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Ion-exchange-induced Phase Separation and Preparation of Porous Glass

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Utilizing the difference in the size of the immiscibility regions with alkali ions, phase separation was induced at the surface of $70SiO_2{\cdot}15B_2O_3{\cdot}15Na_2O$ (mol %) glass by ion exchange in which Na^+ ions were replaced by Li^+ ions in molten $LiNO_3$ salt at 400 °C. The heat treatment after the ion exchange made the phase separation proceed and formed phases which can be dissolved by acid treatment. Through the ion-exchange-induced phase separation, we prepared monolithic glasses, in which only the surface region is porous and the rest is homogeneous and transparent.

In the immiscibility regions of composition for borosilicate glass systems, phase separation occurs resulting in heterogeneous phases consisting of silica-rich and borate-rich domains.[1] When the phase separation occurs through spinodal decomposition, the two phases are continuously interconnected and the interfaces between them are obscure. By acid treatment of the phase-separated glasses with the interconnected phases, the borate-rich phases are dissolved, and as a result porous glasses made of silica-rich phases are obtained.[2–4] The silica-rich porous glasses are utilized to prepare Vycor® glass.[2] They have been also of great interest for applications as carriers of catalysts and enzymes, separation membranes, ionic conductors, and precursors of phosphors.[4,5]

The immiscibility regions of the borosilicate (SiO_2–B_2O_3–M_2O, M = alkali) systems become narrower with atomic number of the alkali atoms from lithium to cesium.[1] Therefore, there exist compositions which are out of the immiscibility regions at a temperature lower than the liquid temperature when alkali ions are larger, but in the regions when the alkali ions are smaller with the same molar composition of SiO_2, B_2O_3, and the alkali oxides. Thus, at first, glasses having such composition are prepared with larger alkali ions; the glasses are homogeneous because the composition is out of the immiscibility regions. Then the alkali ions are replaced by smaller ones through ion exchange. By the replacement of the ions, phase separation will be induced because the composition with the smaller alkali ions is in the immiscibility region. Actually, using this difference in the immiscibility regions with the kind of the alkali ions, Karapetyan et al. have demonstrated that the phase separation is induced by the ion exchange and that the phenomenon is reversible.[6]

When the ion-exchange-induced phase separation takes place through the spinodal decomposition, it is expected that the acid treatment after the phase separation leads to glasses, which are monolithic and partly porous; the other parts of the glasses are homogeneous. In this study we prepared such monolithic glasses, in which only the surfaces are porous, using a sodium borosilicate glass through Na/Li ion exchange and acid treatment.

Glasses with the composition, $70SiO_2{\cdot}15B_2O_3{\cdot}15Na_2O$ (mol %), were prepared from reagent grade raw materials, SiO_2, B_2O_3, and Na_2CO_3, by melting in Pt crucibles at 1400 °C for 1 h. The obtained glasses were annealed at 600 °C for 1 h, cut to $10 \times 10 \times 20\,mm^3$, and polished. The glass transition and softening temperatures were 636 and 684 °C, respectively. The Na/Li ion exchange was carried out by immersing the glass samples in molten $LiNO_3$ salt at 400 °C for 12 h. Post heat treatments at 625 °C for various periods were carried out for the ion-exchanged glasses. Then, the acid treatments were performed in 1 M HNO_3 for 30 min at 90 °C. Vitrification or crystallization was judged by naked eye observation and X-ray diffraction. Surface observation and measurements of distribution of elements along the depth were performed with a scanning electron microscope and an energy dispersive X-ray microanalyzer, respectively. Elemental analyses of the acid solution after the acid treatments were performed by an inductively coupled plasma analysis. The distribution and average of pore size were measured with a mercury porosimeter.

