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# Characterization of pores arising from spinodal phase separation in quenched sodium borosilicate glasses

**Wei-Fang Du,***†[a] **Koji Kuraoka**[b] **and Tetsuo Yazawa**[b]

[a]*New Energy and Industrial Technology Development Organization, Midorigaoka 1-8-31, Ikeda City, Osaka, 563-8577, Japan*
[b]*Optical Materials Department, Osaka National Research Institute, Midorigaoka 1-8-31, Ikeda City, Osaka, 563-8577, Japan*

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**The characterization of pores arising from spinodal phase separation in quenched sodium borosilicate glasses is investigated. Theory predicts that the wavelength of the initial stage for spinodal phase separation on cooling is *ca.* 5–10 nm, whereas after acid leaching, the size of the pore based on so-called spinodal decomposition is much smaller with pores formed in quenched sodium borosilicate glass after leaching being of micropore type with radii of $<1$ nm. The acid leaching model proposed in the present study suggests that the characteristics of the pores in the quenched glass result from the small amplitude of the spinodal decomposition wave on cooling.**

This communication reports a study of the pore structure arising from spinodal phase separation in quenched sodium borosilicate glass. Sodium borosilicate is a typical spinodal phase separation glass and is a source material for porous glasses, which are finding widespread applications in industry.[1–3] The later stages of spinodal decomposition in sodium borosilicate glasses have been extensively studied in previous work by a variety of techniques.[4,5] The separated phase is usually thought to grow by coalescence in this stage. The domain size $r$ of the separated phase is found to increase with the cube root of heat treatment time $t$, *i.e*, $r \propto t^{1/3}$. Based on this spinodal phase separation, porous glasses with highly connective meso- and macro-pores may be obtained and are promising as separation membranes, enzyme and catalyst supports, and photonic materials, *etc.*[6–14]

Despite these efforts, however, the early (initial) stage of spinodal decomposition, *i.e.* the propagation of spinodal phase separation under continuous cooling from the molten state, is still little explored except for the theoretical study by Cahn *et al.*[15–17] in the 1960s. In particular, there are no reports on the relation between the pore characteristics and the phase separation under continuous cooling from the molten state. It is well known that temperature changes imposed upon a homogeneous system result in the spontaneous formation of a new phase. Although the theory of spinodal decomposition has suggested that this effect can be reduced, or even be avoided, at high cooling rates,[15–18] there is still no unambiguous experimental confirmation under rapid-quenching conditions, which prevents us from developing new porous materials with micropores within the rapid-quenched region. Glasses with micropores are thought to be promising materials as membranes with ‘molecular sieving’ properties. So, from the point of view of materials design, it is very important to investigate whether spinodal phase separation exists under rapid-quenching conditions, and the relation between the pore characteristics and phase separation under continuous cooling from the molten state.

Here, we present new data of spinodal phase separation under continuous cooling from the molten state in sodium borosilicate glass, and its influence on the pore distribution.

The sodium borosilicate glass used in our experiments was prepared from reagent grade sodium carbonate, boric acid and silica and was of composition 9.4 $Na_2O$ : 25.4 $B_2O_3$ : 65.2 $SiO_2$ (mol%) separation. First, the reagent-grade chemicals were thoroughly mixed. Then the mixtures were placed in a platinum crucible and fused at 1400 °C in an electric furnace for 60 min. The samples were quenched by pouring *ca.* 25 g melts into carbon molds held at room temperature. Under these conditions the quenching rate was *ca.* $10\ ^\circ C\ s^{-1}$.

