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Very sharp diffraction peak in nonglass-forming liquid with the formation of distorted tetraclusters

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Abstract

Understanding the liquid structure provides information that is crucial to uncovering the nature of the glass-liquid transition. We apply an aerodynamic levitation technique and high-energy X-rays to liquid (*l*)-Er₂O₃ to discover its structure. The sample densities are measured by electrostatic levitation at the International Space Station. Liquid Er₂O₃ displays a very sharp diffraction peak (principal peak). Applying a combined reverse Monte Carlo – molecular dynamics approach, the simulations produce an Er–O coordination number of 6.1, which is comparable to that of another nonglass-forming liquid, *l*-ZrO₂. The atomic structure of *l*-Er₂O₃ comprises distorted OEr₄ tetraclusters in nearly linear arrangements, as manifested by a prominent peak observed at ~180° in the Er–O–Er bond angle distribution. This structural feature gives rise to long periodicity corresponding to the sharp principal peak in the X-ray diffraction data. A persistent homology analysis suggests that *l*-Er₂O₃ is homologically similar to the crystalline phase. Moreover, electronic structure calculations show that *l*-Er₂O₃ has a modest band gap of 0.6 eV that is significantly reduced from the crystalline phase due to the tetracluster distortions. The estimated viscosity is very low above the melting point for *l*-ZrO₂, and the material can be described as an extremely fragile liquid.

Introduction

Determining the liquid structure is the first step in understanding the nature of glass-liquid transitions. However, a diffraction measurement of liquid provides very limited structural information because the liquid structure lacks long-range periodicity, and a Fourier transform of the diffraction data provides only pairwise correlations. Moreover, high-quality measurements are difficult to obtain at high temperatures.

Since glasses play an important role in technology, glass formation has been studied extensively. Zachariasen¹ and

Sun² proposed the basic concepts of glass formation by classifying constituents into glass formers, glass modifiers, and intermediates. Furthermore, Angell³ introduced the concept of “fragility” in glass-forming liquids (GFLs). He interpreted the strong and fragile behavior of liquids in terms of topological differences in potential energy hypersurfaces of the configuration space. Typical strong liquids are SiO₂, GeO₂, and B₂O₃. Their networks are covalently bonded, and the viscosities show an Arrhenius temperature dependence. In contrast, typical fragile liquids are chalcogenides and iron phosphates, the networks of which are mostly ionic and the viscosities of which deviate significantly from the Arrhenius behavior. Many experimental and theoretical structural studies of liquids and glasses have been performed, and with the advent of advanced synchrotron and neutron sources and the development of high-performance computers, they have led to great progress in our understanding of liquid and

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glass structures^{4,5}. The structural analysis of liquids with high melting points has advanced significantly with the advent of the levitation technique⁶, especially in combination with diffraction techniques⁶. The structure of a typical non-GFL, liquid (*l*-) Al₂O₃, and its undercooled liquid have been studied extensively by X-ray diffraction^{7–10}, neutron diffraction^{9–11}, and molecular dynamics (MD) simulations^{9–13}. In addition to the *l*-Al₂O₃ structure, several structures of molten pure oxides with high melting points (T_m) have been studied recently. For example, structures of UO₂¹⁴ and compounds in the UO₂–ZrO₂ system¹⁵ have been investigated for nuclear reactor accidents. The structures of ZrO₂^{16–18}, HfO₂¹⁶, and lanthanide oxides¹⁷ have also been investigated to understand the fundamental properties of high-temperature liquids. Although these investigations are very important not only for materials science but also for preventing severe accidents, the research methods and data are still limited by the high melting points of the materials in question.

Er₂O₃ is a representative nonglass former that is commonly used as a refractory material and dopant for luminescent materials. Because Er₂O₃ has an extremely high melting point ($T_m = 2686$ K), the difficulties in handling the liquid lead to problems in selecting suitable container materials that do not contaminate the sample. To avoid contact with other materials, levitation furnaces have been developed that enable us to measure precise synchrotron X-ray diffraction and thermophysical properties for liquids at extremely high temperatures⁶.

This article presents the results of accurate high-energy X-ray diffraction and density measurements on containerless levitated *l*-Er₂O₃ using an electrostatic levitation furnace (ELF) at the International Space Station (ISS)¹⁹, as it is impossible to measure density data on the ground. We also perform reverse Monte Carlo – molecular dynamics simulations and obtain persistence diagrams from topological analyses to demonstrate liquid properties at the atomic level, comparing *l*-Er₂O₃ with other non-GFLs and a typical GFL, *l*-SiO₂. Furthermore, a sample of *l*-Er₂O₃ is simulated for a short period with the density functional – molecular dynamics method to investigate the electronic structure and to obtain a realistic estimate of the viscosity above the melting point. The combination of an experiment and a simulation allows trends in single-component nonglass-forming liquid oxides to be identified, with a focus on atomic ordering and topology. Furthermore, the article compares the features of single-component nonglass-forming oxide liquids with those of other systems.

Materials and methods

Density measurement

The density of liquid (*l*-) Er₂O₃ was measured with an ELF at the ISS. A sample of 2 mm in diameter was prepared by melting Er₂O₃ powder with a purity of 99.99% and

solidifying it in an aerodynamic levitator. It was charged by friction or contact with other materials in the ISS-ELF and then levitated to the center between six electrodes that applied a Coulomb force. The sample position was stabilized by tuning the voltages between electrodes at 1000 Hz and monitoring the image of the sample backlit by a He–Ne laser. The levitated sample was heated and melted by four 40 W semiconductor lasers (980 nm) under 2 atm of dry air. The temperature of the sample was measured by a pyrometer (1.45–1.8 μm). It was calibrated using an emissivity calculated from the plateau temperature at recalescence and the reference value of the melting point (2686 K). After melting, the nonspherical sample became spherical upon cooling after shutting off the lasers. During cooling, the sample image was observed by an ultraviolet back light and a CCD camera. The pixel size was calibrated against an image of 2.0 mm stainless steel spheres, which were recorded under the same conditions as the sample. The sample volume was calculated from its diameter, obtained from the image. Then, the density was calculated from the volume and weight.

