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Ion-exchange-induced Phase Separation at Dot-like Domains on Glass Surface through a Staining Method

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Staining, which has been used for coloring of glass, was extended as a method for ion exchange in which monovalent ions in the localized fine domains at the surface of glass are replaced by other ions contained in the stain. Here, mixed aqueous $LiNO_3$–poly(ethylene glycol) solution was deposited as dots approximately 100 μm in diameter on a $70SiO_2 \cdot 15B_2O_3 \cdot 15Na_2O$ (mol %) glass by ink-jet printing. Then the glass was heat-treated at 400 °C resulting in the exchange of Li^+ for Na^+ ions at the dot-like domains. This ion exchange induced phase separation at the dots. Subsequent heat treatment at 600 °C and acid leaching made the dot domains porous. Consequently, we succeeded to prepare a glass, at the surface of which dot-like domains were porous and a number of the dots are periodically arrayed.

Staining is a glass-coloring technique in which mixtures called stain, composed of silver or copper inorganic salts, organic resins such as acrylic or cellulose resins, and organic solvents, are applied on glasses, and then the glasses are heat-treated resulting in the coloring of the glass surfaces. The mechanism for the coloring is as follows: during the heat treatment, silver or copper ions in the stain are incorporated into glasses, reduced to metal, and then aggregate in the glasses to form nanoparticles which have intense absorption in the visible region.[1–3] In the staining process, silver or copper ions are incorporated into glasses as replacement for alkaline ions contained in the glasses. This fact means that a similar reaction to ion exchange occurs during the staining process and that the staining, as well as conventional ion exchange using molten salts, can be applied not only for coloring of glasses but also for modification of other properties of glass surfaces. As an example, we reported that staining is applicable to fabricate graded-index waveguides, in which silver or copper ions were incorporated into glass substrates to increase refractive index at the surfaces. In this case, the coloring of the glass was suppressed under the controlled heat treatments during the staining.[4]

In the process of conventional ion exchange, glasses are usually immersed in molten salts at a temperature lower than their glass-transition temperatures. Thus, to exchange ions at localized domains of glass surfaces, e.g., to fabricate channel waveguides with increasing refractive index along lines of several micrometers in width through the incorporation of silver ions, the surface of the glasses should be coated with masks, which are usually prepared by lithography. In the staining process, on the contrary, ions are incorporated into glasses at restricted domains on which stain is applied. Therefore, if the stain is applied on localized fine domains of glass surfaces by means of a printing technique, such as ink-jet or screen printing, the incorporation of ions takes place only at the fine domains. Consequently, it is expected that we can fabricate periodical fine structure of compositional modification in which specific monovalent ions contained in the glass are replaced by others at microordered fine domains on the glass surfaces without relying on lithography. It was demonstrated that by means of staining combined with ink-jet printing we can easily fabricate glasses in which silver ions are incorporated into dot-like domains approximately 100 μm in diameter on the surface of the glasses and a lot of the dots are arrayed with periodicity of several hundred micrometers.[5] This technique will be applicable to fabricate graded-index microoptics such as channel waveguides and microlenses. Thus, in combination with printing technologies, staining should have more extended applications to provide high functionalities to glasses.

As another example, in this work, we performed Li^+ for Na^+ ion exchange for a borosilicate glass by means of the staining combined with ink-jet printing. We used a borosilicate glass with a specific composition in which phase separation to silica-rich and borate-rich phases is induced in the glass through the ion exchange of Li^+ for Na^+.[6,7] This ion-exchange-induced phase separation takes place because of the difference in the immiscibility region between the sodium and lithium borosilicate systems. The region of the latter is larger than that of the former, and then the ion exchange by Li^+ for Na^+ causes the composition of the glass to enter into the immiscibility dome from the outside of the dome. Furthermore, the borate-rich phases are selectively dissolved through acid leaching. Consequently, we succeeded to fabricate a glass, at the surface of which dot-like domains approximately 100 μm in diameter have porous structure.

We chose a composition of the sodium borosilicate glass, $70SiO_2 \cdot 15B_2O_3 \cdot 15Na_2O$ in mol %. The immiscibility temperature of this composition is 550 °C while that of the lithium borosilicate glass of the homologous composition, $70SiO_2 \cdot 15B_2O_3 \cdot 15Li_2O$ is 950 °C.[8] A batch mixture of SiO_2, B_2O_3, and Na_2CO_3 with the appropriate composition was melted at 1300 °C for one hour and cast into a carbon mold. The obtained glass was annealed at 600 °C for one hour. The glass-transition and softening temperatures determined with a dilatometer were 636 and 684 °C, respectively. The glass was colorless and transparent; no phase separation was macroscopically observed. This is because the immiscibility temperature of this composition was lower than the glass-transition temperature. The glass was cut to the size, $10 \times 10 \times 2\,mm^3$, and both sides were polished.

