

Structure of an extremely fragile liquid

Glass formation from liquids is an important topic in glass science, and several theories of glass formation were established in the last century. Zachariasen [1] and Sun [2] proposed the basic concepts of glass formation by classifying constituents into glass formers, glass modifiers, and intermediates. Angell [3] introduced the concept of 'fragility' in glass-forming liquids (GFLs) on the basis of the relationship between glass transition temperature and viscosity: liquids can be classified as 'strong' and 'weak' according to their glass-forming ability. ZrO₂ is one representative of nonglass formers and is commonly used as a refractory material, suggesting that liquid (1)-ZrO₂ is indeed a non-GFL. As ZrO₂ has an extremely high melting point $(T_m = 2,715^{\circ}C)$, the difficulties in handling the liquid at high temperatures lead to problems in selecting suitable container materials that prevent contamination effects. We have developed a beamline aerodynamic levitation furnace that enables us to perform precise synchrotron X-ray diffraction measurements of containerless liquids at extremely high temperatures. Using the levitation furnace, we performed high-energy X-ray diffraction measurements on containerless levitated /-ZrO2 [4] at beamlines BL04B2 and BL08W. We also carried out large-scale density functional (DF)-MD simulations to clarify the liquid properties at the atomic and electronic levels. Furthermore, we compared I-ZrO₂ with a typical GFL, I-SiO₂ [5] to reveal the relationship between structure and glass-forming ability in liquids.

Figure 1(a) shows the Bhatia-Thornton [6] numbernumber partial structure factor $S_{NN}(Q)$ for I-ZrO₂ at 2,800°C compared with that for I-SiO₂ at 2,100°C. Only I-SiO₂ exhibits the first sharp diffraction peak (FSDP) at Qr_{AX} = 2.7 (r_{AX} is the atomic cation (A) – anion (X) distance in AX polyhedra). Since the Bhatia-Thornton $S_{NN}(Q)$ can eliminate the weighting factors for X-rays, the absence of an FSDP in $S_{NN}(Q)$ for I-ZrO₂ is a distinct signature of a non-GFL.

The coordination number distributions of I-SiO₂ and I-ZrO₂ calculated from the structural models are shown in Fig. 1(b). SiO₄ tetrahedra are predominant in I-SiO₂, whereas I-ZrO₂ comprises ZrO₅, ZrO₆, and ZrO₇. This comparison supports our view that the variety of oxygen coordination around cations in I-ZrO₂ is another characteristic feature of non-glass-forming behavior, because it can disturb the evolution of intermediate-range ordering.

To obtain structural features beyond the first coordination distance, polyhedral connection analysis was performed for I-SiO₂ and I-ZrO₂. Figure 1(c)

shows the fractions of corner-sharing, edge-sharing, and face-sharing polyhedral units in the liquids. The corner sharing of oxygen is prevalent in I-SiO₂, which is a unique feature of GFLs according to Zachariasen [1]. However, I-ZrO₂ exhibits a considerable amount of oxygen edge sharing, implying that the variety of polyhedral connection is another characteristic feature of single-component non-GFLs.

Electronic structure analysis was carried out in terms of the electronic density of states (DOS) to obtain snapshots of the high-temperature phases of crystalline (*c*-) ZrO_2 and *I*- ZrO_2 . The projections (P-DOS) reveal that the electronic spectrum is mainly associated with oxygen (O-2*p* orbitals) and the Zr semicore states, and the gap between the valence and the conduction bands in *I*- ZrO_2 is narrower than that in *c*- ZrO_2 .

The difference between the electronegativities of Zr (1.3) and O (3.5) indicates that the chemical bonding between the two elements is mainly ionic. The effective charges calculated by the Bader method are +2.62*e* and -1.31*e* for Zr and O in *I*-ZrO₂, respectively, which reflect the ionic bonding.