High-energy synchrotron X-ray diffraction measurement

The high-energy X-ray diffraction measurement of *l*-Er₂O₃ was performed at the BL04B2 beamline²⁰ of SPring-8 using an aerodynamic levitator²¹. The energy of the incident X-rays was 113 keV. The 2-mm Er₂O₃ sample was levitated in dry air and heated by a 200 W CO₂ laser. The temperature of the sample was monitored by a two-color pyrometer. The background of the instrument was successfully reduced by shielding the detector and by optimizing a beam stop. The measured X-ray diffraction data were corrected for polarization, absorption, and background, and the contribution of Compton scattering was subtracted using standard analysis procedures²². The corrected data sets were normalized to give the Faber–Ziman²³ total structure factor $S(Q)$, and the total correlation function $T(r)$ was obtained by a Fourier transform of $S(Q)$.

Molecular dynamics – reverse Monte Carlo simulation

To determine the atomic configuration of *l*-Er₂O₃, a molecular dynamics – reverse Monte Carlo (MD-RMC) simulation was performed with 5000 particles in a cube to reproduce the X-ray $S(Q)$. The MD simulation was carried out with a Born-Mayer type of pairwise potential with a Coulomb interaction and a repulsive component, given by the following equation:

$$U_{ij}(r) = \frac{e^2}{4\pi\epsilon_0} \frac{Z_i Z_j}{r} + B_{ij} \exp\left(-\frac{r}{\rho_{ij}}\right), \quad (1)$$

where r is the interatomic distance, Z is the effective charge, B is the repulsion, e is the elementary charge ($Z_{\text{Er}} = 2.1$, $Z_{\text{O}} = -1.4$), ϵ_0 is the permittivity of the

Table 1 The parameters for the Born-Mayer potential used in the MD simulation.

	B_{ij} (eV)	ρ_{ij} (Å)
Er-O	3771	0.28
O-O	390	0.36

vacuum, and ρ is the softness parameter. The parameters used in the MD simulation are summarized in Table 1.

The simulations were carried out for a system of 2000 Er and 3000 O atoms in the unit cell with a random atomic configuration. The cell volume was determined from the number densities of l -Er₂O₃ at the melting point, which were calculated with the density measured by the ISS-ELF. Periodic boundary conditions were used, and the long-range Coulomb interaction was treated with Ewald's summation. A time step of 1 fs was used in the Verlet algorithm. First, the temperature of the system was maintained at 4000 K for 20,000 time steps and then cooled to 2923 K over 20,000 steps. The structural model was finally annealed at 2923 K for 150,000 steps. After the MD simulation, RMC refinement was conducted using the RMC++ code²⁴. The benchmark RMC runs were performed using simulation boxes with 250, 500, 1000, and 3000 particles.

Density functional – molecular dynamics simulation

The simulations based on the density functional theory (DFT) of the electronic structure were performed with the projector augmented wave (PAW) method²⁵, implemented in the VASP software^{26,27}. The PAW potentials supplied within VASP for Er ($5p$, $5d$, and $6s$, with 11 $4f$ electrons frozen in the core) and O ($2s$, $2p$) were tested and used (see supplementary information for a comparison between the frozen core approximation and the treating of the Er- $4f$ electrons explicitly, Fig. S1). For a liquid sample of 500 atoms, the energy cutoff of the plane waves was set to 400 eV, with a single Γ -point in the Brillouin zone. In comparison, the bulk crystalline (c)-Er₂O₃ unit cell was fully relaxed until the forces on all atoms were below 0.01 eV/Å with a Γ -centered $2 \times 2 \times 2$ k-point grid and a plane-wave energy cutoff of 550 eV. The PBE functional²⁸ was used for the geometry optimization and the molecular dynamics simulations, whereas the HSE06 hybrid functional²⁹ was used to obtain the electronic densities of states (DOSs) and their projections to produce more realistic electronic band gaps and test the effect of the $4f$ electrons in c -Er₂O₃. The effective charges and atomic volumes were evaluated by Bader analysis^{30–32} using the PBE functional.

The density functional – molecular dynamics (DF-MD) simulations were performed with a Nöse-Hoover thermostat³³ and a time step of 2 fs, with an initial atomic

configuration given by the benchmark RMC model mentioned above with 500 atoms. The system was simulated at 2923 K (~ 2650 °C) for a total of 30 ps, where the last 25 ps were used for data collection (Fig. S2). The electron occupancy was described with a Fermi smearing corresponding to the $k_B T$ value at the target temperature. The mean-square displacements (MSDs) of the atoms show a liquid (diffusion) behavior where equilibrium is already achieved during the first few picoseconds.

Topological analysis using a persistent homology

The homology of atomic configurations has been investigated using the persistence diagram D_1 , which consists of two-dimensional histograms showing a persistent homology. The details of the analysis are described elsewhere³⁴. The persistence diagram D_1 of a set of atoms is given by the following thickening process of spheres: (1) place a sphere with a radius r at the center of each atom, (2) increase the radii of the spheres from 0 to a sufficiently large value, and (3) encode the pair of birth and death radii (b_i , d_i) for each ring c_i consisting of a set of spheres. The persistence diagram is then constructed by the two-dimensional histogram on the birth and death plane obtained by the pairs for independent c_i , $i = 1, \dots, K$. Here, the birth (death) radius is defined as the radius of spheres at which the ring c_i first appears (disappears). The birth radius has information about the distances between atoms of the ring c_i , and the death radius has information about the size of the ring. The persistence diagram provides statistical information on the shapes of all independent rings and thereby provides insight into intermediate ordering in the liquid structure. The rings and cavities detected by this process are recorded for the computation of the persistence diagrams; hence, their geometric shapes can be identified for further analysis. The persistence diagrams were calculated using the HomCloud package³⁵.

Results and discussion

Density data

Figure 1 shows the density of l -Er₂O₃ as a function of temperature, which exhibits a linear temperature dependence. The least-squares fit to the data is given by the following equation:

$$\rho(T) = \rho_m [1 - \alpha(T - T_m)] (\text{kg/m}^3), \quad (2)$$

where ρ_m is the molten density at T_m (8170 kg/m³) and α ($=1/\rho_m[d\rho(T)/dT]$) is the thermal expansion coefficient and is assumed to be constant ($1.0 \times 10^{-4} \text{ K}^{-1}$) at any temperature of the liquid. The correlation coefficient of this fitting is 0.98. The uncertainty in the measurements is estimated to be 2% from the image resolution (640×480 pixels) and from the uncertainty in the mass measurement (± 0.1 mg).

