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Identification of nanometer-scale compositional fluctuations in silicate glass using electron microscopy and spectroscopy

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ABSTRACT

Silicate glasses are indispensable for optical and photonics applications, and their properties are affected by phase-separated structures. Understanding the phase separation behavior inside the glasses is thus crucial for controlling their optical properties. Here, we attempt to identify the phase-separated structure inside silicate glass by high-angular annular dark field-scanning transmission electron microscopy (HAADF-STEM) combined with a multi-slice image simulation. In addition to the phase-separated structure, we also demonstrate that the identifications of the type and stage of the phase-separation are possible by the HAADF observation in combination with a phase separation simulation.

Silicate glass is widely used in industry and technology, such as optical fibers, cover glasses for displays, and building windows. Its widespread applications arise from its varied properties, such as electric conductivity [1,2], high mechanical property [3,4], and ionic conductivity [5–7], which are achieved while maintaining its optical transparency.

To achieve optical transparency, the fabrication of homogeneous glass without dielectric interfaces that scatter optical light is important. However, some multicomponent silicate glass systems are known to separate into two or more phases and possess dielectric interfaces; this phenomenon is called phase separation. Although phase separation is usually not preferable for some optical glasses because of a degradation in the optical transparency, the active use of phase separation to enhance the optical property has also been reported [8,9]. An understanding of the mechanism of the phase separation in silicate-based glass and knowledge of how to control this phenomenon are crucial for the development of additional advanced optical glasses.

A phase-separated structure, especially on the nanometer scale, has been identified by using a scattering method, namely the structure has been observed in a Fourier space. These observations and theoretical analyses revealed the statistical behavior of phase separation and its structure [10,11]. Consequently, some theories have been developed. However, these theories are not ideal because they ignore interactions among the phases, which are difficult to treat in the Fourier space. For a greater understanding of the phase separation behavior, a real space observation of the phase separation and determining the interaction among phases have to be clarified.

Recently, scanning transmission electron microscopy (STEM) equipped with a spherical aberration corrector has achieved a sub-nm scale spatial resolution, and observation of phase-separated structures on the tens-nanometer order [12]. In these studies, the phase-separated structures were generally identified by some spectroscopic methods, such as electron energy loss spectroscopy (EELS) or energy dispersive X-ray spectroscopy (EDX), because they are commonly chemical sensitive [13,14]. However, an imaging method, such as the bright-field (BF) and high angular annular dark field (HAADF) methods, is usually used to obtain complementary information to the EELS or EDX mapping. It is known that the contrast of the HAADF-STEM method is almost proportional to the square of the atomic number [15,16]. Since HAADF image observations require a shorter duration time than those with EELS or EDX, the HAADF method is expected to provide the benefits of less damage and a shorter time for observation. These advantages are really important to observe beam-sensitive materials, such as silicate glasses, with high resolution to obtain detailed information about the phase-separated structure. However, even though there have been some reports on the identification of the phase separation of metallic glass using HAADF, to date, there have only been a few reports on the identification of the phase separation of nanometer scale silicate glass [12].

Here, we attempt to identify the nm-scale phase-separated structure in silicate glass by HAADF-STEM. In addition to the identification of the phase-separated structure, we also discuss the possibility for determining the thermodynamic meaning of the distribution of the HAADF intensity obtained by observation with sub-nm resolution.

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The silicate-based glass 20 CaO-10 Al_2O_3-70 SiO_2 (mass%) (22.0–6.1–71.9 mol%) was selected in this study because this composition is known to be located at the edge of the immiscibility region of the phase diagram and has been reported to separate into a major Ca-rich region and minor Si region [8]. The glasses with the similar compositions have been investigated, and a growth of the phase separated structure has been reported [17,18]. The bulk glass samples were prepared by the conventional melt-quench method. The mixed batch materials (analytical reagent grade) of SiO_2, Al_2O_3 and $CaCO_3$ were melted in an electric furnace at 1650 °C in a $Pt_{90}Rh_{10}$ crucible for 3 h. The melt was quenched into water to produce small fragments, and then mixed and re-melted in the crucible at 1680 °C for 3 h to further homogenize the glasses. The second melt was cooled by being cast onto a carbon plate to obtain cylindrical glass. Some of the samples were annealed at 900 °C in air for 900 min. The quenched sample without annealing is hereafter referred to as the "0-min sample", and the annealed sample for 900 min is called "900-min sample". From the thermodynamic theory, a much larger phase separated structure should be observed in the 900-min sample.

To avoid changes in the phase-separated structure of the glass by further heating and ion irradiation, the transmission electron microscopy (TEM) sample was fabricated by the crushing method [19]. STEM observation was performed using an aberration-corrected scanning transmission electron microscope (JEM-ARM200F, JEOL Ltd.) equipped at an accelerating voltage of 200 kV. The high-angle annular dark-field (HAADF), and electron energy loss spectra (EELS) were observed [3,20,21]. The convergent and detection angles for the HAADF image were approximately 40 and from 68~280 mrad, respectively. The thickness measurement was performed using EELS by the log-ratio method with the inelastic mean free path of 155 nm [22].

