Amorphous Oxides Prepared from Organometallic Compounds
Part 1. Preparation of Sodium Borosilicate Gels

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and

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SYNOPSIS

Sodium borosilicate gels of compositions similar to that of Vycor^R glass like $80SiO_2.15B_2O_3.5Na_2O$ (wt%) were prepared from hydrolysis and polycondensation of tetra-ethyl orthosilicate, trimethyl borate, and sodium methylate under the HCl catalysis. Variation of the gelation time is examined as a function of the mixing ratio of the starting materials and the catalyst. The thermal behavior of the gels has been discussed on the basis of their TG and DTA traces.

1. INTRODUCTION

The sol-gel process has a potential not only to prepare the precursor powders for ceramics[1,2] but to prepare monolithic amorphous solids[3,4]. Dried gels have a large volume fraction of pores that the sol-gel process is suitable for preparing porous materials with determined pore size distribution and pore volume if we can control gelation reactions and drying-heating process. In the present experiment[5] we prepared several compositions of sodium borosilicate gels as a candidate of monolithic porous material. We have examined the variation of gelation time depending on the mixing ratio of the starting materials and the catalyst and discussed the thermal behavior of the gels by the use of TG and DTA technique.

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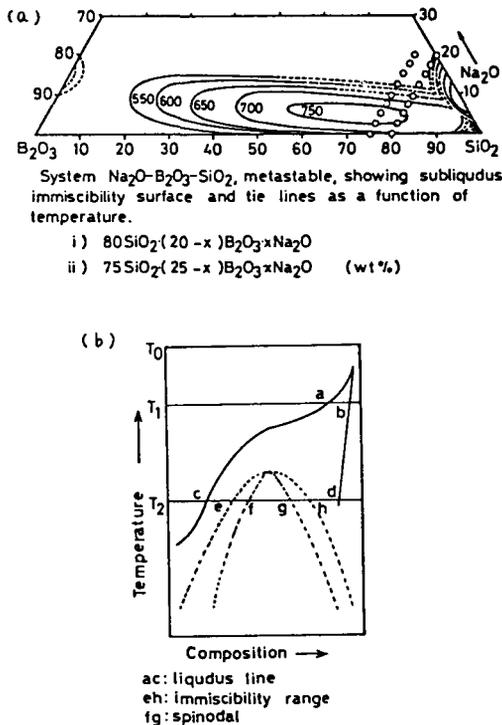(a) System $Na_2O-B_2O_3-SiO_2$, metastable, showing subliqudus immiscibility surface and tie lines as a function of temperature.

i) $80SiO_2 \cdot (20-x)B_2O_3 \cdot xNa_2O$
ii) $75SiO_2 \cdot (25-x)B_2O_3 \cdot xNa_2O$ (wt%)

(b) ac: liqudus line
eh: immiscibility range
fg: spinodal

Procedure II   Procedure I

Fig. 1(left). Composition of the borosilicate gels prepared and the immiscible region in melt-quenched glass.[6]
Fig. 2(right). Procedure of preparation of the borosilicate gels.[7]
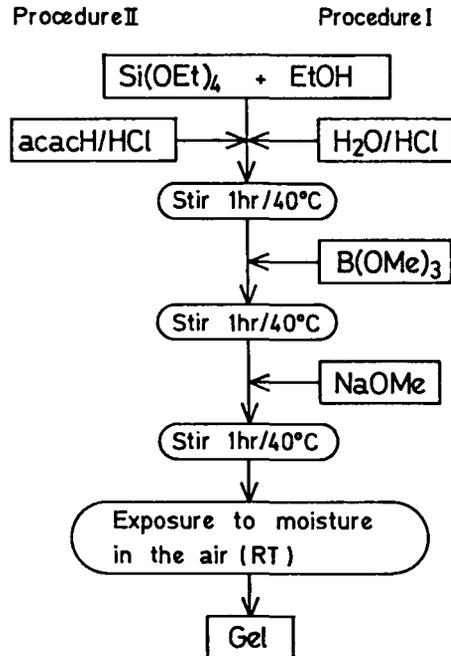
2.EXPERIMENTAL