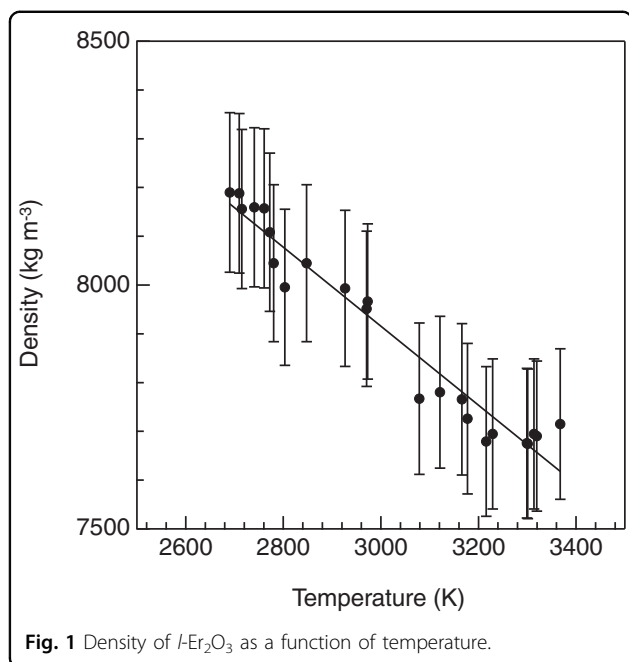


Fig. 1 Density of $l\text{-Er}_2\text{O}_3$ as a function of temperature.

Table 2 Densities at T_m and the thermal expansion coefficients.

	SiO_2 ³⁶	Al_2O_3 ³⁷	ZrO_2 ¹⁸	Er_2O_3
Density at T_m (kg/m^3)	2140	2930	5050	8170
Thermal expansion coefficient (10^{-4}K^{-1})	1.0	1.2	1.8	1.0

The density and the expansion coefficient for $l\text{-Er}_2\text{O}_3$, together with those for $l\text{-SiO}_2$ ³⁶ and other non-GFLs^{18,37}, are compared in Table 2. Although the density trends increase with increasing cation atomic number, they do not show a clear relation. On the other hand, the thermal expansion coefficients show a similarity as each value approaches $1 \times 10^{-4} \text{K}^{-1}$. The thermal expansion coefficient of $l\text{-Er}_2\text{O}_3$ is especially close to those of $l\text{-SiO}_2$ and $l\text{-Al}_2\text{O}_3$.

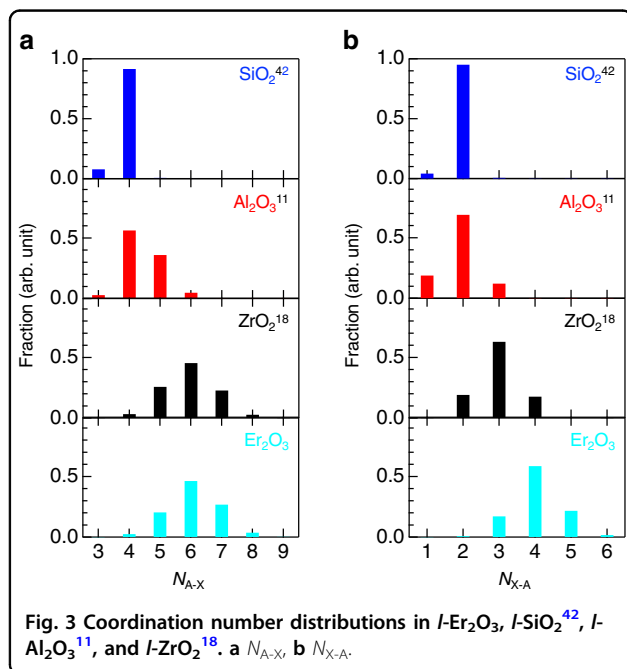
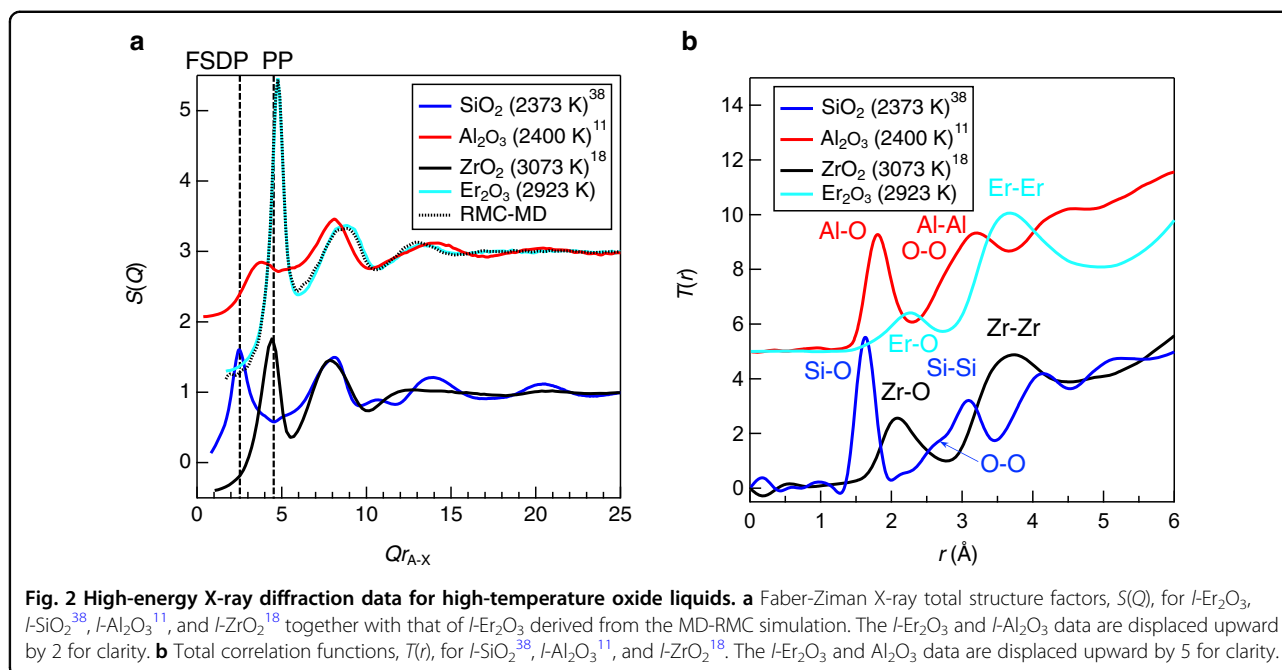
Structure factors and real-space functions