The glasses prepared by the above method were then etched using aqueous 3 M $HNO_3$ at 98 °C, and were washed with water and dried. The boron and silica contents of the leaching solution were analysed using an induction-coupled plasma (ICP) analyser (Model SPS 1200A, Seiko Co.). The specific surface areas and the pore size distribution of the samples were measured by nitrogen adsorption (Belsorp 28, Bel Japan Inc.). Prior to the measurement, the samples were evacuated at 150 °C for 3 h. The specific surface areas were calculated by the BET method,[19] and pore size distributions were determined by the MP method.[20]

According to the pore diameter within a given solid, porous materials are classified as microporous when the pore diameter is $<2$ nm, mesoporous when the pore diameter is between 2 and 50 nm and macroporous with pore diameters $>50$ nm, according to the International Union of Pure and Applied Chemistry.[21] These porous solids usually exhibit different hysteresis behavior in nitrogen adsorption–desorption cycles in comparison to non-porous solids when they are exposed in a closed space to nitrogen at a given pressure.[22–28] The essential features of the adsorption–desorption isotherms of porous and non-porous solids are illustrated in Fig. 1.[29]

In sodium borosilicate glasses, if spinodal phase separation occurs, pores with high connectivity can be obtained by selectively leaching out with acid the aggregative boron in the phase-separated glasses. Otherwise, such pores are not formed

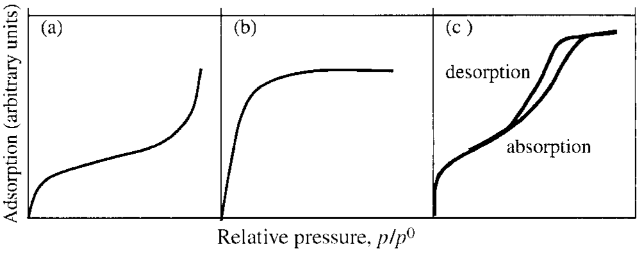

**Fig. 1** The essential features of adsorption isotherms for (a) non-porous solids, (b) microporous solids and (c) mesoporous solids.

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†Present address: Optical Materials Department, Osaka National Research Institute, Midorigaoka 1-8-31, Ikeda City, Osaka 563-8577, Japan. E-mail: du@onri.go.jp

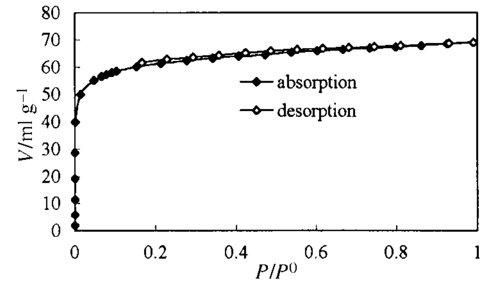

**Fig. 2** Adsorption–desorption isotherm curve of a quenched sodium borosilicate glass sample after leaching at 98 °C.

after the acid leaching of the glasses. Thus, one can confirm whether phase separation occurs in the sodium borosilicate glasses by the nitrogen adsorption–desorption behavior after leaching. A typical adsorption–desorption isotherm of a leached sample is shown in Fig. 2. The sample clearly possesses an extensive pore network of the micropore type characterized by a large amount of adsorption at a low relative pressure followed by a plateau which is nearly horizontal, as shown in Fig. 1. Thus, spinodal phase separation has obviously taken place on quenching. The selective extraction of boron during acid-leaching is confirmed by ICP atomic emission analysis, as seen in Fig. 3. Removal of boron is primarily responsible for micropore development in the sample.

In the initial stage of spinodal decomposition, as coalescence of the domain structure does not yet occur, the phase separation is caused only by compositional fluctuation due to diffusion. Thus, it is assumed that the cooling rate $v_{\max}$ which is required to avoid phase separation is dependent solely on the diffusion flux and is given by eqn. (1)

$$v_{\max} > KD \qquad (1)$$

where $D$ is the diffusion coefficient of the glass and $K$ is a constant. At a cooling rate of $v_{\max}$, we assume that the cooling process is more rapid than the diffusion process, so that compositional fluctuation is inhibited and thus the phase separation is avoided entirely. Cahn and Charles have studied extensively the characteristic kinetics of phase separation by spinodal decomposition.[17] It was found that, upon cooling, the most rapid decomposition occurs at *ca.* 10% of the spinodal temperature. If a cooling rate is rapid enough to inhibit decomposition at this temperature, then spinodal phase separation can be avoided entirely during cooling. The value of $v_{\max}$ was precisely deduced in ref. 17 by eqn. (2)

