Phase separation of borosilicate glass containing sulfur

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A 10Na2S·30B2O3·60SiO2 (mol %) glass was prepared, and the changes in glass structure and chemical state of sulfur caused by phase separation were investigated. In the as-prepared and heat-treated glasses, sulfur was present as S2− anion and polysulfide S3− and S4− anions, and Si–S and B–S bonds were not confirmed. A phase separation by spinodal decomposition was observed after heat-treatment, where sulfur was preferentially distributed to borate-rich phase. Even after the phase separation, formation of non-bridging oxygen was not recognized. The preferential distribution of sulfur anions in the present glass was explainable on the basis of the change in population of sodium ions, which compensated the negatively-charged sulfur anions.

1. Introduction

Phase separation of borosilicate glass is well known. In Na2O–B2O3–SiO2 glass, glasses with low Na2O content separate into SiO2- and B2O3-rich phases due to heat-treatment at temperatures higher than glass transition temperature.1,2) It has been widely used in production of porous glass and SiO2 substitution. Recently, novel utilization methods of phase separation of borosilicate glass has been developed for the recycling of wastes containing SiO2, such as waste glass,3) radioactive waste,4) blast furnace slag5) and municipal waste slag.6) In the recycling process, B2O3 is added to the wastes, preparing borosilicate glasses, from which high SiO2 glass can be recovered by using phase separation.

In the blast furnace slag5) and municipal waste slag6) measurable amount of sulfur (<5 mass %) is included, which originate from iron ore, paper, kitchen wastes, vulcanized rubbers, etc. In recycling the sulfur-containing wastes to raw materials of glassware, sulfur should be removed from the wastes, because sulfur is a possible cause of coloration. Little is known concerning the chemical states of sulfur in borosilicate melts7–9) and glasses.10,11) According to Asahi et al.,10,11) sulfurs in Na2S–B2O3–SiO2 glass are present with a negative charge in the glass, and Si–S bonds are confirmed only when non-bridging oxygen (NBO) atoms are formed in the glasses.

To the knowledge of the authors, no report has been published on the phase separation of sulfur-containing glasses. Then, in the present study, phase separation of a glass in Na2S–B2O3–SiO2 system has been investigated. Sulfur-containing 10Na2S·30B2O3·60SiO2 glass (mol %) and sulfur-free 10Na2S·30B2O3·60SiO2 glass for comparison were prepared. The glass composition was chosen because of the similarity with Vycore® glass. Chemical state of sulfur in the sulfur-containing glass was investigated from optical absorption, and chemical composition was determined with inductively-coupled plasma (ICP) emission spectrometry. Glass structure was examined with using 11B and 29Si MAS-NMR spectrometries. Texture after phase separation was observed with scanning electron microscope (SEM). From these analyses, changes in glass structure and chemical states of sulfur caused by phase separation were studied.

2. Experimental

The glasses with compositions given in Table 1 were prepared by a conventional melt-quenching method. The raw materials of reagent grade Na2S, Na2CO3, B2O3 and SiO2 were mixed thoroughly and melted in an alumina crucible with a lid of alumina placed in an electric furnace at 1400°C for 30 min. In preparing the sulfur-free glass, a platinum crucible with a lid of alumina was used. The melts were poured onto an iron plate and quenched by being pressed with another iron plate to form glass plates with a thickness of 2–3 mm. Differential thermal analyses (DTA) were carried out with a heating rate of 10 K/min in order to determine glass transition and crystallization temperatures, Tg and Tc, respectively.

Heat treatments for phase separation were performed at the temperatures 600 and 650°C, which were between Tg and Tc. After the heat treatment, the glasses were immersed in nitric acid of 1.0N for 16 and 48 h, and the insoluble residues were recovered with vacuum filtration. After being rinsed in water and dried in an oven, silica-rich glasses were obtained.