The Faber-Ziman X-ray total structure factors, $S(Q)$, for $l\text{-Er}_2\text{O}_3$, $l\text{-SiO}_2$ ³⁸, $l\text{-Al}_2\text{O}_3$ ¹¹, and $l\text{-ZrO}_2$ ¹⁸, together with the results of the MD-RMC simulation for $l\text{-Er}_2\text{O}_3$, are compared in Fig. 2a. It is noted 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 $l\text{-Er}_2\text{O}_3$ (solid cyan curve) is well reproduced by the MD-RMC simulation (dotted black curve) using the liquid density measured by the ISS-ELF shown in Fig. 1. A well-defined first sharp diffraction peak (FSDP)³⁹ is observed only for $l\text{-SiO}_2$ (GFL) at $Qr_{A-X} = 2.6$, while a principal peak (PP)³⁹ is observed in both the $l\text{-ZrO}_2$ and $l\text{-Er}_2\text{O}_3$ data at

$Qr_{A-X} \sim 4.5$. On the other hand, $l\text{-Al}_2\text{O}_3$ gives rise to a small peak between the FSDP and PP, suggesting that the structure of $l\text{-Al}_2\text{O}_3$ is intermediate¹⁷ between $l\text{-SiO}_2$ and $l\text{-ZrO}_2/l\text{-Er}_2\text{O}_3$. It is well known that the PP reflects the packing of oxygen atoms in neutron diffraction data⁴⁰, since neutrons are sensitive to oxygen. For the same reason, a PP is not observed in the X-ray $S(Q)$ for $l\text{-SiO}_2$ (see Fig. 2a), and the origin of the PP in $l\text{-ZrO}_2$ and $l\text{-Er}_2\text{O}_3$ is ascribed to the packing of cations. The X-ray total correlation functions $T(r)$ for $l\text{-Er}_2\text{O}_3$, $l\text{-SiO}_2$ ³⁸, $l\text{-Al}_2\text{O}_3$ ¹¹, and $l\text{-ZrO}_2$ ¹⁸ are shown in Fig. 2b. The first peak observed at approximately 2.2 Å is assigned to the Er–O correlation, and a tail to ~ 3 Å implies the formation of distorted ErOn polyhedra in the liquid. The second peak, observed at 3.7 Å, can be assigned mainly to the Er–Er correlation, and the O–O correlation peak is unclear due to its small weighting factor for X-rays. The Er–O correlation length of 2.2 Å, as well as that of Zr–O (2.1 Å), is longer than those of Si–O (~ 1.63 Å at 2373 K) and Al–O (~ 1.78 Å at 2400 K) owing to substantial differences between the ionic radii of the elements. The increased cation–oxygen correlation length in the liquid phases of Er–O and Zr–O suggests that the oxygen coordination number around cations is higher than 4 because the Er–O correlation length (2.2 Å) or Zr–O correlation length (2.1 Å) is close to the sum of the ionic radii⁴¹ of oxygen (1.35 Å) and six-fold erbium (0.89 Å) or zirconium (0.72 Å), respectively. The structures of $l\text{-Er}_2\text{O}_3$ and $l\text{-ZrO}_2$ therefore consist of large interconnected polyhedral units and are very different from those of $l\text{-SiO}_2$ and $l\text{-Al}_2\text{O}_3$. This behavior is consistent with the fact that the peaks observed at $Qr_{A-X} \sim 4.5$ in Fig. 2a are not the FSDP, which is typically associated with intermediate-range ordering in oxide glasses and liquids; thus, there is no such ordering in $l\text{-Er}_2\text{O}_3$ and $l\text{-ZrO}_2$ due to a very densely packed structure.

Coordination number distributions from the simulation

The coordination number distributions, N_{A-X} and N_{X-A} , for $l\text{-Er}_2\text{O}_3$, $l\text{-SiO}_2$ ⁴², $l\text{-Al}_2\text{O}_3$ ¹¹, and $l\text{-ZrO}_2$ ¹⁸ obtained from the simulation are compared in Fig. 3a, b, and their average values are summarized in Table 3. The Er–O coordination number (up to 3.0 Å) is found to be 6.1 from our combined MD-RMC simulation, which is rather close to the crystalline phase⁴³, and the O–Er coordination number can be estimated to be 4.1. It is suggested that the cations are tetrahedrally coordinated in $l\text{-SiO}_2$ (GFL), while they are octahedrally coordinated in $l\text{-ZrO}_2$ and $l\text{-Er}_2\text{O}_3$ (non-GFLs), and the cation–oxygen coordination number in $l\text{-Al}_2\text{O}_3$ is intermediate¹⁷ between GFL and $l\text{-ZrO}_2/l\text{-Er}_2\text{O}_3$, although $l\text{-Al}_2\text{O}_3$ is a non-GFL. This behavior is consistent with that of the first correlation peaks in experimental real-space functions (see Fig. 2b) and with the fact that the viscosity of $l\text{-ZrO}_2$ is approximately one-tenth of that in $l\text{-Al}_2\text{O}_3$ ¹⁸. Another interesting behavior is observed for the oxygen–cation coordination numbers. It is



demonstrated that oxygen is twofold in l - SiO_2 , which is a signature of the formation of a sparse network, while triclusters (XA_3) are dominant in l - Al_2O_3 and l - ZrO_2 . The formation of tetraclusters (XA_4) is confirmed in l - Er_2O_3 , suggesting that this behavior is a distinct feature of this liquid. We suggest 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

