

Formation of a zirconium oxide crystal nucleus in the initial nucleation stage in aluminosilicate glass investigated by X-ray multiscale analysis

Glass ceramics are composed of precipitated crystals and a glass matrix, which exhibit unique characteristics that are not observed in conventional glasses, such as high mechanical strength and excellent thermal shock resistance owing to the presence of encrusted crystals [1]. Glass ceramics are synthesized by annealing the quenched pristine glass above the glass transition temperature to obtain homogeneous crystallization. Zirconium oxide is a commonly used nucleation agent in various glass ceramics, in which it aids in controlling the crystallization process [1]. The environments around Zr^{4+} ions in pristine glass and sufficiently crystallized glass ceramics have been studied using various experimental techniques, but the Zr^{4+} environment in the early stages of nucleation in glass is still not well understood.

In this study, we examined ZrO_2 -doped lithium aluminosilicate glass and its glass-ceramic, which is an important commercial material. The lithium aluminosilicate glass-ceramics in the initial nucleation stage were prepared by thermal treatment of pristine glass with small amounts of ZrO_2 (2.9 mol%) at 770°C for various durations. To investigate the structural changes associated with a small amount of Zr (1 mol%) in the glass and glass-ceramics at both the short- and intermediate-range scales, we conducted anomalous X-ray scattering (AXS) [2] measurements at SPRing-8 BL13XU [3]. Furthermore, the nanoscale structures of the pristine glass and glass-ceramics were analyzed using a combination of small-angle X-ray scattering (SAXS) and in-house X-ray diffraction (XRD) measurements. Thus, we performed a state-of-the-art multiscale structural analysis that demonstrated the behavior of a small number of Zr cations from the atomic scale to the nanoscale during the initial nucleation stage in commercially available glass-ceramic materials [4].

The in-house XRD patterns of the samples annealed for longer than 4 h showed subtle diffraction peaks assigned to cubic (c-) or tetragonal (t-) ZrO_2 , indicating that glass-ceramics suitable for investigating the structural changes during the initial nucleation stage were obtained. The SAXS profiles of the samples prepared with various annealing durations are shown in Figs. 1(a,b). A relatively low scattering intensity was observed for the 0-h-annealed sample, indicating that the pristine glass had an internal inhomogeneous structure. The SAXS peak height

gradually increased with the annealing duration, indicating that the electron density contrast between the scatterers increased. These results indicate that the structural change in the ZrO_2 -doped lithium aluminosilicate glass-ceramics during the initial nucleation stage originated from the separation of the Zr-rich and Zr-poor regions. Notably, these structural changes occurred without any change in the spatial nanoscale geometry because the distance between scatterers, which was calculated using $d = 2\pi/Q$ (Q is the peak position in the SAXS profile), did not show any notable change with increasing annealing duration.

The differential structure factors $\Delta_{\text{Zr}}S(Q)$ for 0-, 2-, and 4-h-annealed samples obtained from the AXS measurements are shown in Fig. 2(a). $\Delta_{\text{Zr}}S(Q)$ markedly changed in the high- Q region ($Q > 0.5 \text{ \AA}^{-1}$), indicating that the Zr-related structure at short- and intermediate-range scales changed upon thermal treatment. Differential total correlation functions, $\Delta_{\text{Zr}}T(r)$, for the 0-, 2-, and 4-h-annealed samples obtained from the Fourier transforms of $\Delta_{\text{Zr}}S(Q)$ are shown in Fig. 2(b). In addition to the Zr–O correlation peak located at 2.1 \AA , the second Zr–Zr correlation peak with a shoulder on the low- r side was observed at 3.6 \AA for all $\Delta_{\text{Zr}}T(r)$. The shoulder peak on the low- r side of the second peak was likely composed of the tail of the asymmetric Zr–O peak and other Zr-related correlation peaks observed at approximately $2.8\text{--}2.9 \text{ \AA}$ for all $\Delta_{\text{Zr}}T(r)$. Because only six partials (Zr–Zr, Zr–Si, Zr–Al, Zr–Na, Zr–P, and Zr–O) contributed to $\Delta_{\text{Zr}}S(Q)$ and the weighting factors for

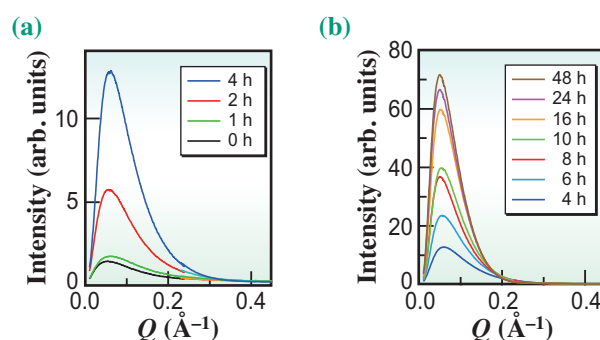


Fig. 1. (a) SAXS profiles of the Zr-doped lithium aluminosilicate glass and glass-ceramic samples annealed for less than 4 h. (b) SAXS profiles of the Zr-doped lithium aluminosilicate glass-ceramic samples annealed for more than 4 h. [4]

Zr–Si and Zr–Al correlations were relatively large except for the Zr–O correlation in $\Delta_{Zr}S(Q)$, the shoulder peak was assigned to the Zr–Si and/or Zr–Al correlation. The Zr–(Si/Al) distance of 2.8–2.9 Å was considerably short for a Si or Al at the center of a (Si/Al)O₄ tetrahedron sharing an oxygen at the corner with a ZrO_x polyhedron. Therefore, the short Zr–(Si/Al) distance indicated the formation of edge-sharing polyhedral connections between ZrO_x and (Si/Al)O₄.