The origin of the FSDP associated with the



Fig. 1. (a) Bhatia-Thornton number-number partial structure factor $S_{\rm NN}(Q)$ for l-ZrO₂ at 2,800°C derived from DF-MD simulation (black curve) [4] compared with that for l-SiO₂ at 2,100°C (blue curve) [5]. The momentum transfer Q was scaled by $r_{\rm AX}$, which is the first coordination distance between A and X in the real-space function. (b) Coordination number distribution of oxygen atoms around the cations in l-ZrO₂ at 2,800°C [4] and l-SiO₂ at 2,100°C [5]. CS, corner sharing of oxygen; ES, edge sharing of oxygen; FS, face sharing of oxygen.

formation of intermediate-range ordering in oxide glasses and liquids remains controversial [7], because the inherent disorder complicates the ability of AX polyhedral connections to form an A-X network. SiO₂ has exceptionally high glass-forming ability, and the origin of the FSDP in SiO₂ has often been studied. The random network model of Zachariasen [1], which was modified for an oxide glass, demonstrates that the intermediate-range ordering arises from the periodicity of boundaries between successive small cages in the network formed by connected, regular SiO₄ tetrahedra with shared oxygen atoms at the corners [7]. It has also been suggested that the small cages are topologically disordered, resulting in a broad distribution of ring sizes from threefold to twelvefold rings centered at sixfold rings [8]. This is reflected in $S_{NN}(Q)$ for I-SiO₂ (Fig. 1(a)), where the FSDP width is larger than that of the corresponding Bragg peak in the crystalline phase (β -cristobalite, c-SiO₂), where only a sixfold ring contributes. Figures 2(a) and 2(b) show the three-dimensional atomic configurations and schematic illustrations of c-SiO₂ and I-SiO₂, respectively. The crystalline phase exhibits only sixfold rings of six SiO₄ tetrahedra, resulting in longrange periodicity (dashed lines in Fig. 2(a)). However, some pseudo-Bragg planes (dashed lines in the left panel of Fig. 2(b)) can be recognized in /-SiO₂. Although the introduction of different ring sizes can easily modify the crystalline topological order (Fig. 2(b)), the interconnection of regular SiO₄ tetrahedra with shared oxygen atoms at corners only yields the broadened Bragg peak as the FSDP.

As can be seen in Fig. 1(a), an FSDP is absent in $S_{NN}(Q)$ for *I*-ZrO₂. This is because the variety of shortrange structural units with large oxygen coordination, ZrO₅, ZrO₆, and ZrO₇, and the large contribution of oxygen edge sharing prevent the formation of intermediaterange ordering. Short-range structural disordering in I-ZrO₂ is further demonstrated in the three-dimensional atomic configuration and the schematic illustration of I-ZrO₂ (Fig. 2(c)). The periodicity of boundaries (dashed lines) is suppressed by the edge sharing of oxygen associated with the formation of ZrO₅, ZrO₆, and ZrO7. Although ZrO2 forms a network structure by interconnecting AX polyhedra in the liquid phase, we have shown that the various short-range structural units and their connectivity cause disorder in the intermediate range and prevent the evolution of an FSDP for the liquid. The absence of an FSDP in $S_{NN}(Q)$ of I-ZrO₂ suggests that I-ZrO2 is an extremely fragile liquid. The fragility of I-ZrO2 is confirmed by its very low viscosity $(-2 \times 10^{-3} \text{ Pa} \cdot \text{s}^{-1} \text{ at } 2,800^{\circ}\text{C})$ and the short lifetime of the Zr-O bond (DF-MD simulation showed that 50% of the bonds break within 185 fs at 2,800°C).

In this study, we have succeeded in uncovering the relationship between structure and glass-forming ability

in single-component oxide liquids. Finally, we stress that the containerless preparation and measurement techniques provide new tools for the study of unique features of extremely high temperature liquids, and we demonstrate the importance of combining experiment and theory for understanding the nature of liquids at the atomic (structure and dynamics) and electronic (chemical bonding) levels.





Fig. 2. Atomic configurations and schematic illustrations of (a) c-SiO₂, (b) l-SiO₂, and (c) l-ZrO₂. The periodicity of the cage boundaries is highlighted by dashed lines and curves.

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