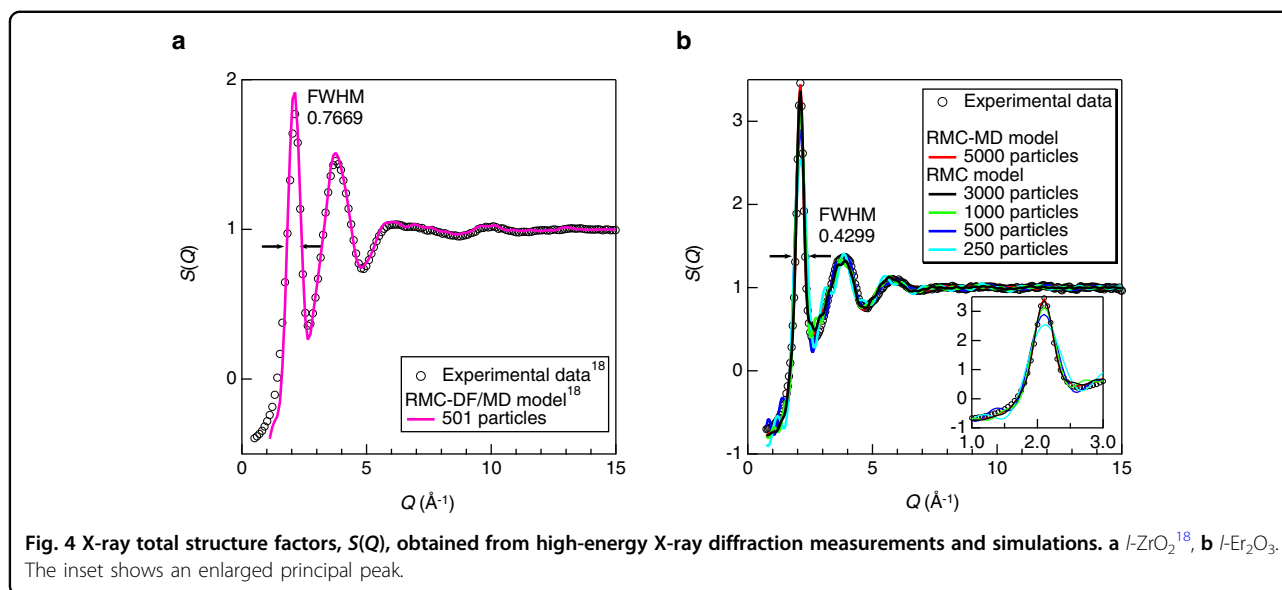
Table 3 Average coordination numbers derived from the simulations.

	SiO_2 ⁴² (2273 K)	Al_2O_3 ¹¹ (2400 K)	ZrO_2 ¹⁸ (3073 K)	Er_2O_3 (2923 K)
N_{A-X}	3.9	4.4	6.0	6.1
N_{X-A}	2.0	2.9	3.0	4.1

are small, which results in tetrahedral coordination, although the Al-O coordination number is greater than four on average. The tetracluster formation is caused by the ratio of Er and O in Er_2O_3 .

Very sharp principal peak (PP) in l - Er_2O_3

As shown in Fig. 2a, the PP of l - Er_2O_3 is very sharp compared to that of l - ZrO_2 . The FWHM of the PP in l - Er_2O_3 is 0.4299, in comparison to 0.7669 in l - ZrO_2 (see Fig. 4). A simulation box with 501 particles was used in the previous RMC – density functional (DF) simulation for l - ZrO_2 ¹⁸, where a good agreement was observed between the experimental data and simulation (see Fig. 4a). However, as can be seen in the inset data of Fig. 4b, a simulation box of 500 particles is insufficient to reproduce the sharp PP in l - Er_2O_3 ; larger atomic models are needed to reproduce this feature. Insight into the structure of l - Er_2O_3 , in comparison with those of l - SiO_2 and other non-GFLs, can be obtained by calculating the Faber-Ziman partial structure factors, $S_{ij}(Q)$, and the Bhatia-Thornton⁴⁴ number – number partial structure factor, $S_{NN}(Q)$, which



indicates the topological order in a system:

$$S_{\text{NN}}(Q) = c_{\text{A}}^2 S_{\text{AA}}(Q) + c_{\text{X}}^2 S_{\text{XX}}(Q) + 2c_{\text{A}}c_{\text{X}} S_{\text{AX}}(Q), \quad (3)$$