The Li staining combined with ink-jet printing was performed as follows. Mixed aqueous solution of 1 or 2 M $LiNO_3$–0.1 M poly(ethylene glycol) (PEG), hereafter called Li stain, was used for ink-jet deposition. The deposition was carried out using a piezo-actuated ink-jet device (Microjet IJET-2000C). The

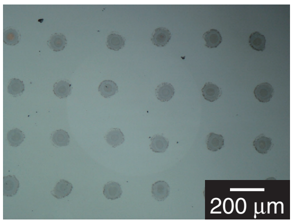

Figure 1. Photograph of the surface of glass observed with an optical microscope. Ten droplets of Li stain were deposited for each dot on the glass. Then, the glass was heat-treated at 400 °C for 12 h and residual stain was flushed with water.

nozzle diameter was 50 µm. The driving signals were rectangular pulses with 14–19 µs width, 113 Hz frequency, and 96–118 V amplitude. These conditions were adjusted to minimize the dot diameter and to suppress satellite droplet formation. The deposited solution on the glass was dried, and the glass was heat-treated at 400 °C for 12 h. During the heat treatment, Li^+ ions were supposed to be exchanged for Na^+ ions as shown below. After the heat treatment at 400 °C, residual Li stain was flushed with water and the glass was furthermore post-heat-treated at 600 °C for 48 h. Subsequently, the glass was immersed in 1 M HNO_3 solution at 90 °C for 5 or 30 min.

Surface observations for the glass were performed by means of a scanning electron microscope (SEM, Hitachi S-800) and atomic force microscope (AFM, Toyo Corporation Nano-R™). Sodium line profiles were measured using an energy-dispersive X-ray microanalyzer (EDX, Hitachi EMAX-7000) equipped with the SEM.

Figure 1 shows a photograph of the surface of the glass which was heat-treated at 400 °C for 12 h after the deposition of the Li stain. Traces of dots were clearly observed. The size of the traces became larger with increasing the number of droplets for each dot deposition, approximately 50, 80, and 130 µm for one-, five-, and ten-droplet deposition for each dot, respectively. In the previous study, we carried out ion exchange by Li^+ for Na^+ in $LiNO_3$ molten salt for a borosilicate glass which has the same composition with that in the present study.[7] The ion exchange induced phase separation at the surface region of the glass. This is due to the immiscibility temperature of the Li^+-incorporated region was elevated while the glass-transition temperature lowered; two glass transitions were observed at 513 and 585 °C for the glass ion-exchanged in the $LiNO_3$ molten salt. The transparent glass turned opaque at the ion-exchanged region. Therefore, it is supposed that the observed traces as seen in Figure 1 are due to the phase separation induced by the ion exchange at the Li-stain-deposited domains. The traces became smaller with polishing the surface and finally disappeared at the depths of approximately 15, 30, and 40 µm, for one-, five-, and ten-droplet deposition, respectively. This fact means that the diffusion depth of Li^+ ions reached at least ten to several tens of micrometers. Figure 2 shows the line profile of sodium along with the aligning dots measured with EDX. The sodium concentration was clearly decreased at the dots, which supports that the ion exchange by Li^+ for Na^+ occurred.

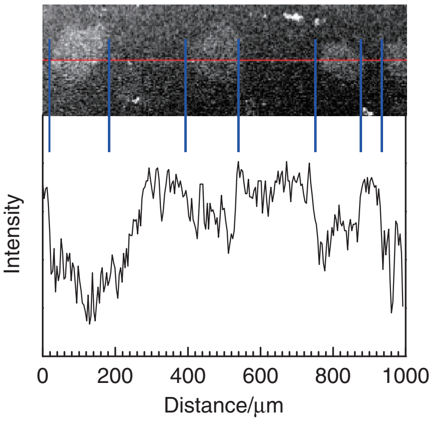

Figure 2. SEM image and the line profile of sodium along with the aligning dots measured with EDX. Five droplets were deposited for each dot on a glass and then the glass was heat-treated and residual stain was flushed with water.

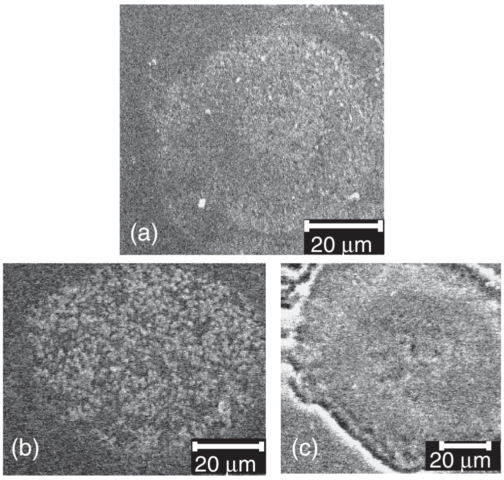

Figure 3. SEM images of one-droplet dots after acid treatments at 90 °C for 5 min in 1 M HNO_3 on the glass (a) without post heat treatment and (b) with post heat treatment at 600 °C for 48 h. (c) The dot after acid-treated at 90 °C for 30 min in 1 M HNO_3 on the glass with post heat treatment at 600 °C for 48 h.

