

Very sharp diffraction peak in dense oxide liquid with the formation of distorted tetraclusters

Determining the liquid structure is the first step in understanding the nature of glass-liquid transitions, and high-quality diffraction and density data are very important in obtaining a reliable structure model by modeling or simulation. However, it is difficult to obtain the data of single-component oxides with high melting temperatures (T_m) in liquid states, because the liquids are easily contaminated with container materials or nucleated from the heterogeneous interface between the container and the liquid. To overcome such problems, we have developed levitation furnaces, which maintain high-temperature liquids without any contact [1,2].

Although liquid (l-) Er_2O_3 ($T_m = 2686$ K) is a representative non-glass-forming liquid (non-GFL), its structure has not been well understood. To elucidate the atomic structure [3], the density data were measured using an electrostatic levitation furnace (ELF) onboard the International Space Station (ISS) and the diffraction data were measured using an aerodynamic levitation furnace at the highenergy X-ray diffraction beamline, SPring-8 BL04B2. A combined molecular dynamics (MD) - reverse Monte Carlo (RMC) simulation was also performed to obtain an atomistic model that reproduces diffraction data. Persistence diagrams (PDs) were obtained on the basis of the structural model in a comparison with other non-GFLs and a typical GFL, *l*-SiO₂. The combination of an experiment and a simulation allows trends in single-component non-GFL oxides to be identified, with a special focus on atomic ordering and topology. Furthermore, we compared the features of single-component non-GFL oxide liquids with those of other systems.

The Faber–Ziman total structure factors, S(Q), for *l*-Er₂O₃ [3], *l*-SiO₂ [4], *l*-Al₂O₃ [5], and *l*-ZrO₂ [1], together with the results of the MD-RMC simulation for *l*-Er₂O₃, are shown in Fig. 1. Note that the scattering vector Q is scaled by multiplying by r_{A-X} (distance between the center and corners of the polyhedron). The experimental S(Q) of l-Er₂O₃ (solid cyan curve) is well reproduced by the MD-RMC simulation (dotted black curve) with the liquid density measured using the ISS-ELF. A well-defined first sharp diffraction peak (FSDP) is observed only for *l*-SiO₂ (GFL) at Qr_{A-X} = 2.6. The FSDP originates from the intermediate-range ordering [1,4] arising from the periodicity of boundaries between successive small cages in the network composed of connected polyhedra with shared oxygen atoms at the corners.



Fig. 1. Faber–Ziman X-ray total structure factors, S(Q), for *l*-Er₂O₃ [3], *l*-SiO₂ [4], *l*-Al₂O₃ [5], and *l*-ZrO₂ [1] together with that of *l*-Er₂O₃ derived from the MD–RMC simulation. Scattering vector Q is scaled by multiplying by r_{A-X} (distance between the center and corners of the polyhedron).

l-Al₂O₃ gives rise to a small FSDP at $Qr_{A-X} = 3.8$, suggesting that the structure of l-Al₂O₃ is intermediate between those of l-SiO₂ and l-ZrO₂ /l-Er₂O₃. A very sharp principal peak (PP) is observed in both the l-ZrO₂ and l-Er₂O₃ data at $Qr_{A-X} \sim 4.5$. The PP originates from the packing of cations since X-rays are sensitive to heavy atoms.

The coordination number distributions, N_{A-X} and N_{X-A} , for *l*-Er₂O₃ [3] were obtained from the MD–RMC simulations. They show that the Er-O coordination number (up to 3.0 Å) is 6.1, which is rather close to that of the crystalline phase, and the O-Er coordination number can be estimated to be 4.1. These results suggest that cations are fourfold in *l*-SiO₂ (GFL)[4], whereas they are sixfold in *l*-ZrO₂ [1] and *l*-Er₂O₃ (non-GFLs), and the cation-oxygen coordination number in *l*-Al₂O₃ is intermediate [5] between those of GFL and *l*-ZrO₂/*l*-Er₂O₃, although *l*-Al₂O₃ is a non-GFL. This behavior is consistent with that of the first correlation peaks in experimental real-space functions [3] and with the fact that the viscosity of l-ZrO₂ is approximately one-tenth of that in *l*-Al₂O₃ [5]. Another interesting behavior is observed for the oxygencation coordination numbers. It is demonstrated that oxygen is twofold in *l*-SiO₂, which is a signature of the formation of a sparse network, while triclusters (XA₃) are dominant in *l*-Al₂O₃ and *l*-ZrO₂. The formation of tetraclusters (XA₄) is confirmed in *l*-Er₂O₃, suggesting that this behavior is a distinct feature of this liquid.

Moreover, it is implied that the behavior of the coordination numbers in a series of oxide liquids is affected by both the composition and the ionic radii between the constituent anions and cations. For instance, the ionic radii of Si and Al are small, which results in tetrahedral coordination, although the Al–O coordination number is greater than four on average. The tetracluster formation is governed by the ratio of Er to O in Er_2O_3 .

As shown in Fig. 1, the PP of l-Er₂O₃ is much sharper than that of the extremely fragile *l*-ZrO₂ [1]. The FWHM of the PP in *l*-Er₂O₃ is 0.43 in comparison with 0.77 in l-ZrO₂. To reveal the origin of the very sharp PP in *l*-Er₂O₃, the bond angle distributions of the liquid and crystal were calculated. A pronounced difference was found between the liquid and crystal data for the O-Er-O and Er-O-Er distributions. The O-Er-O bond angle distribution exhibits two peaks at 80° and 140°, suggesting that ErO₆ polyhedra are highly distorted in the liquid. Another interesting feature is that the Er-O-Er bond angle distribution exhibits a peak at ~180°, which is not observed for the crystal or in l-ZrO₂, in addition to the peak at ~90° [1]. This two-peak structure in the Er-O-Er bond angle distribution indicates the formation of a distorted OEr₄ tetracluster network in the liquid phase (Fig. 2(a)), whereas tetraclusters are symmetric in the crystalline phase. This behavior suggests that the coordination of OEr4 tetraclusters is more octahedrallike and hence is tolerant to disorder even in the liquid owing to the distortion, resulting in the very sharp PP in *l*-Er₂O₃ and a linear arrangement reflected by the prominent peak observed at 180° in the Er-O-Er bond angle distribution. This is clearly visible in Fig. 2(b), where linear atomic arrangements are highlighted by magenta lines.

To shed light on the similarity in topology between the crystal and liquid phases, the PDs for l-Er₂O₃ in both phases were calculated (Fig. 3). The figures show the similarity between the crystal and liquid phases. In particular, neither the Er-centric nor O-centric PD for



Fig. 2. (a) Visualization of the OEr_4 tetracluster network in l- Er_2O_3 . Pink, oxygen; blue, erbium. (b) Visualization of the nearly linear arrangements of Er-O-E in l- Er_2O_3 .

l-Er₂O₃ shows a vertical profile along the death axis, which is a pronounced feature in a typical GFL such as l-SiO₂ [4]. The short lifetime of the profile as indicated by the small death value demonstrates that both the crystal and liquid phases exhibit a very densely packed structure associated with the formation of tetraclusters in both phases. We hypothesize that this similarity is a signature of non-GFL behavior and a factor hindering glass formation.



Fig. 3. Er-centric (a) and O-centric (b) persistence diagrams for Er_2O_3 .

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