As-prepared glasses were colorless and transparent. After the Na/Li ion exchange, however, they became opaque from the surface up to about 1 mm inside as shown in Figure 1. After the post heat treatments at 625 °C for the ion-exchanged glasses, the parts became more opaque while no variations were observed for the transparent parts inside of the glasses. Figure 1 also shows the X-ray diffraction patterns of the glass before ion exchange and the opaque parts of the ion-exchanged glasses before and after the post heat treatments for various periods. Only halo pattern was observed for the ion-exchanged glass before the post heat treatment suggesting that becoming opaque is not because of the crystallization but to the phase separation. In fact, line expansion curves showed a characteristic pattern to the phase-separated glasses, in which two glass transition points were

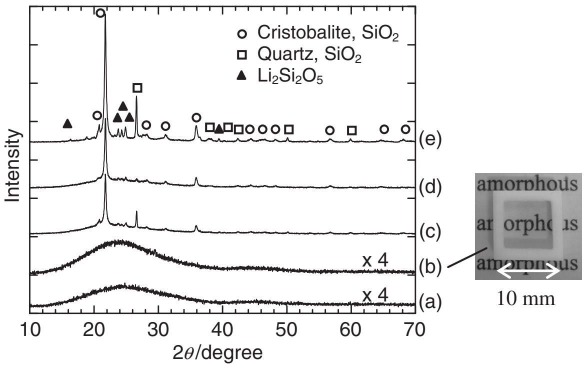

Figure 1. X-ray diffraction patterns of the $70SiO_2{\cdot}15B_2O_3{\cdot}15Na_2O$ glasses, (a) before ion exchange, (b) after ion exchange, and after ion exchange and post heat treatment at 625 °C for (c) 1, (d) 12, and (e) 48 h. The photograph of (b) is also presented.

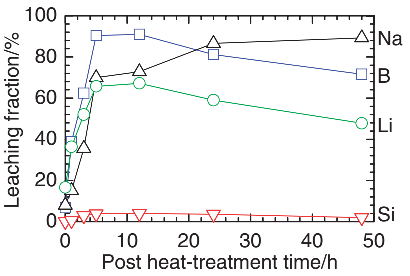

Figure 2. Post heat-treatment time dependences of leaching fractions of ions in the acid treatment.

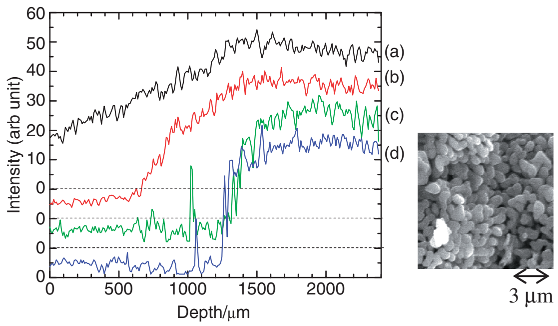

Figure 3. Depth profiles of Na in the ion-exchanged glasses, (a) without the post heat treatment and before the acid treatment, and with the post heat-treated at 625 °C for (b) 1, (c) 5, (d) 24 h, and after the acid treatment. Photograph shows the SEM image of sample (d).

observed at 513 and 585 °C. After the post heat treatment, diffraction lines assigned to cristobalite and quartz were observed and those of $Li_2Si_2O_5$ crystal in the glasses heat-treated for longer period. These diffraction lines became stronger with the heat-treatment time.

Figure 2 shows that heat-treatment time dependence of the leaching fractions of ion into 1 M HNO_3 solution in which the ion-exchanged glasses were immersed at 90 °C for 30 min. The fractions were defined as the ratio of the leaching ions to the incorporated ions for lithium, and for the other elements, the ratios of the leaching ions to the ions which presented before the acid treatment in the ion-exchanged parts, i.e., from the surface to the diffusion depth of Li^+ ions. The diffusion depth of Li^+ was determined by the line profile of Na^+ distribution (Figure 3). The amount of Na^+ ions present in the region was estimated by the subtraction of the amount of the incorporated Li^+ from the amount of the Na^+ present in the region before the ion exchange. Figure 2 shows that Si hardly leached regardless of the heat-treatment time. On the other hand, although the leaching fractions for lithium, sodium, and boron were small for the glasses before the post heat treatment, they increased up to 70% with increasing the heat-treatment time then slightly decreased for lithium and boron beyond 12 h.