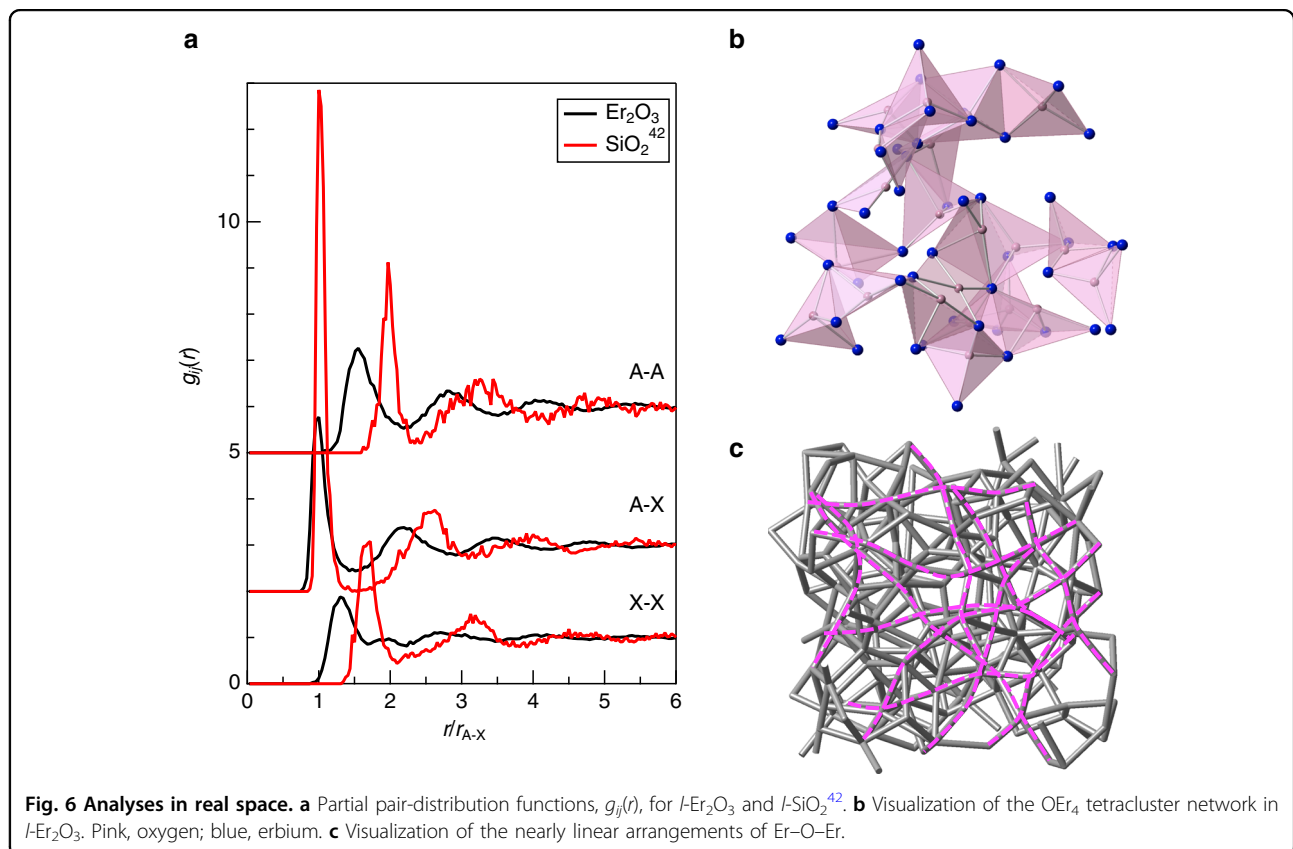
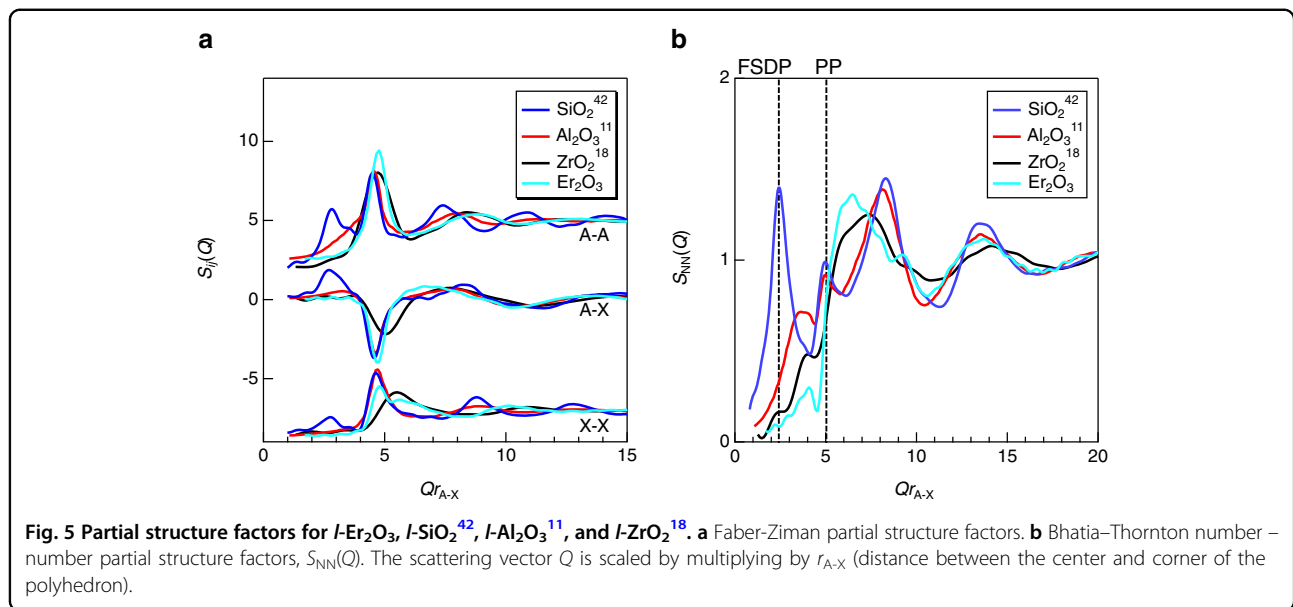
where $S_{ij}(Q)$ is a Faber-Ziman partial structure factor and c_i denotes the atomic fraction of chemical species i . Moreover, it is possible to compare data for the four liquids while ignoring the difference in the sensitivity of elements to X-rays because the weighting factors for X-rays are eliminated in $S_{\text{NN}}(Q)$. The $S_{ij}(Q)$ values calculated from the simulation models for l -Er₂O₃, l -SiO₂⁴², l -Al₂O₃¹¹, and l -ZrO₂¹⁸ are shown in Fig. 5a. It is confirmed that a very sharp PP in l -Er₂O₃ can be assigned to the Er-Er correlation. The $S_{\text{NN}}(Q)$ for l -Er₂O₃ and those for l -SiO₂ and other non-GFLs are compared in Fig. 5b. As mentioned above, only l -SiO₂ exhibits an FSDP at $Qr_{\text{A-X}} = 2.6$. The Q_{FSDP} position arises from an underlying periodicity of $2\pi/Q_{\text{FSDP}}$ that originates, for example, from the formation of pseudo-Bragg planes with a finite correlation length of $2\pi/\Delta Q_{\text{FSDP}}$ in l -SiO₂, while neither l -Al₂O₃, l -ZrO₂, nor l -Er₂O₃ show an FSDP in $S_{\text{NN}}(Q)$, as discussed in Kohara et al.¹⁸. Since the Bhatia-Thornton $S_{\text{NN}}(Q)$ can eliminate the weighting factors for X-rays, the absence of an FSDP in $S_{\text{NN}}(Q)$ is characteristic of a non-GFL. Another important feature in $S_{\text{NN}}(Q)$ is that l -SiO₂ and l -Al₂O₃ exhibit a second PP at $Qr_{\text{A-X}} \sim 5$, while a PP is not distinct in the l -ZrO₂ or l -Er₂O₃ data.

The absence of an FSDP in the l -ZrO₂ and l -Er₂O₃ data suggests that both cations and oxygen are densely packed. To confirm this in real space for l -Er₂O₃, the partial pair distribution functions, $g_{ij}(r)$, of l -Er₂O₃ are compared with those of l -SiO₂ in Fig. 6a. The atomic distance r is scaled by dividing by $r_{\text{A-X}}$ (distance between the center and

corners of the polyhedron). It is found that the scaled first A-A and X-X correlation distances of l -Er₂O₃ are much shorter than those of l -SiO₂, demonstrating that l -Er₂O₃ has a much more densely packed structure, manifested by the formation of the OEr₄ tetracluster network shown in Fig. 6b. This network cannot be found in l -Al₂O₃ nor in l -ZrO₂, suggesting that the very sharp PP in l -Er₂O₃ is a specific signature of the formation of a tetracluster network with long-range periodicity.