2.1. Preparation

The compositions of the gels and glasses were

i) $80SiO_2 \cdot (20-x)B_2O_3 \cdot xNa_2O$ [wt%] $(0<x<20)$
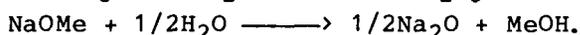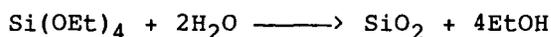ii) $75SiO_2 \cdot (25-x)B_2O_3 \cdot xNa_2O$ [wt%] $(0<x<20)$

and were indicated in Fig. 1 together with the region of the phase separation reported by Haller et al.[6]   Some of the above glasses are located in the region of spinodal decomposition which results in an entangled phase separation structure. A glass of composition $80SiO_2 \cdot 15B_2O_3 \cdot 5Na_2O$ (wt%), denoted as (80S-15B-5N), is known as the starting glass for the Vycor[R] type porous glass and has been chosen as the target material in this experiment.

The procedure of preparing the gels was schematically shown in Fig. 2 after Mukherjee[7]. A mixture of 21.6 ml tetraethyl orthosilicate (TEOS) and ethanol (EtOH) (TEOS/EtOH=1/3 in volume) was prepared in a 100 ml beaker under stirring. Method I: After addition of H_2O to the

Table 1. Appearance of 80S-15B-5N gels prepared
with various catalysts.

Catalyst	pH	Gels
No catalyst	6.2	Opaque
HCl	0.58-0.85	Transparent
$(NH_4)_2CO_3$	7.5-9.03	Opaque
Anyline	8.0-9.8	Opaque
NH_4OH	12.0	Opaque

mixture so as to attain the molar ratios H_2O/TEOS = 1/2, 1, 3/2, 2 and
5/2, HCl or NH_4OH solution was added as the catalyst. The pH of the
solutions was varied as shown in Table 1. The molar ratios HCl/TEOS
were indicated in Table 2. Full hydrolysis and polymerization of the
alkoxides such as TEOS, $B(OMe)_3$ and NaOMe need 2, 3/2 and 1/2 moles of
H_2O, respectively:

$$Si(OEt)_4 + 2H_2O \longrightarrow SiO_2 + 4EtOH$$

$$B(OMe)_3 + 3/2H_2O \longrightarrow 1/2B_2O_3 + 3MeOH$$

$$NaOMe + 1/2H_2O \longrightarrow 1/2Na_2O + MeOH.$$

Thus the stoichiometric ratio of H_2O/TEOS for the full polymerization
of the gel of the composition 80S-15B-5N was

$$H_2O/TEOS = [2M(SiO_2) + 3M(B_2O_3) + M(Na_2O)]/M(SiO_2)$$
$$= 2.63$$

where M's represent molar fraction of the component oxides. If H_2O was

Table 2. Mixing molar ratios of the starting materials
and catalyst HCl for 80S-15B-5N gel.

Sample	Temp.	HCl/TEOS[a]	HCl/H_2O	H_2O/TEOS	Appearance
1	RT[b]	1/100	1/100	1	Transparent
2	40°C	1/100	1/100	1	Transparent
3	40°C	1/300	1/100	1/3	Transparent
4	40°C	1/500	1/100	1/5	Transparent
5	40°C	1/100	1/5	1/20	Transparent
6	40°C	1/100	1/150	3/2	Transparent
7	40°C	1/100	1/200	2	Translucent
8	40°C	1/100	1/250	5/2	Translucent
			HCl/acac-H[c]		
9	40°C	1/100	1/100	1	Transparent

a: Tetraethyl orthosilicate   b: Room temperature
c: Acetyl acetone

added to the gelling solution in excess over the stoichiometric ratio,
the solution became opaque and inhomogeneous. The ratio of H_2O to
TEOS was hence varied in the range H_2O/TEOS < 2.63. Method II:
Acetylacetone (later denoted as acac-H) was used in place of H_2O, and
3.64ml $B(OMe)_3$ and 1.36g NaOMe was added one after another to the
mixture of TEOS and acac-H. H_2O needed for the hydrolysis and poly-
merization should be supplied from the air. In both methods the final
solution prepared was poured into a plastic petri dish (35mm in diame-
ter and 10mm high) or sample bottles (27.5mm in diameter and 55mm
high) in size). The containers were then covered with plastic film
having pin holes, and left in air at room temperature for hydrolysis
and polymerization.