$$v_{\max} > 8\pi^2 D\theta^2/\lambda^2 V_{\mathrm{m}}^2 \qquad (2)$$

where $D$ is the diffusion coefficient of the glass, $\theta$ is the temperature below the spinodal temperature, defined as the point of the most rapid decomposition occurring under cooling, which is *ca.* 10% of the spinodal temperature, $V_{\mathrm{m}}$ is the molar volume and $\lambda$ is the wavelength of the wave with most rapid decomposition, which is independent of cooling rate and typically in the range 5–10 nm. Comparison of eqn. (1) with eqn. (2) gives eqn. (3)

$$K = 8\pi^2\theta^2/\lambda^2 V_{\mathrm{m}}^2 \cong 5.6\times10^{18} - 6.2\times10^{19} \qquad (3)$$

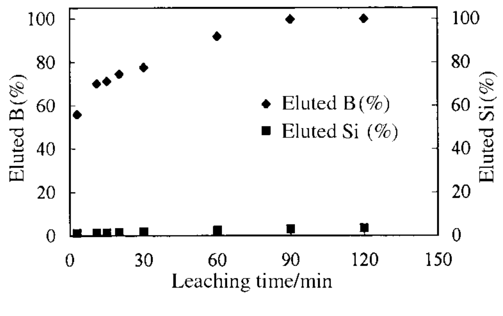

**Fig. 3** Dependence of the elution of boron and silicon upon leaching time at 98 °C.

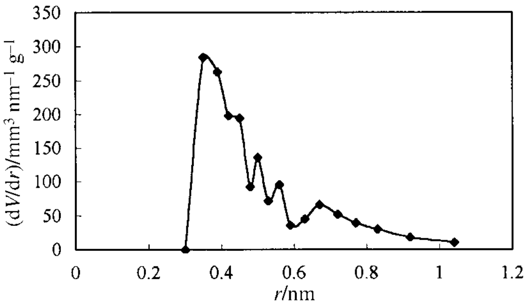

**Fig. 4** Pore size distribution of a quenched sodium borohydride glass sample after leaching at 98 °C.

$D$ is usually $>10^{-8}$ cm$^2$ s$^{-1}$ and can be as large as $10^{-5}$ in fluid melts of sodium borosilicate glass.[17] In such melts, from the theoretical point of view, spinodal phase separation at a cooling rate of 10 °C s$^{-1}$ can not be avoided, which further supports our experimental results.

Previous investigations of the kinetics of spinodal phase separation show that the main bulk of the homogeneous fluid begins to form stationary waves that initially only grow in amplitude.[15–17] Furthermore, Cahn and Charles suggested that the decomposition wavelengths were independent of the cooling rate.[17] Theoretical calculations indicate that the wavelength of the wave caused by the most rapid decomposition under cooling is typically in the range 3–10 nm for silicate glass. However, the pore size distribution of the samples after acid leaching in the present case is $<1$ nm (Fig. 4), which is markedly lower than the theoretical prediction. This phenomenon is assumed to be caused by the fact that the amplitude of the decomposition wavelength is small upon rapid cooling.

