Composition fluctuations in silica glass containing water

By Emily M. Aaldenberg and Minoru Tomozawa

Water and water vapor can degrade the mechanical strength of glass, promote crack growth, and cause fatigue.[1,2]

Water has been found to enter through the fracture surface of glasses,[3,4,5] indicating that water ahead of the crack tip promotes the growth of cracks. Both structural[6] and stress relaxation[7] were found to occur faster at the glass surface than in the bulk when exposed to water. Liquid water or water vapor in the air can enter the glass through diffusion. At low temperatures, molecular water can remain in the glass. At high temperatures, most of the diffused molecular water readily reacts with the glass network to form immobile hydroxyls, ≡Si-OH.[8,9]

Although the large effect of water on glass properties and relaxation behavior has been observed, the mechanism by which a small quantity of water in the glass can cause this behavior has remained elusive. It is proposed that water entering the glass causes fluctuations in the composition that can lead to dynamic mechanical relaxation[10] and pathways for crack growth. This research will establish the presence of composition fluctuations caused by water in silica glass, the primary network former in many glasses.

Composition fluctuations, crack growth, and relaxation

Fluctuations may play an important role in both the fracture process and the relaxation process in the presence of water. Zarzycki[11] proposed that glass, which has density fluctuations, would have low density domains which would act as pathways for a moving crack or as closed Griffith flaws in the glass. When water is present, this interpretation of crack propagation could be extended to composition fluctuations in which the crack may grow through water-rich pathways. The presence of tensile stress or damaged sites may also promote these composition fluctuations, as will be demonstrated by the formation of bubbles at low temperatures in damaged glass.

Water in glass can also lead to dynamic mechanical[12] or delayed elastic behavior representative of a time-dependent modulus giving rise to stress relaxation behavior. The relaxation strength of the glass becomes large as composition fluctuations increase approaching the spinodal temperature.[13] Here, the presence of composition fluctuations in the silica glass-water system was examined through three experiments: the memory effect, small angle X-ray scattering (SAXS), and the formation of bubbles at low temperature.

Memory effect

The memory effect in glass, where glass "remembers its past thermal history," takes place when glass has multiple relaxation times resulting from composition fluctuations.[14] This effect can be demonstrated through the crossover experiment in which glass is cooled from its equilibrium fictive temperature $T_f = T_1$ toward a temperature T_2. When the glass T_f reaches the crossover temperature T_x, where $T_2 < T_x < T_1$, the temperature of the furnace is switched to T_x. T_f can be seen to change with time rather than remaining constant because portions of the glass relax faster and slower than the average. The memory effect in glass has been shown to occur in silica glass containing fluorine or OH, but not for pure silica glass.[15] Further confirmation that the memory effect is caused by composition fluctuations rather than density fluctuations can be gained by testing at temperatures approaching the spinodal.[16]

In this study, the memory effect of a silica glass containing 800–1,000 wt. ppm OH was investigated at various T_1, T_2, and T_x (example in Figure 1), with the differences $T_1 - T_2$ and $T_1 - T_x$ constant. The sample tested at higher temperatures showed no discernible memory effect, while samples tested at lower temperatures showed that T_f initially increases and subsequently decreases following the crossover to T_x.

The presence of composition fluctuations in silica glass containing OH can be confirmed because composition fluctuations increase at lower temperatures.[17] As the temperature of the crossover experiment was reduced, the spinodal temperature was approached, so larger fluctuations in composition led to a noticeable distribution in structural relaxation times for glass containing OH.