2.2. Gelation time and thermal treatment

The change in the viscosity of the solution was monitored with a
viscotester (Rion Co. Ltd., VT-02) in order to obtain the gelation
time, t_{gel}, which denotes the time when the viscosity reaches 6 poise.
The solutions became viscous as the hydrolysis and polymerization
reactions proceeded. The viscosity data less than 0.3 poise and larger
than 8 poise were omitted because of the lesser reliability. DTA and
TG curves were taken for the dried gels at a rate of $20^{\circ}C$/min up to
$1000^{\circ}C$. The X-ray diffraction traces were taken for the samples
before and after the thermal analysis.

Thermal expansion/contraction behavior of the dried (as-prepared)
and heat-treated gels shaped into a cylinder 0.3cm in diameter and
1.0cm - 1.5cm long was traced by Rigaku thermomechanical analyzer
(TMA) heating at a rate of $1^{\circ}C$/min up to $600^{\circ}C$, by the use of a SiO_2
glass rod as the reference. Thermal contraction was observed for as-
prepared gels.

3. RESULTS AND DISCUSSION

3.1. Gelation and appearance of gels

Figure 3 shows the variation of the viscosity of 80S-15B-5N solu-
tion as a function of time for gelling. The numerical figures repre-
sent the sample numbers summarized in Table 2. Comparison of curves
1 and 2 indicates that higher temperature for preparing the sol consi-
derably reduces the gelation time, t_{gel}, (No.1 at room temperature,
and No.2 at $40^{\circ}C$). For gels of a constant ratio HCl/TEOS, the sol
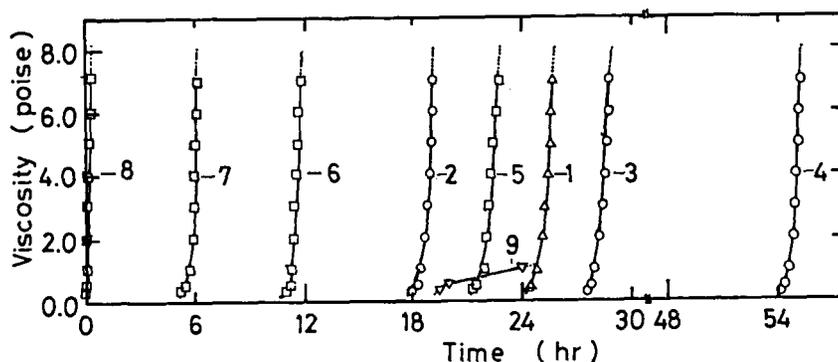with a higher molar ratio H_2O/TEOS becomes gel in shorter time with

Fig. 3. Variation of viscosity of the solutions during gelation reactions. The numerical figures are the sample numbers in Table 2. The gelation time is the time the viscosity reaches 8 poise.

more opaqueness. Fig. 4 shows the effect of the molar ratio H_2O/TEOS on the gelation time of the solutions with the constant ratio HCl/TEOS (= 1/100). The gelation time decreases with increase in the water content.