X-ray diffraction (XRD) measurement was done to confirm the

Table 1. Batch and ICP analytical compositions of the samples

<table>
<thead>
<tr>
<th>Component</th>
<th>10Na2S·30B2O3·60SiO2</th>
<th>10Na2O·30B2O3·60SiO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch/ mol %</td>
<td>Analytical/ mol %</td>
<td>Batch/ mol %</td>
</tr>
<tr>
<td>Na2S</td>
<td>10.0</td>
<td>6.87 (3.28)</td>
</tr>
<tr>
<td>Na2O</td>
<td>—</td>
<td>0.31 (3.92)</td>
</tr>
<tr>
<td>B2O3</td>
<td>30.0</td>
<td>27.7</td>
</tr>
<tr>
<td>SiO2</td>
<td>60.0</td>
<td>65.2</td>
</tr>
<tr>
<td>Al2O3*</td>
<td>—</td>
<td>2.65</td>
</tr>
</tbody>
</table>

*1: Tentative content under the assumption that sulfurs are present as an S2− anionic state.
*2: Final content estimated from the results of 11B MAS-NMR. The average charge of S is estimated as −0.94.
*3: External content.

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specimens remaining in amorphous state. Chemical composition of the specimens, such as the glasses before phase separation and the acidic solutions and insoluble residues after acid treatment was determined by an inductively coupled plasma (ICP) emission spectrometry. Optical absorption was evaluated by a spectrophotometer with a wavelength range of 250–750 nm, and the diffuse reflection measurement was applied for the specimens after acid treatment. Phase separation was confirmed by a scanning electron microscope (SEM) observation, where the specimens were etched in 5% HF solution for 60 s. Local structures around Si, B and Al atoms were investigated with $^{29}$Si, $^{11}$B and $^{27}$Al MAS-NMR measurements, respectively. For the $^{29}$Si MAS-NMR measurement, 0.2 mol% of Gd$_2$O$_3$ was added to the glass batches in order to shorten the relaxation time. NMR measurements were carried out at 7.05 T on a Varian Unity Inova 300 spectrometer, and the respective conditions of $^{29}$Si, $^{11}$B and $^{27}$Al NMR measurements were as follows: frequency = 59.6, 90.2 and 79.2 MHz, sample spinning speed = 5.0 kHz (all), pulse duration = 4.0, 0.6 and 0.6 μs, repetition time = 1.0 s (all), chemical shift standard = poly (dimethyl siloxane) (PDMS), BPO$_3$ andaq.AI Cl$_3$.

3. Results

3.1 As-prepared glasses

The analytical composition of the glasses is shown in Table 1, in which Na$_2$S and Na$_2$O contents (1 in Table 1) are tentatively given based on the assumption that sulfurs are present as an S$^{2-}$ anionic state. In both glasses, SiO$_2$ content increases as compared with the nominal compositions, indicating that parts of Na$_2$S, Na$_2$O and B$_2$O$_3$ were volatilized during the melting process. In the sulfur-containing glass, Al is also confirmed, which is eluted from the alumina crucible used. The remaining rate of sulfur in the as-prepared glass is estimated at 63%. Figure 1 shows the DTA curves of the as-prepared glasses. $T_e$ and $T_x$ of the sulfur-containing as-prepared glasses are 473 and 657°C, respectively, and those of the sulfur-free glass are 486 and 672°C. The difference in $T_e$ and $T_x$ between the glasses are not so clear, and the difference in coloration is, however, quite clear.

As shown in Fig. 2, the sulfur-containing glass is faint blue, and the sulfur-free glass is colorless. In the optical transmission spectra shown in Fig. 3, the sulfur-containing glass shows lower transmittance at λ > 300 nm than the sulfur-free glass, and a strong and weak absorptions are confirmed at 585 and 400 nm, which are attributed to S$_2^-$ and S$_3^-$, respectively. According to Ashih et al., low molecular-weight sulfur anions such as S$_2^-$, S$_3^-$ and S$^{2-}$ are present in the space between the glass networks without forming Si–S and B–S bonds in the case of low alkali glasses colored faint blue or blue, and in the case of high alkali glasses colored yellow or red, S$^{2-}$ anions are substituted for NBO ions in SiO$_2$ and BO$_3$ units at the end of the glass networks, and polysulfide anions S$_n^{2-}$ with larger size are also present in the space between the glass networks. It is well known in borosilicate glass that NBOs are not produced in the glasses with Na$_2$O/B$_2$O$_3$ molar ratio < 0.5. In the present glasses, Na$_2$S(Na$_2$O)/B$_2$O$_3$ ratio is small (< 1/3), and hence NBOs are expected to be absent. It is consequently suggested that the coloration of faint blue is due to the optical absorption at 585 nm of S$_2^-$ anions present in the space between the glass networks. As indicated, S$_2^-$ and S$_3^-$ anions other than S$^{2-}$ anions are confirmed in the as-prepared glasses, and hence the average charge of sulfur anions should be less negative than –2. The chemical states of sulfur will be discussed later.

