Nanoscale local stress mapping of phase-separated glass by scanning transmission electron microscopy-cathodoluminescence

Yamada, T.[1], Ohtsuka, M.[1], Yoshino, H.[2], Amma, S.[2] and Muto, S.[3]

[1] Graduate School of Engineering, Nagoya University, Japan, [2] Asahi Glass Co., Ltd., Japan, [3] Institute of Materials & Systems for Sustainability, Nagoya University, Japan

Phase-separated glass, such as borosilicate glass, is widely used to manufacture scientific apparatus and kitchenware because of its hardness and heat resistance. Determining the local stress distribution of this type of glass helps clarify its fracture mechanism, thus providing important information to develop stronger glass. One of the most promising methods to visualize nanoscale physical/chemical properties involves using a nano-electron probe based on scanning transmission electron microscopy (STEM). The local stress can be measured by the wavelength shift observed for the doped luminescent element (piezoelectroluminescence effect). While these measurements have been conducted using scanning electron microscopy, measurements based on high-resolution transmission electron microscopy (TEM) are desired. In the present study, we conducted STEM-cathodoluminescence (CL) experiments on Sm-doped phase-separated glass composed of SiO_2, CaO, and Al_2O_3.

A silicate glass sample with composition of 20 CaO-10 Al_2O_3-70 SiO_2 (mass %) (22.0 - 6.1-71.9 in mol %), doped with 5000 mol ppm of Sm^{3+} as the luminescent element, was prepared by the conventional melt-quench method. The annealed sample was ground and dispersed in ethanol, and a drop of this dispersion was taken on a carbon microgrid. STEM-CL experiments were performed by a JEOL JEM-2100 scanning transmission electron microscope equipped with a Gatan Vulcan TEM-CL system. The typical CL spectrum of the doped sample is shown in Figure 1(a). To detect the small peak shift, we focused on the strongest peak at ~600 nm with a wavelength resolution of 0.2 nm/channel using a diffraction grating of 1200 lines/mm, as shown in Figure 1(b). The peak shift of the CL spectrum was obtained by the centroid method [1] because the peak position could be determined regardless of the peak asymmetry.

The annular dark field (ADF)-STEM image of the sample showed a sea-island structure, as seen in typical of phase-separated glass, and the size of the islands was approximately 100 nm (Figure 2). STEM-energy dispersive X-ray spectrometry measurements showed the elemental distribution in the glass (Figure 3); the results showed that the islands were enriched with Si, while the sea was enriched with Al and Ca. Thus, the stress distribution was expected to be correlated with the compositional distribution.

The STEM-CL spectrum image data were acquired for the area indicated by the dotted line in Figure 4(a). Figures 4(b) and (c) show the associated ADF-STEM images and the relative peak shift map calculated by the centroid method, respectively. The island structure roughly corresponded to the area where the peak was shifted to the lower wavelength side, whereas the sea structure corresponded to the area where the peak was shifted to the higher wavelength side. In the presentation, photoluminescence measurements will be reported using a four-point bending test to relate the peak shift direction to the nature of stress (compressive or tensile).

[1] Kurita M, Amano J, Sakamoto I (1982) Statistical Analysis of X-Ray Stress Measurement by Centroid Method. The Society of Materials Science, 31(345): 83-89.

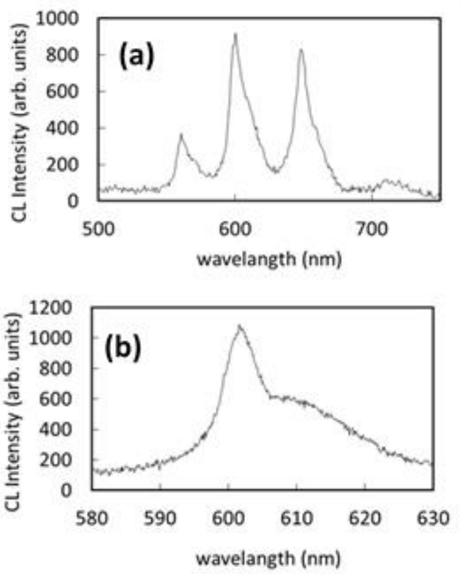

Fig. 1 (a) CL spectrum in the range 500–750 nm
(b) High-resolution CL spectrum in the range 580–630 nm

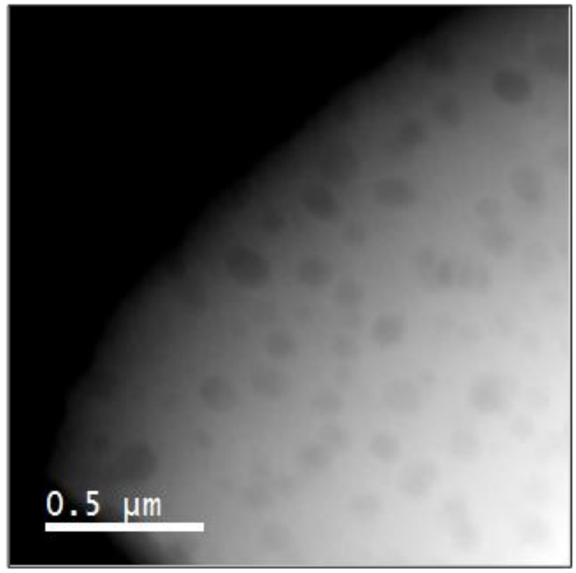

Fig. 2 ADF-STEM image of phase-separated glass

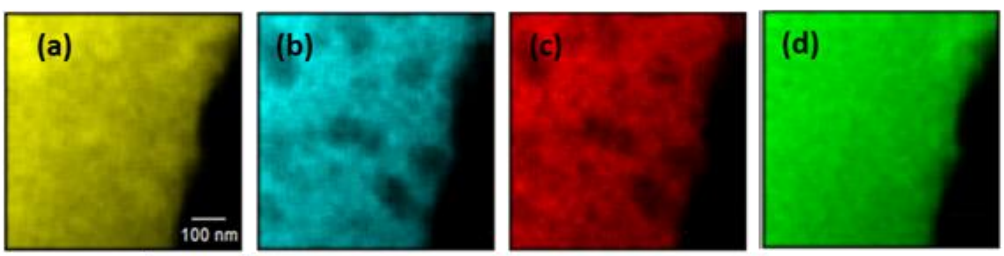

Fig. 3 Elemental maps of (a) Si (b) Ca (c) Al (d) O

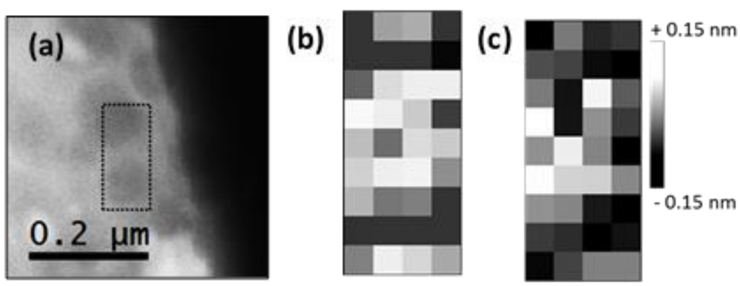

Fig. 4 (a) Survey image (b) ADF-STEM image (c) Peak shift map