The solution containing acac-H instead of H_2O was separated into two phases in the course of measuring the viscosity change: a viscous liquid in the center part where the measuring cup was rotating, and a translucent gel near the wall of the container. The comparison of curve 2 with curve 9 for the sols with the constant ratio HCl/TEOS shows that the solution with acac-H has a larger value of t_{gel}
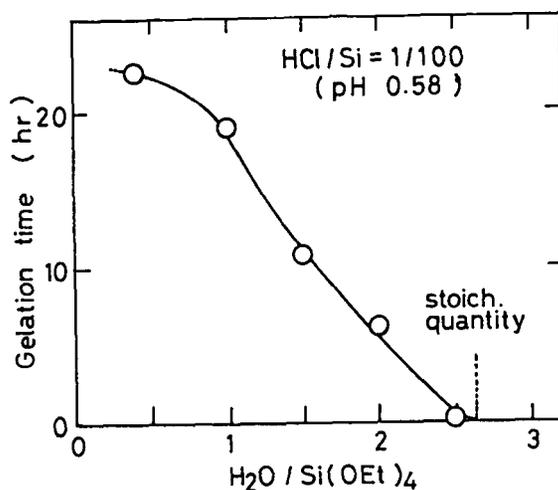

Fig. 4. The effect of the molar ratio H_2O/TEOS on the gelation time of 80S-15B-5N solution.
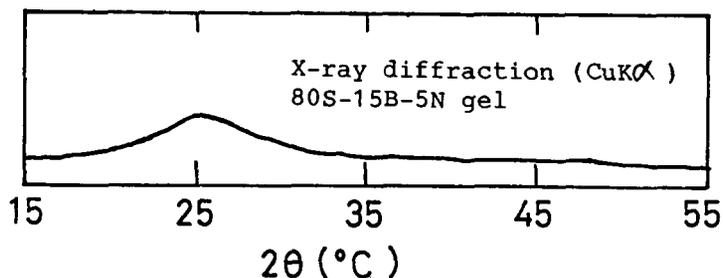
Fig. 5. The X-ray diffraction pattern for the 80S-15B-5N gel dried for one month in air.

because the sols should catch water in air for gelation.

Homogeneous and transparent gels were obtained in the composition range $2.5 < x (= wt\% \ Na_2O) < 10$ in both series of 80 and 75 wt% SiO_2. The gels prepared by method II with acac-H were orange in color. We will focus our discussion on the gels prepared through procedure I in the following. Fig. 5 is an X-ray diffraction pattern for the 80S-15B-5N gel dried for a month. Those of other compositions have a similar diffraction pattern, indicating that they are all amorphous.

3.2. Thermal behavior of the borosilicate gels

Figure 6 shows the DTA and TG curves for as-prepared 80S-15B-5N gel aged and dried in air for over one month after gelation. The deeper
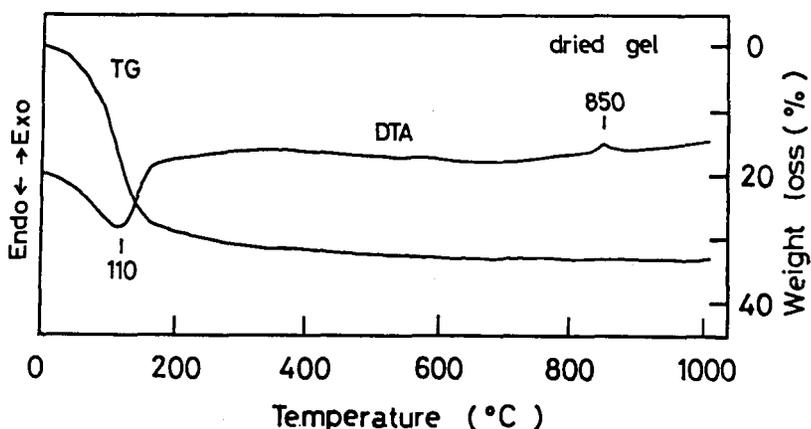

Fig. 6. DTA and TG traces for the dried 80S-15B-5N gel. The exothermic peak near 850°C is due to precipitation of cristobalite.

