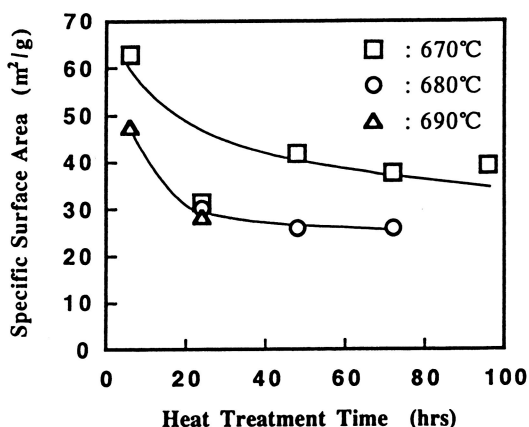


Figure 3 Changes in specific surface area of porous glass with heat-treatment temperature and time.

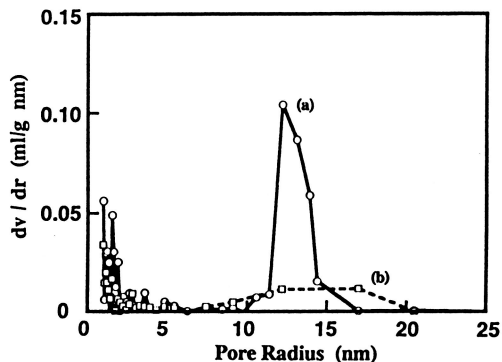


Figure 4 Change in pore size distribution of porous glass with the condition of leaching;
(a) : 96 hrs in 1N- H_2SO_4 .
(b) : 48 hrs in 0.1N- H_2SO_4 .

Table 2. Estimated compositions of skeletal glasses and leached phases.
(in mol%)

	Present Study		Shirasu-Type Glass [9]	
	skeleton	Leached phase	skeleton	Leached phase
SiO ₂	75~84	28~34	75.24	30.05
Al ₂ O ₃	5	7~9	4.31	1.40
B ₂ O ₃	5	20~26	13.52	29.46
Na ₂ O	4~8	3	5.10	5.78
K ₂ O	2~5	1	0.93	0.42
CaO	3~8	29~32	0.13	32.39
MgO	-	2	0.64	0.17
Fe ₂ O ₃	-	-	0.14	0.33

Change in Pore Structure with Heat-Treatment

Changes in S_g and bulk density with isothermal heat-treatment are shown in Fig. 5 and 6. The glass phase was separated at 680°C-48 hrs and then leached with 1N H₂SO₄ solution. The value of S_g quickly decreased by heating at 800°C, and the glass was completely densified within 6 hrs. Also, the collapse of pores proceeded at an appreciable rate at 750°C, with complete densification occurring within 25 hrs. During this time, the bulk density increased from 1.42 g/cm³ to that of the skeletal glass at 2.40 g/cm³. The porous glass soaked at 700°C, however, remained uncollapsed, although its S_g decreased slightly in the early stage of heat-treatment. Densification at 750°C is lower by about 150°C compared to the same HSG with similar pore structure. This is low enough to fabricate quantum dots materials containing some semiconductor particles such as CdS before their sublimation becomes intensive. But the temperature is still too high to embed PbS without decomposing into PbO or PbSO₄.

Figure 7 shows the UV-Vis spectra for the porous glass measured in both air and water and for the completely densified glass. The scattering loss observed on the spectrum for the porous glass measured in air was reduced from that measured in water to an acceptable level for effective irradiation of UV light for photo-patterning. The fully dense glass had good transparency over the wavelength region of interest, showing that the glass can be used in optical devices.

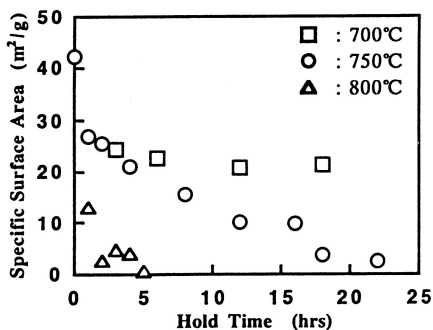


Figure 5 Changes in specific surface area of porous glass with isothermal heat-treatment.

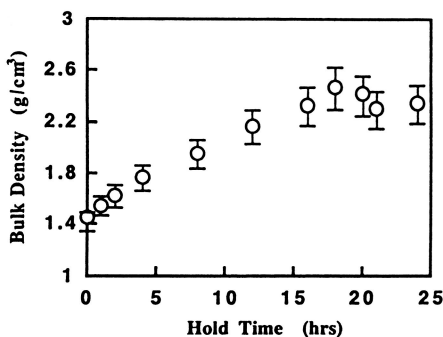


Figure 6 Change in bulk density of porous glass with isothermal heat-treatment at 750°C.

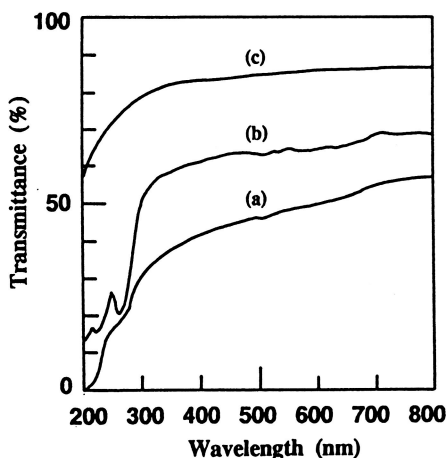


Figure 7 UV-vis transmission spectra of the porous glass and densified glass; (a) : Porous glass in air. (b) : Porous glass in water. (c) : Densified glass.