It is well known that alkali borate-rich phases leach out with acid treatment for glasses which are phase-separated through spinodal decomposition because the separated phases have continuously interconnected structure.[9,10] In the previous study, we found that no elements leached out with acid treatment from the sodium borosilicate glass in which phase separation was induced through the ion exchange in $LiNO_3$ molten salt.[7] However, leaching of boron and alkaline (sodium and lithium) ions was observed from the glasses which were ion-exchanged and subsequently heat-treated at 600 °C or temperatures higher than that. The leaching fraction of these elements increased with the heat-treatment period and reached more than 60% for the glass heat-treated at 600 °C and 90% at 625 and 650 °C. This fact indicates that the post heat treatment evolved interconnected structure of the phases separated through ion exchange in the glasses like spinodal decomposition. Furthermore, the acid treatment turned the phase-separated domains to porous structure with pore size of approximately 200 nm. In this study, similar behaviors were observed for the ion-exchanged dot domains through Li staining. As shown in Figure 3a, no variation in the dot was found after acid treatment for the Li-stained, i.e., the ion-exchanged, glass without post heat treatment. However, for

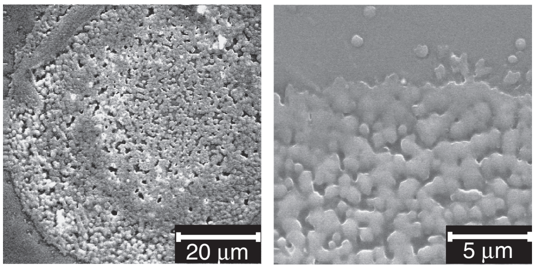

Figure 4. SEM images of a ten-droplet dot on the glass with post heat treatment and acid treatment, showing a characteristic interconnected phase structure.

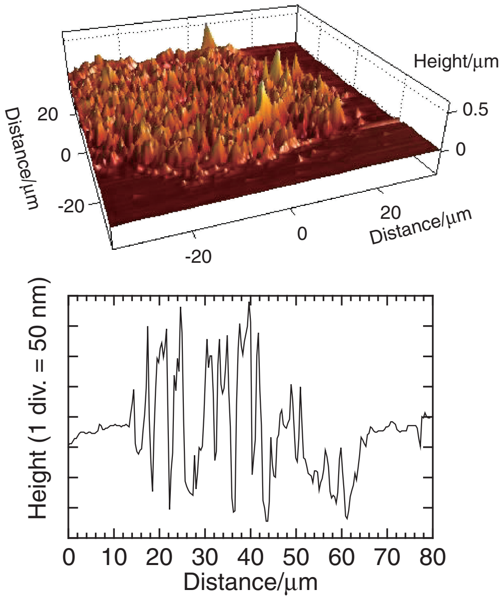

Figure 5. Three-dimensional AFM image and the side-view profile of a dot at the surface of glass which was Li-stained, i.e., ion-exchanged, followed by post heat treatment and acid treatment.

the glass which was Li-stained, and subsequently heat-treated at 600 °C for 48 h and treated in 1 M HNO_3 at 90 °C for 5 min, the dot domains became porous as shown in Figure 3b. Through the acid treatment for 30 min, on the other hand, the dot domains were completely removed as shown in Figure 3c. Furthermore, the characteristic interconnected structure was also observed as shown in Figure 4.

Figure 5 shows three-dimensional AFM image and the side-view profile of a dot at the surface of the glass which was Li-stained followed by post heat treatment and acid treatment. Porous structure was also clearly observed at the dot. Another characteristic feature is that the dot domain increased by 100 to 200 nm from the glass surface. We observed that the increase had already occurred after the Li staining (before heat and acid treatments). Although the mechanisms for the increase are not clear, at least two possibilities are considered. One is that a volume expansion occurred through the rearrangement of the network structure accompanied by the ion-exchange-induced phase separation. Another possibility is that a reaction with water, e.g., hydration, occurred at species which appear through the phase separation because flushing with water was carried out after the Li staining for the AFM observation. Further experiments are continued in order to clarify the mechanism for these phenomena.

In summary, Na^+ ions were replaced by Li^+ ions at dot-like domains on the surface of a $70SiO_2 \cdot 15B_2O_3 \cdot 15Na_2O$ glass through Li staining combined with ink-jet technology. The replacement induced phase separation at the dots. The subsequent acid leaching turned the phase-separated dot domains to porous structure. Consequently we could prepare glasses, at the surfaces of which localized fine domains of micrometer size were porous and the other regions were transparent and homogeneous. As is well known, extensive investigations have been performed on applications of porous glasses prepared through conventional phase separation and acid leaching.[10,11] Furthermore, research has been recently reported on the preparation of glasses with characteristic properties utilizing the immiscibility phenomena.[12] We can expect, therefore, that the newly prepared glasses, in which phase separation occurs at localized fine domains and the domains have porous structure, will have potential applications expanding into a wider area.

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