To investigate the HAADF image, we performed HAADF image simulation using the multi-slice method. The glassy structure of SiO_2 possessed 3240 Si atoms and 6480 O atoms in a 2.13 × 2.13 × 32.09 nm cell. Since HAADF intensity is changed by atom densities, thickness, and composition, their dependences on the HAADF intensity were separately considered by preparing calculation cells with different atom densities, thicknesses, and compositions. The atom density was changed by changing the cell size. The composition was changed by randomly replacing some Si atoms with Al atoms and Ca atoms. Furthermore, simple simulations of the phase separations were performed to discuss the phase separation behavior from the HAADF intensity,

Fig. 1(a) shows the HAADF image of the 900-min sample. From the HAADF image, it was observed that the contrast was not uniform, and dark droplet-like areas 20 nm to 60 nm in diameter were clearly observed. It is known that a droplet-type phase-separated structure is formed when the volume fractions of the two phases in the phase diagram are asymmetric. According to the phase diagram of the present system, the formation of the droplet shapes is thus reasonable [8]. The HAADF intensity ratio between the bright region and the dark region was 1.15–1.25. Furthermore, the area fraction between the bright and dark regions was around 0.36 (dark region/bright region). From the convergent and detection angles of the present HAADF-STEM observation, the following three causes for the HAADF intensity deviation can be considered: the differences in 1) atom density, 2) thickness, and 3) composition. To determine the origin of the HAADF intensity deviation, first we simulated the image contrast by using a multi-slice method [23], and then confirmed it using EELS.

Fig. 2 shows the dependence of the HAADF intensity on the atom density, thickness, and composition. Basically, the intensity linearly increased with an increase of them. First, we focused on the effect of the atom density. As described above, density was changed by changing the cell-size of the simulated model without compositional change. As shown in Fig. 2(a), an increase of approximately 18% in the atom density was needed to cause a HAADF intensity change. Since the Young's modulus of SiO_2 is 73.0 GPa [24], a compressed/tensile stress of 3.94 GPa was necessary to result in the bright/dark contrast in the HAADF image.

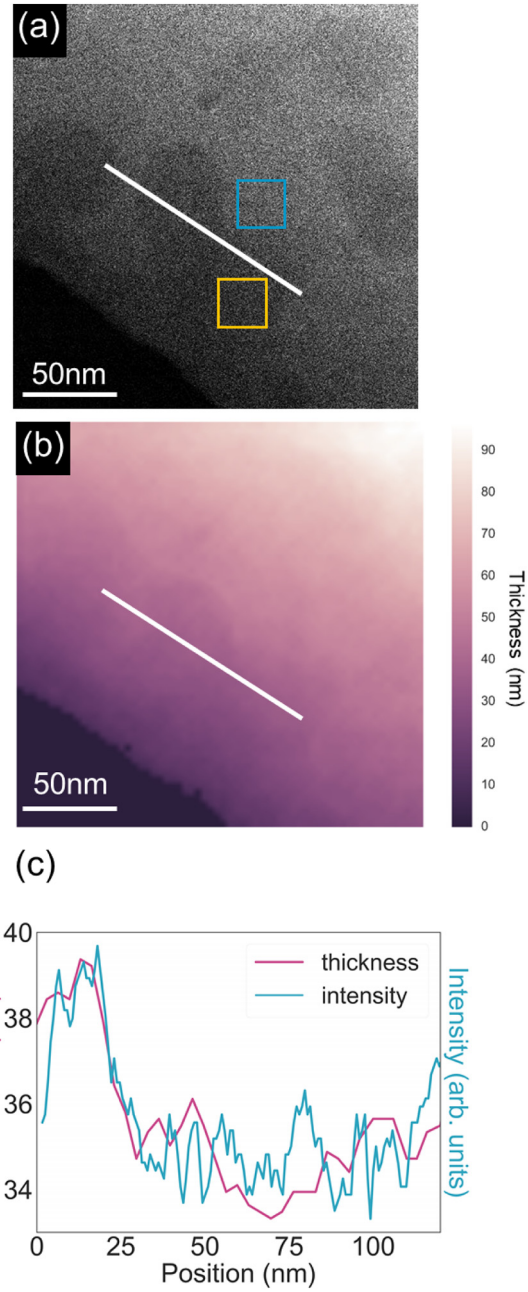

Fig. 1. (a) HAADF image of the 900-min sample. Intensity ratio between the bright region and dark region is approximately 1.15 to 1.25. (b) Thickness mapping obtained by EELS. (c) Line profiles along the white lines in panels (a) and (b).

Namely, a very localized and strong compressed/tensile stress is necessary. Such a nano-sized and abrupt stress distribution is unrealistic, and thus the atom density was not the main factor for the HAADF intensity deviation.

If the difference in the HAADF intensity was caused by the difference in thickness, the bright region needed to be approximately 20% thicker than the dark region (Fig. 2(b)). To confirm the thickness of the observed area, the thickness was measured using EELS (Fig. 1(b)), and found that the thickness gradually changed from the edge (approximately 10 nm) to the inside (approximately 90 nm) of the sample. The line profile of the thickness from the bright to dark regions along the dashed lines is shown in Fig. 1(c). The thicknesses at the bright and dark regions were approximately 38.5 nm and 34.5 nm, respectively, which indicated that a difference of only 8.9% was observed for