DISCUSSION

The remarkable reduction in densification temperature and good transparency of the new porous glasses show that the composition of the mother glass was properly selected. Although it is still desirable to modify the glass composition further to reduce densification temperature, it is also of significance to discuss the sintering behavior of the new porous glass with respect to pore structure and viscosity of the skeletal glass at this stage.

According to Scherer [10], the sintering behavior of low density, open-pore materials which are densified by viscous flow and driven by surface energy, can be described by using a model consisting of a cubic array formed by intersecting cylinders. In such a model, the pore diameter, D , is given by Eq.(1):

$$D=2(L-2R)/\sqrt{\pi} \quad (1)$$

where L is the length of the cubic cell, and R is the cylinder radius. The volume of the solid phase in the cubic cell, V_s , and the bulk density, ρ , are given by Eqs. (2) and (3):

$$V_s = 3\pi R^2 [L - (8\sqrt{2}/3\pi) R] \quad (2)$$

$$\rho = (3\pi \left(\frac{R}{L}\right)^2 - 8\sqrt{2} \left(\frac{R}{L}\right)^3) \rho_s \quad (3)$$

where ρ_s is the density of the cylinder.

The applicability of this model to the porous glass in the present study can be examined by comparing the estimated surface area, S_g , on this model with the measured value. The estimated S_g of the model cubic cell was 33 m²/g by correlating the experimental data, $\rho_0=1.42$ g/cm³, $\rho_s=2.40$ g/cm³ and $D=23.4$ nm with Eqs. (1) and (3) and substituting into Eq. (4):

$$S_g = \frac{1}{R\rho_s} \left(\frac{6\pi L - 24\sqrt{2}R}{3\pi L - 8\sqrt{2}R} \right) \quad (4)$$

Good agreement between estimated and measured S_g values at 30-40 m²/g assumes that the change ρ/ρ_s , which represents the sintering behavior of the porous glasses, can be expressed using reduced time, $(\gamma \eta L_0)(\rho_s \rho_0)^{1/3}(t - t_0)$. Here, γ is the surface tension, η is the viscosity of the skeletal glass, L_0 is the initial value of L , and t_0 is the fictitious time at which $x(=a/l)$ equals zero.

Figure 8 shows the results for the estimating the change in ρ/ρ_s at various values of viscosity, assuming that $\gamma=0.3$ J/m² (300 ergs/cm²). Since ρ/ρ_s increases from an initial value of 0.57 to 0.94 in 20 hrs by isothermal heat-treatment at 750°C, the viscosity of the skeletal glass at that temperature is known to be in the range $1-1.5 \times 10^{-13}$ dPa · s. When these values are plotted against the reciprocal of the

absolute temperature, the viscosity of the skeleton of the porous glass is estimated to be about 10^{-14} dPa · s at 700 °C. This value is reasonable since the glass transition temperature determined by dilatometry is $726 \pm 5^\circ\text{C}$.

The results for similar estimation at constant viscosity of 10^{-13} dPa · s on the densification time for the material of viscous pore diameters are shown in Fig. 9. It is known from this figure that the densification time of the porous glass with 25 nm pores is about 170 hrs at this viscosity, and that the densification time can be reduced to a half by decreasing the pore diameter from 25 nm to 10 nm. Heat-treatment time of 100 hrs for densification will be within an acceptable range for practical fabrication of quantum dots materials.

Although the phase separated glass with the pore diameter of 10 nm did not maintain integrity under the leaching conditions of present study, it may not be impossible to obtain a porous glass with such a pore structure without disintegration after optimization. Then, the possibility of application to optical and photonic devices will be remarkably increased.

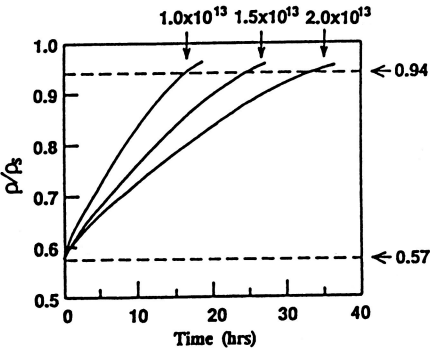


Figure 8 Estimation of densification time at various values of viscosity.

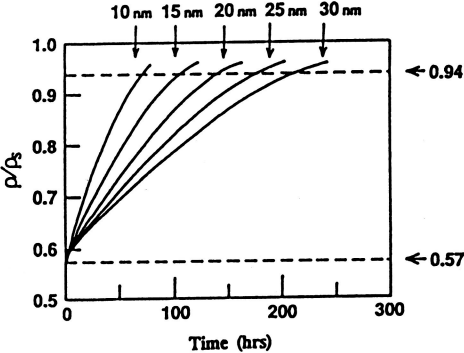


Figure 9 Estimation of densification time for materials with various pore diameters at constant viscosity.

CONCLUSIONS

Preparation of a porous glass having a pore structure similar to that of high silica porous glass of the Vycor-type, but that which densifies at lower temperatures, was studied in order to develop a material applicable to the fabrication of quantum dots materials, optical integrated circuits and other components important for optical and photonic devices.

The following conclusions were obtained:

- (1) A porous glass having average pore diameter of 23.4 nm and specific surface area of 40 m²/g was obtained by the heat-treatment and acid leaching of a Shirasu-type glass with modified composition.
- (2) The porous glass showed a good transparency in the UV-Vis region to allow photo-patterning of dopants.
- (3) The porous glass completely densified at 750°C and can be applied to the fabrication of quantum dots materials containing non-oxide semiconductors.

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