To obtain clear insights into the initial nucleation stage from the atomic level to the nanoscale, a schematic representation of the structural change from pristine glass to glass-ceramic (4-h-annealed sample) was constructed, as shown in Figs. 3(a–d). As shown by the SAXS results, the pristine glass exhibited an inherent separation of the Zr-rich and Zr-poor regions (Fig. 3(a)). Thermal treatment of the pristine glass for 4 h caused the aggregation of ZrO_x and an increase in contrast in the electron density between the Zr-rich and Zr-poor regions (Fig. 3(b)). Figures 3(c,d) show schematic representations of the intermediate-range structure in the Zr-rich region for the pristine glass and the 4-h-annealed sample, respectively. SiO₄, AlO₄, and only a few PO₄ tetrahedra formed a tetrahedral network, whereas Zr⁴⁺, Li⁺, and Na⁺ cations were distributed around the network in the pristine glass (Fig. 3(c)). Several ZrO_x polyhedra formed an edge-sharing with the (Si/Al)O₄ polyhedra in the structure of the pristine glass. After annealing for 4 h, the Zr⁴⁺ ions congregated and formed an ordered arrangement, whereby additional edge-sharing connections were formed between the ZrO_x polyhedra and the surrounding (Si/Al)O₄ tetrahedra, as shown in Fig. 3(d). The Zr-related specific configuration could be the initial crystal nucleus of the Zr-doped lithium aluminosilicate glass-ceramic. The ZrO₂ nanocrystal surrounded by the (Si/Al)O₄ tetrahedral network shown in Fig. 3(d) corresponds to the core–shell structure, which acted as a nucleation barrier that inhibited

the increase in the size of ZrO₂ crystals [5]. Although Zr–(Si/Al) correlations beyond the nearest-neighbor distance have rarely been observed using conventional approaches, we succeeded in their observation using Zr-specific pair distribution function analysis with AXS data. These findings may provide new insights into the intermediate-range structures of nucleation agents in glasses and promote a better understanding of the nucleation mechanism in the initial stages of glass-ceramic materials.

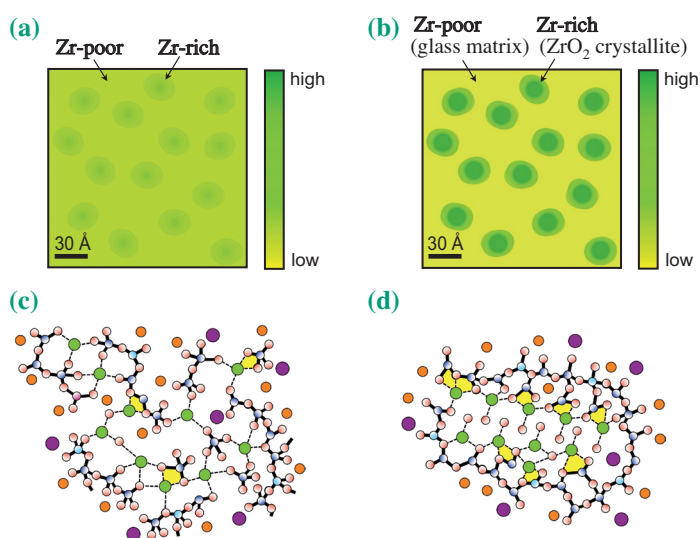


Fig. 3. Schematic representation of the initial nucleation stage in the Zr-doped lithium aluminosilicate glass-ceramic. (a) Nanoscale structures of the pristine glass and (b) 4-h-annealed sample. (c) Representations of the intermediate-range structure in the Zr-rich region of the pristine glass and (d) the 4-h-annealed sample. Green: zirconium, blue: silicon, cyan: aluminum, magenta: phosphorus, orange: lithium, purple: sodium, and red: oxygen. The yellow polyhedra indicates edge-sharing polyhedral connections. [4]

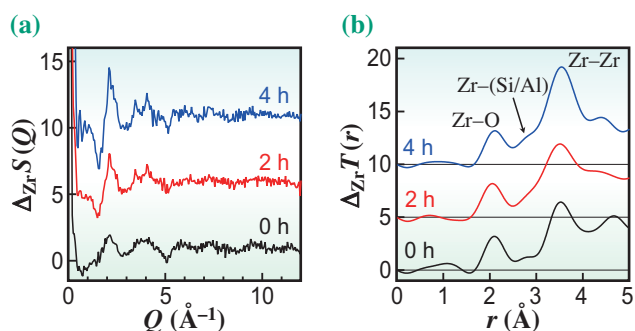


Fig. 2. (a) Differential structure factors $\Delta_{Zr}S(Q)$ and (b) differential total correlation functions $\Delta_{Zr}T(r)$ of the Zr-doped lithium aluminosilicate samples annealed for 0 h (black), 2 h (red), and 4 h (blue). [4]

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