endothermic peak in the DTA trace between 80°C and 150°C is due to the loss of organic solvent or water trapped in open pores. The smaller exothermic peak in the range from 300°C to 450°C has been ascribed to the combustion of organic compounds or some structural evolution. Above 750°C, DTA curve shows a small exothermic peak corresponding to the crystallization of cristobalite (JCPDS 11-695), which is verified by the X-ray diffraction pattern shown in Fig. 7.
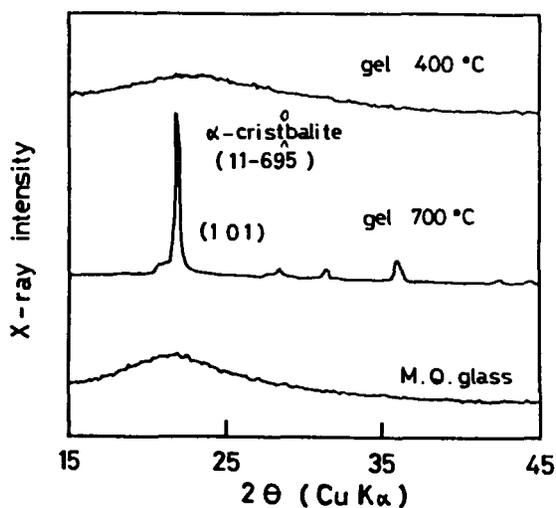

Fig. 7.
X-ray diffraction patterns for the 80S-15-B-5N gel heated at 400° and 700°C for 5h, and the melt-quenched glass of the same composition treated at 700°C for 5h.

The TG curve shows scarce weight loss above 450°C. The thermal expansion curve in Fig. 8 shows that the dried gels begin to shrink slowly at about 120°C and remarkably around 450°C. The shrinkage of the gel is as large as about 14 percent in the longitudinal direction. After the shrinkage measurement the transparent cylindrical gel turned opaque. This shrinkage is caused by the development of continuous glass networks due to pore collapse as well as the phase separation process in the high temperature region above 650°C. A transmission electron microscope observation is unsuccessful to determine whether the opacity of the gels comes from residual micropores or from phase separation. Villegas and Navarro[8] proposed the phase separation in the solidified gels.

4. CONCLUSION

Sodium borosilicate gels of compositions near the Vycor[R] glass, $80SiO_2 \cdot 15B_2O_3 \cdot 5Na_2O$ (wt%) have been prepared and their thermal beha-
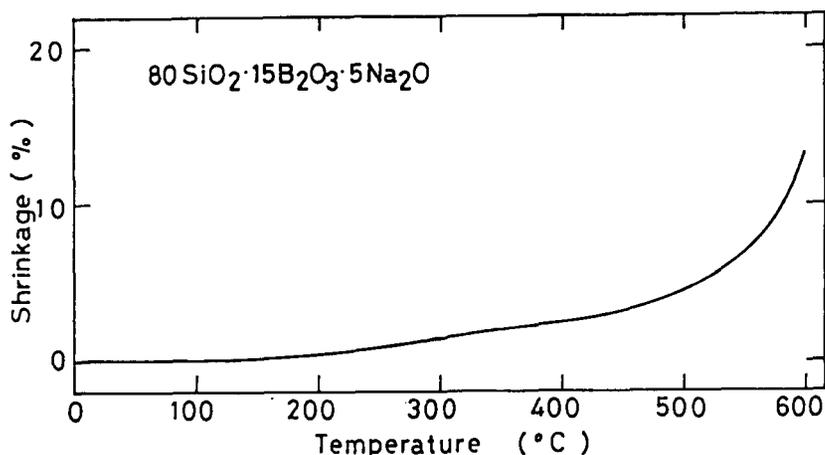
Fig. 8. Thermal expansion (shrinkage) curve for the dried
gel of composition 80S-15-B-5N.

vior has been examined due to TG and DTA technique. Addition of
acetylacetone is not suitable for the control of the hydrolysis and
condensation reactions of the starting materials. For the solutions
of the molar ratio HCl/TEOS=1/100, the gelation time decreases rapidly
with increase in the ratio H_2O/TEOS. An opaque gel is obtained as soon
as the stoichiometric amount of water is added to the metal alkoxides
solution. The dried gels are all amorphous regardless to their compo-
sition but shows precipitation of cristobalite after the measurement
up to 1000°C in a DTA apparatus. Thermal shrinkage as much as 16% has
been observed for the 80S-15B-5-N gel below 600°C.

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