According to the phase diagrams of the SiO_2–B_2O_3–M_2O (M = Li and Na) systems, the immiscibility temperature of the composition, $70SiO_2{\cdot}15B_2O_3{\cdot}15Na_2O$, is lower than 550 °C while that of $70SiO_2{\cdot}15B_2O_3{\cdot}15Li_2O$ is over 950 °C.[1] Although the phase diagrams show the immiscibility temperatures when the melts of the composition are cooled, they suggest that the immiscibility temperature of the glass, $70SiO_2{\cdot}15B_2O_3{\cdot}15Na_2O$, rapidly increased by the Na/Li ion exchange. Furthermore, the glass transition temperature of the ion-exchanged glass decreased to 513 °C which was lower than the temperature of the post heat treatments. Then it is expected that the phase separation through the spinodal decomposition occurred at the regions where some parts of the Na^+ ions were replaced by Li^+ ions. This leads to the borate-rich phase dissolution by the acid treatment as shown in Figure 2. Another possibility is that the crystallization as shown in Figure 1 induced the formation of the phases which can dissolve in acid. Further investigations are in progress to elucidate the mechanism of the phase separation in detail.

Figure 3 shows the line profiles of Na distribution along with the depth for the glasses after the acid treatment. Assuming that the Li^+ ions replaced only Na^+ ions, the Li^+ ions diffused to about 1300 μm. The line profiles did not vary by the post heat treatments within the resolution of the measurement. However, they varied by the acid treatment showing that Na^+ ions leached from the surface to the inside of the glasses with the heat-treatment time. For the glass which was heat-treated for 5 h, Na^+ leached almost completely until the depth where the Li^+ ions reached by diffusion. The acid treatment made the glasses porous from the surface to the inside of the glasses. This is shown by the photograph in Figure 3 presenting glass which was post heat-treated for 24 h and then was immersed in HNO_3 solution. The pore size distribution of the glass measured with a porosimeter showed two peaks at 200 nm and about 10 μm. The intensities of both sized-pores were almost the same for the 24-h post heat-treated glass.

In summary, Na^+ ions until 1300 μm in depth in the $70SiO_2{\cdot}15B_2O_3{\cdot}15Na_2O$ glasses were partly replaced by Li^+ ions through the ion exchange in molten $LiNO_3$ salt at 400 °C for 12 h. The phase separation was induced by the ion exchange and proceeded by the post heat treatment at 625 °C, resulting in the formation of phases which can dissolve in acid. Furthermore, we demonstrated that the monolithic glasses, which are partly porous, are obtained through the ion-exchange-induced phase separation and acid treatment.

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References

1 a) W. Haller, D. H. Blackburn, F. E. Wagstaff, R. J. Charles, *J. Am. Ceram. Soc.* **1970**, *53*, 34. b) O. V. Mazurin, G. P. Roskova, E. A. Porai-Koshits, in *Phase Separation in Glass*, ed. by O. V. Mazurin, E. A. Porai-Koshits, North-Holland Physics Publishing, New York, **1984**, Chap. IV, pp. 103–142.
2 a) H. P. Hood, M. E. Nordberg, U.S. Patent, 2106744, **1938**. b) M. Nordberg, *J. Am. Ceram. Soc.* **1944**, *27*, 299.
3 T. Yazawa, H. Tanaka, K. Eguchi, S. Yokoyama, *J. Mater. Sci.* **1994**, *29*, 3433.
4 T. Yazawa, *Key Eng. Mater.* **1996**, *115*, 125.
5 a) T. Yazawa, H. Tanaka, K. Eguchi, *J. Mater. Sci. Lett.* **1994**, *13*, 494. b) T. Araki, Y. Daiko, A. Mineshige, M. Kobune, N. Toyoda, I. Yamada, T. Yazawa, *J. Am. Ceram. Soc.* **2010**, *93*, 127. c) L. Yang, M. Yamashita, T. Akai, *Opt. Express* **2009**, *17*, 6688.
6 a) G. O. Karapetyan, V. V. Loboda, D. K. Tagantsev, *Glass Phys. Chem.* **1999**, *25*, 288. b) G. O. Karapetyan, V. V. Loboda, D. K. Tagantsev, *J. Non-Cryst. Solids* **2000**, *270*, 154.