Small angle X-ray scattering

SAXS can demonstrate the presence of density and composition fluctuations in glass. Pure silica glass has only density fluctuations, which give rise to a SAXS intensity at zero scattering vector $I(q=0)$ proportional to temperature.[18] $I(0)$ measured at room temperature can be seen to increase with increasing equilibrium T_f because the structure of the glass becomes frozen-in upon rapid cooling. The presence of composition fluctuations leads to an additional contribution to $I(0)$, as has been demonstrated for fluorine-doped silica.[19]

In order to show the presence of composition fluctuations in silica containing OH, two silica glasses were measured with equilibrium T_f=900–1,300°C. One glass

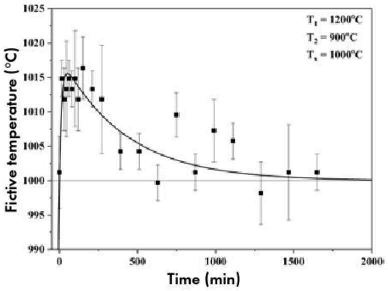

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Figure 1. Time dependent T_f after cross-over to T_x. Data fit (solid line) estimated from a model of two relaxation times.

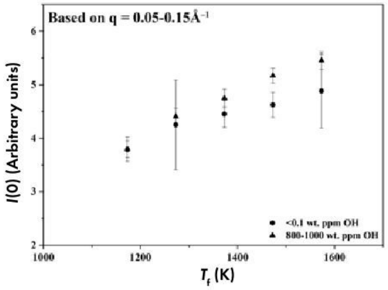

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Figure 2. SAXS intensity as a function of the glass fictive temperature for two silica glasses.

contained 1,000 wt. ppm chlorine and <0.1 wt. ppm OH; the other contained 800–1,000 wt. ppm OH. The addition of chlorine was found to have no effect on the scattered intensity.[20] $I(0)$ was calculated from a linear fit of the measured region q=0.05–0.15 Å^{-1}. For a constant T_f, the glass containing OH has a greater scattering intensity (Figure 2). This is consistent with the hypothesis that the OH in the glass causes composition fluctuations.

Low temperature bubble formation

The previous two experiments involved composition fluctuations for silica glass containing predominantly reacted water, ≡Si-OH formed at high temperatures. This third study involves the diffusion of water at low temperatures, where molecular H_2O is present. A silica sample with a final polish of cerium oxide was found to contain bubbles beneath the glass surface (Figure 3a), following a six-day water diffusion treatment in 250°C saturated water vapor pressure (29,800 Torr). The sample is estimated to have OH and H_2O diffusion depths of about 14 µm.[21] Subsurface damage was revealed by etching the surface layer of a separate polished sample in an HF solution (Figure 3b).

The formation of bubbles typically occurs at temperatures above the glass transition temperature, T_g. It is surprising, then, that silica glass was able to form bubbles at temperatures so far below T_g. Bubbles form as a result of supersaturation of diffused water in glass. The subsurface damage may serve as a nucleation site for the bubbles (phase separated regions) to form because without any subsurface damage present, no bubbles formed after the same heat-treatment. This type of polishing-induced damage, which represents closed cracks below the glass surface, is caused by dragging blunt ceria particles across the surface and is only revealed by etching.[22,23] Fluctuations and phase separation in the silica-water system at low temperatures are especially important because the crack growth and relaxation processes are typically studied at low temperatures, where molecular H_2O is present.

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Editor's note

Aaldenberg will present the 2019 Kreidl Award Lecture at the Glass and Optical Materials Division Annual Meeting in Boston, Mass., on June 11, 2019.

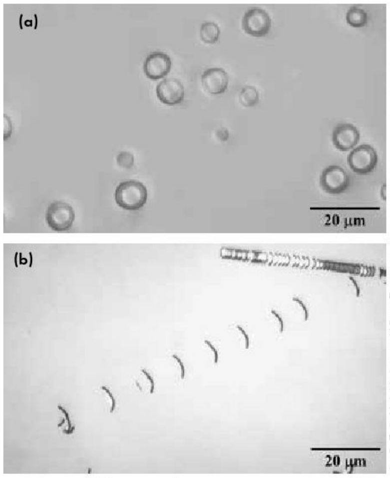

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Figure 3. (a) Optical microscope image of bubbles formed after heat treatment of silica at 250°C saturated water vapor pressure. (b) Subsurface damage revealed by etching.

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