Figure 4 shows $^{29}$Si MAS-NMR spectra. In the as-prepared glasses, a peak at δ ~ –105 ppm is commonly observed, which is assigned to Q$_4$ species, that is, SiO$_4$ unit consisting of four bridging oxygen (BO) atoms. If Si–S bonds were present, peaks would be observed at around –20 and –60 ppm. In the present glass, however, these peaks are not recognized in Fig. 4a.
suggesting that sulfur atoms are not bound to Si atoms and present in the space between the glass networks.

The result of $^{11}$B MAS-NMR measurement is shown in Fig. 5. The sharp peak at $\delta \approx 0$ ppm and the asymmetric broad peak at 20−290 ppm are associated with four- and three-coordinated boron (B4 and B3) atoms, respectively. The relative amount of B4 with respect to total amount of boron is designated as $N_{B4} \equiv B4/(B3 + B4)$, which is estimated from the peak separation of $^{11}$B MAS-NMR spectrum. Comparing the as-prepared glasses, the sulfur-containing glass shows smaller $N_{B4}$ value than the sulfur-free glass. As shown in Table 1, the incorporation of Al from the Al crucible used is confirmed. Al atoms in the sulfur-containing glass are present in tetrahedral $\text{AlO}_4$ units, which is identified from $^{27}$AlMAS-NMR measurement. It is well known that tetrahedral $\text{AlO}_4$ units take part in glass networks, and $\text{AlO}_4$ units possess a negative charge so that network modifiers such as Na$^+$ ions are consumed to compensate the negative charge of $\text{AlO}_4$ units. Na$^+$ ions are also used for the compensation of sulfur anions present in the space between the glass networks, and hence the amount of remaining Na$^+$ ions in the sulfur-containing glass is less than that in the sulfur-free glass. That is the reason for the difference in $N_{B4}$ value between the sulfur-containing and sulfur-free glasses.

3.2 Changes due to heat treatment

As shown in Fig. 1, $T_q$ and $T_c$ of the as-prepared glasses were not so different regardless of sulfur. Thereby, the heat-treatment temperatures were chosen at 600 and 650°C. As shown in Figs. 2 and 3, the heat-treatments result in the changes of the appearance and optical transmittance of the glasses. The sulfur-containing glass turns murky blue, and the sulfur-free glass becomes translucent white, and the decrease in optical transmission is observed in UV to visible region. It was confirmed from XRD measurement that all the samples remained in amorphous state after the heat treatments. It is therefore suggested that the decrease in optical transmission is caused by the phase separation in the glasses, and it is also expected that the size of the separated phases is comparable with the wavelength of the scattered light.

Figure 6 shows the SEM photographs of the surface of the heat-treated samples. Regardless of sulfur, spinodal phase separation is commonly confirmed in the heat-treated glasses. The size of the phase-separated texture is ca. 200 nm, and there is little difference between the sulfur-containing and sulfur-free glasses.

After the heat-treatments, $^{29}$Si NMR peak is broadened slightly to lower magnetic field side, and another peak component is confirmed at around −90 ppm (Fig. 4). In Si NMR spectra of alkali silicate glasses, $^{29}$Si peaks at −85−−92 ppm are attributed to Q1 species (SiO$_2$ unit consisting of three BOs and one NBO). In the present glasses, however, absence of NBO is expected from the glass composition even after the heat-treatments. It is consequently concluded that the −90 ppm peak is attributable to Q3 species neighboring of tetrahedral BO$_4$ units. As described below, most Si atoms are present in SiO$_2$-rich phase after the phase separation, and little B atoms are present in the SiO$_2$-rich phase. It is thereby supposed that the −90 ppm peak is not derived from Si atoms in the SiO$_2$-rich phase. However, little Si atoms should be distributed to the B$_2$O$_3$-rich phase, and it is therefore supposed that the contribution of Si atoms in the B$_2$O$_3$-rich phase giving the −90 ppm peak is emphasized for some reason. Gd$_2$O$_3$ was added to the glass batches for the $^{29}$Si MAS-NMR measurement. If more Gd atoms are distributed to the B$_2$O$_3$-rich phase after the phase separation, relative intensity of the −90 ppm peak will be enhanced than the case of even distribution of Gd atoms.