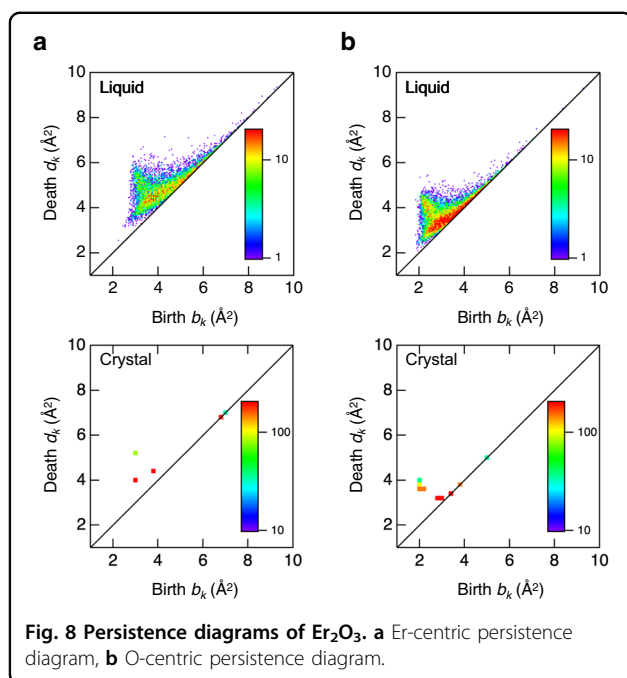
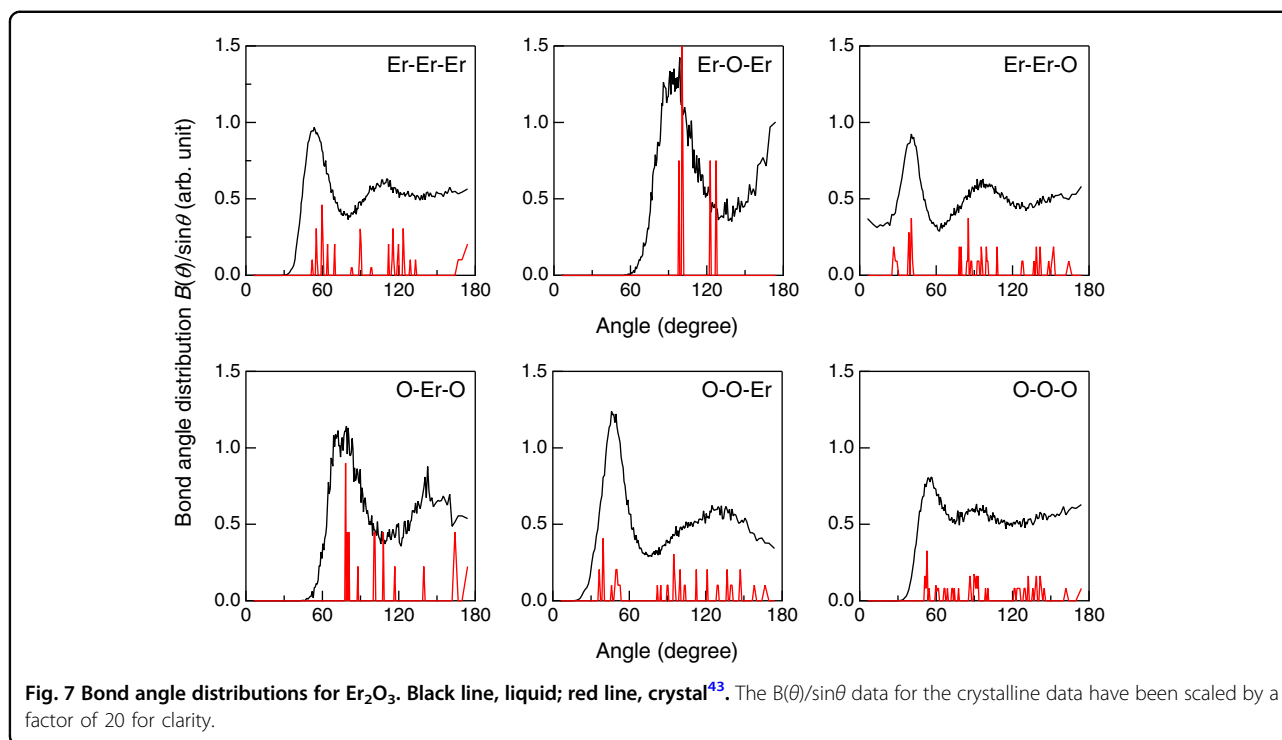
Topology and homology in l -Er₂O₃

To reveal the origin of the very sharp PP in l -Er₂O₃, we calculated the bond angle distributions of the liquid and crystal⁴³ and summarized them in Fig. 7. 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° in addition to the peak at ~90°, which is not observed for the crystal⁴³ nor in l -ZrO₂¹⁸. This two-peak structure in the Er-O-Er bond angle distribution indicates the formation of a distorted OEr₄ tetracluster network, whereas tetraclusters are symmetric (comprising regular tetrahedra) in the crystalline phase. This behavior suggests that the coordination of OEr₄ tetraclusters is more octahedral-like and hence tolerant of disorder even in the liquid due to the distortion, providing a linear arrangement manifested by a prominent peak observed at 180° in the Er-O-Er bond angle distribution. This is clearly visible in Fig. 6c, where linear atomic arrangements are highlighted by the magenta lines.