It is well known that one of the important characteristics for spinodal decomposition is the non-spherical shape and high connectivity of the separated phase. Thus, after leaching out the boron-rich phase, pores with high connectivity, so-called spinodal pores, could be obtained. However, inside boron- or silica-rich phases, composition gradients still exist according to the theory of spinodal decomposition at the initial stage of spinodal decomposition (Fig. 5). These lead to complexity of the relation between the spinodal pore size and the decomposition wavelength since the distribution of the spinodal pores is determined not only by the boron-rich phase but also by the

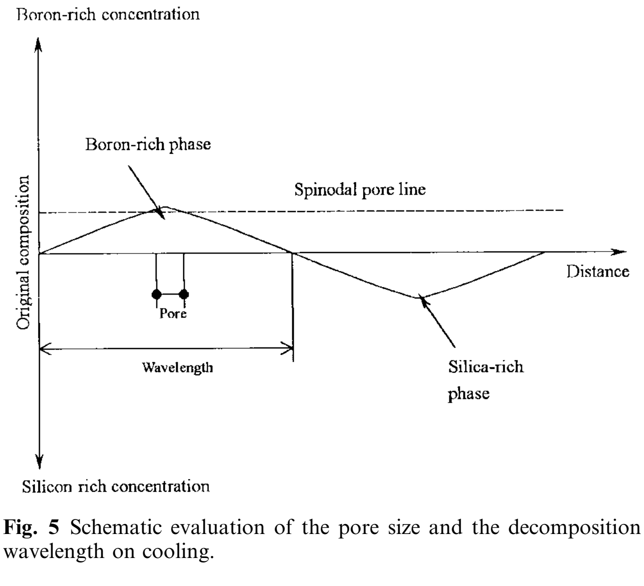

**Fig. 5** Schematic evaluation of the pore size and the decomposition wavelength on cooling.

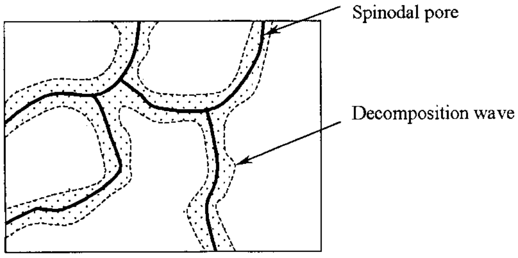

**Fig. 6** Illustration of the relation between spinodal pores and the decomposition wave.

topology of the boron and silica network. In the boron-rich phase, as the boron concentration near the edge of the decomposition wave is low and approaches the original composition, it is thought that these boron atoms are still wrapped by a silica network. After leaching out the boron in the boron-rich phase, spinodal pores with high connectivity can not be formed in such regions (Fig. 6) and it is supposed that a spinodal pore line occurs at the initial stage of the spinodal decomposition (Fig. 5). The boron-rich phase above the spinodal pore line allows disturbance of the silica network and thus leads to connective pores after leaching. However, the boron-rich phase below the spinodal pore line cannot give rise to connective pores because the miscibility of the topology between the boron and the silica is still very high. The proposed model can be confirmed by experimental data of the leaching process. As shown in Fig. 3, the measurement of eluted boron indicates that all the borate oxide in the glass is completely removed during acid-leaching. According to the composition of the glass and the density of $B_2O_3$, it is easy to calculate the percentage volume occupied by leached borate oxide. However, this calculated value (10.5%) does not coincide with the experimental measurement of the pore volume by the $N_2$ adsorption method and the volume of the spinodal pore is smaller than the volume of the eluted borate oxide (16%). This confirms that only part of the leached boron contributes to the formation of spinodal pores. Finally, the proposed leaching model gives a reasonable explanation for the experimental result of the pore size distribution (Fig. 4). Since only part of the boron-rich phase contributes to the formation of spinodal pores, the size of the spinodal pores after acid leaching is therefore less than the wavelength of the spinodal wave.

In summary, we find that spinodal phase separation occurs upon quenching a boron silicate glass at a rate of $10\,^{\circ}\mathrm{C\,s^{-1}}$. After acid leaching, fine spinodal pores with radii $<1$ nm were formed. The size of the pores based on the so-called spinodal phase separation is much less than the theoretical wavelength associated with the decomposition owing to the small amplitude of the decomposition wavelength upon rapid cooling. The experimental results suggest that spinodal pores are formed only by part of the boron-rich phase which is above the spinodal pore line in a acid leaching model proposed in present study.

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