As shown in $^{11}$B MAS-NMR spectra (Fig. 5), $N_{B4}$ value decreases slightly after the heat-treatments regardless of sulfur in the glasses. According to Dell et al., $N_{B4}$ value is dependent only on Na$_2$O/B$_2$O$_3$ molar ratio in the NBO-free glasses such as Na$_2$O/B$_2$O$_3 < 0.5$. In the present sulfur-free glass, Na$_2$O/B$_2$O$_3$ ratio is almost constant at 1/3 even after phase separation, and hence $N_{B4}$ value should not change. The reason for the change in $N_{B4}$ value is discussed later.

3.3 Changes due to acid treatment

The chemical composition of the glass phases after the phase separation was estimated as follows; the B$_2$O$_3$-rich phase is
soluble to HNO₃ solution, and hence the composition of the B₂O₃-rich phase was determined from the concentration of the elements in the acid solution after the acid-treatment. The SiO₂-rich phase is insoluble to HNO₃ solution but is soluble to HF solution, and hence the insoluble solids obtained after immersing HNO₃ solution were completely dissolved by HF solution, from which the composition of the SiO₂-rich phase was determined. The result for the glass heat-treated at 650°C for 16 h is shown in Table 2. Sulfur is completely eluted to HNO₃ solution, indicating that sulfur is preferentially introduced to the B₂O₃-rich phase during the phase separation.

Figure 7 shows the optical absorption spectra, in which the photograph of a specimen after acid-treatment is also shown. The specimen after acid-treatment is porous and opaque, and hence diffuse reflectance measurement was used to obtain the absorption spectra shown in Fig. 7. The peaks at 585 and 400 nm associated with S⁺ and S⁻, respectively, are not observed after acid-treatment, which is consistent with the composition analyses.

4. Discussion

4.1 Glass composition and chemical states of sulfur

As shown in Fig. 5, the fraction of four-fold coordinated boron atoms, \( N_4 \) in the sulfur-containing glass is less than that in the sulfur-free glass. In the sulfur-containing glass, sulfur anions and AlO₄ units are present, and Na⁺ ions are consumed to compensate the negative charge of these negative species. Tetrahedral BO₄ units also possess a negative charge, and equivalent amount of Na⁺ ions are required for charge compensation. According to Dell et al.,††\( N_4 \) value is predicted as \( N_4 = \frac{Na_2O}{B_2O_3} \) molar ratio in the NBO-free borate and borosilicate glasses. \( N_4 \) value of the sulfur-containing as-prepared glass is 23.3%, and the amount of Na₂O used to produce BO₄ units is therefore expected as 6.5 mol%. In addition, 2 mol% of Na₂O is required to form AlO₄ units, and total amount of Na₂O consumed for the BO₄ and AlO₄ units is 8.5 mol%. However, the analytical amount of Na₂S + Na₂O is only 7.1 mol%, which is insufficient to compensate the negatively-charged species.

According to Nanba et al.,†† the fraction of four-fold coordinated boron atoms in borosilicate glass is predicted based on the optical basicity, \( \Lambda \), which is calculated from glass composition and electronegativity of the glass constituents. Based on their prediction, 1.9 mol% of Na₂O is enough to obtain \( N_4 = 23.3\% \) for the glass at B₂O₃:SiO₂ = 27.7:65.2. Then, 1.9 and 2.0 mol% of Na₂O is consumed to form BO₄ and AlO₄ units, respectively. Consequently, 3.2 \( \times \) 2 mol% of Na⁺ ions is remaining to compensate 6.8 mol% of negatively-charged sulfur atoms, and the average charge of sulfur anions is thereby estimated at \(-0.94\). The composition of the sulfur-containing as-prepared glass is finally given as 3.2Na₂S:13.3Na₂O:27.7B₂O₃:65.2SiO₂ + 2.0Al₂O₃.

The composition of the B₂O₃-rich phase in the sulfur-containing glass after a heat-treatment (650°C-16h) is also estimated in the same way, resulting in 3.6Na₂S:12.5:18.5Na₂O:76.9B₂O₃:1.0SiO₂ + 2.1Al₂O₃. The average charge of sulfur anions after the heat-treatment is estimated at \(-0.38\), which is much less than the charge of \(-0.94\) before the heat-treatment. As shown in Fig. 7, the absorption peaks at 585 and 400 nm increase in intensity due to the heat-treatment, indicating the increase in the polysulfide anions of \( S_3^2^- \) and \( S_2^- \), that is, the polymerization of \( S^2^- \) anions. After the heat treatment, the elimination of sulfur is not confirmed from ICP analysis, which also indicates the polymerization of sulfur anions or the increase of zero-valence molecular sulfurs such as \( S_2^- \). At phase separation, sulfurs and Al₂O₃ are selectively incorporated in B₂O₃-rich phase, which is explainable by the distribution of Na⁺ ions. In the present glass, sulfurs are present as anions, such as S²⁻ and polymerized S₃⁻ and S₂⁻ polysulfides. These negatively-charged sulfide anions are associated with Na⁺ ions as a charge compensator. Na⁺ ions also compensate negatively-charged BO₄ and AlO₄ units. At phase separation, Na⁺ ions are preferentially distributed to B₂O₃-rich phase, and the distribution shift of Na⁺ ions to B₂O₃-rich phase is accompanied by the segregation of negatively-charged species, resulting in the condensation of sulfurs and Al₂O₃ into B₂O₃-rich phase.

4.2 Fraction of BO₄ units

As shown in Fig. 5, the \( N_4 \) value decreases slightly after the heat-treatment regardless of sulfur in the glasses. As above mentioned, no NBOs are formed in the present glasses even after the heat-treatment, and hence the decrease in \( N_4 \) value is not explainable by the formation of NBOs. In borosilicate glass, Chen et al.¹⁷ reported the change in \( N_4 \) after heat-treatment, where they claimed that phase separation, formation of NBO and structural rearrangement of borate groups were responsible for the change in \( N_4 \). In the present glass, however, NBOs are not formed after the phase separation, and hence the total amount of BO₄ units should be kept even after the structural rearrangement.

As above mentioned, Nanba et al.¹⁸ reported the prediction of BO₄ fraction, in which it was revealed that \( N_4 \) value increased with increasing SiO₂/B₂O₃ molar ratio. Before phase separation,
SiO$_2$/B$_2$O$_3$ ratio is $\sim 60/30 = 2.0$, and after phase separation, SiO$_2$/B$_2$O$_3$ ratio in B$_2$O$_3$-rich phase decreases to almost nothing (1.0/76.9 = 0.01 from Table 2). It is consequently concluded that the difference in $N_i$ between as-prepared and heat-treated glasses is responsible for the change in composition from borosilicate to borate glasses.

5. Conclusion

Ternary Na$_2$S–B$_2$O$_3$–SiO$_2$ glasses were prepared by a conventional melt-quenching method, and the distribution behavior of sulfurs due to phase separation was investigated. After heat-treatment, the decrease in optical transmission was observed, and a spinodal phase separation was confirmed from SEM observation. $^{28}$Si MAS-NMR spectra suggested that Si atoms were present in $Q_4$ species, and Si–S and Si–NBO bonds were not produced in the glasses even after the phase separation. It was also indicated that sulfurs were present in the space between the glass networks as anions, such as $S^{2-}$ and polymerized $S_2^{2-}$ and $S_3^{3-}$ polysulfides. Na$^+$ ions were consumed to compensate the sulfur anions, and hence the fraction of BO$_4$ units in the sulfur-containing glasses was smaller than that in the sulfur-free glasses. After acid-treatment, absence of sulfur was confirmed in the insoluble solids, and the optical absorption of polysulfides also disappeared. The distribution behavior of sulfurs was successfully explained by the population shift of Na$^+$ ions.

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References