To shed light on the similarity in topology between the crystal and liquid phases, we calculated the persistence diagram for *l*-Er₂O₃ and compared it with the crystal data in Fig. 8. The figures show the similarity between the crystal⁴³ and liquid phases. In particular, both the

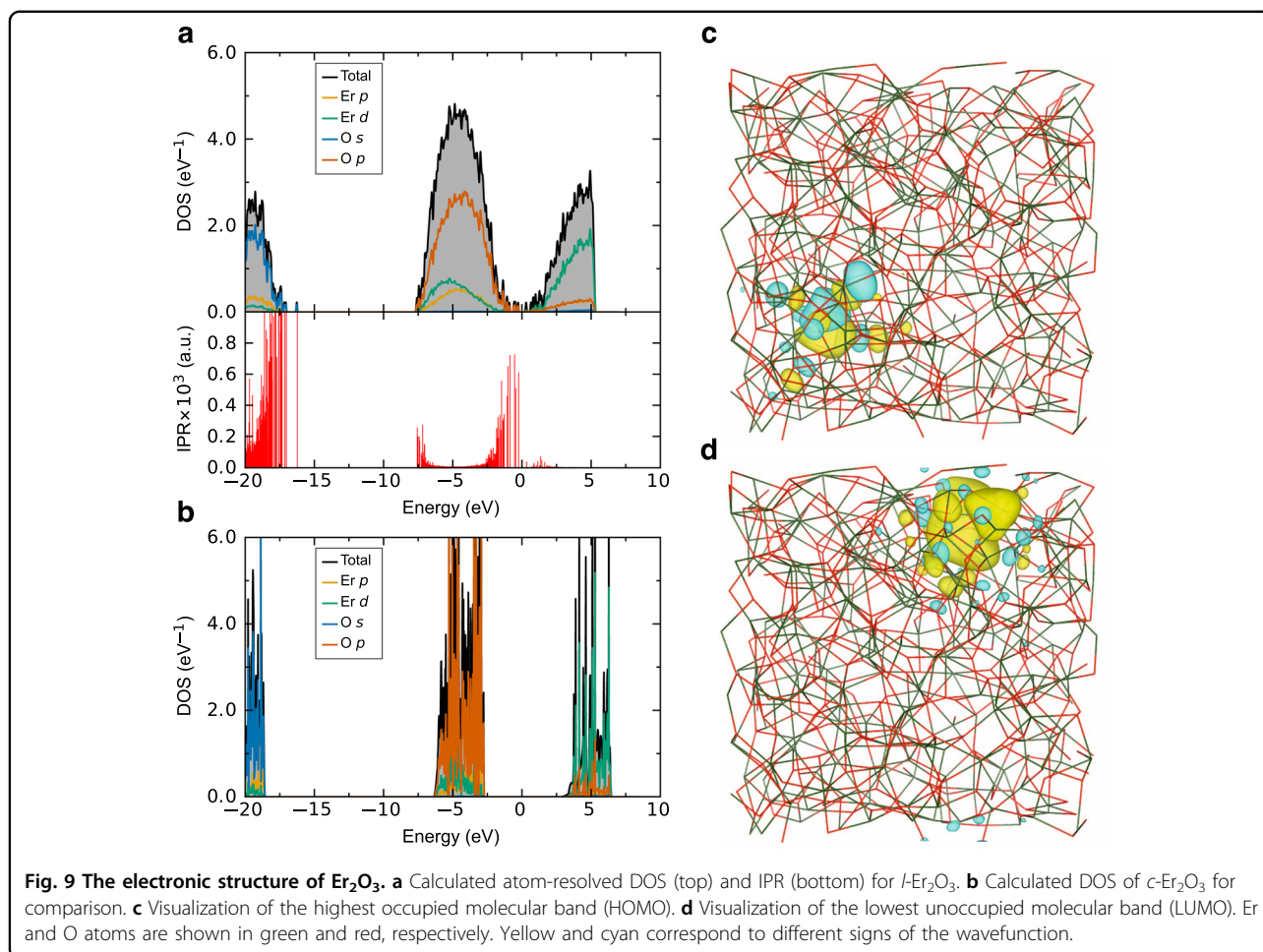
Er-centric and O-centric persistence diagrams for *l*-Er₂O₃ do not show a vertical profile along the death axis, which is a pronounced feature in a typical GFL, such as *l*-SiO₂⁴². The short lifetime of the profile manifested by the small death value demonstrates that both the crystal and liquid



phases exhibit a very densely packed structure associated with the formation of tetraclusters in both phases. We suggest that this similarity is a signature of non-GFL behavior.

Electronic structure and viscosity of $l\text{-Er}_2\text{O}_3$

As previously mentioned, a 500-atom RMC model of $l\text{-Er}_2\text{O}_3$ appeared to be too small in reproducing the very sharp PP accurately (see Fig. S3). Nevertheless, we used this model as a starting structure in our DF-MD simulations to study the electronic structure and atomic diffusion in the liquid phase. The electronic density of states (DOS) and effective charges were calculated for snapshots of $l\text{-Er}_2\text{O}_3$ atomic structures and a fully DFT-relaxed (0 K) $c\text{-Er}_2\text{O}_3$ unit cell. The DOSs of $l\text{-}$ and $c\text{-Er}_2\text{O}_3$ are shown in Fig. 9a, b. The valence band consists mainly of O-2p states, while the conduction band consists mainly of Er-5d states. As a measure of the orbital localization, we also present the inverse participation ratios (IPRs) for $l\text{-Er}_2\text{O}_3$. The IPRs show increased weight at the valence band maximum (VBM), indicating stronger localization, whereas the states around the conduction band minimum (CBM) are delocalized. The obvious broadening of the valence and conduction bands in $l\text{-Er}_2\text{O}_3$ is caused by the distortion of the ErO_n polyhedra at elevated temperatures. The DOS for $l\text{-Er}_2\text{O}_3$ reveals a band gap of 0.57 eV in comparison to the substantially large band gap of 5.46 eV in $c\text{-Er}_2\text{O}_3$. Previously, a vanishing band gap was reported for $l\text{-ZrO}_2$ ¹⁸, but we ascribe this effect to the PBE functional, which is known to underestimate the real value, whereas the hybrid HSE06 functional used here predicts a more correct band gap.



The difference in electronegativities of Er (1.24) and O (3.44) suggests predominantly ionic chemical bonding between the two atoms. This becomes clear from the partial DOS in Fig. 9a, and the calculated atomic charges are summarized in Table 4. The effective charges for *l*-Er₂O₃ are +1.96 *e* and −1.31 *e* for Er and O, respectively, similar to those in *c*-Er₂O₃ (see Table 4). These values are in agreement with previous works on *l*-ZrO₂¹⁸, glassy MgO-SiO₂⁴⁵, and CaO-Al₂O₃⁴⁶ and are consistent with the nominal charges Er³⁺ and O²⁻ (systematically scaled down by a factor of $\sim \frac{2}{3}$). As for ZrO₂¹⁸, the increased atomic volume of oxygen in the transition from *c*- to *l*-Er₂O₃ compensates for the corresponding decreased oxygen coordination, which results in similar atomic charges for the two phases. Note here also the similarity with the charges used in the classic MD force field (+2.1 and −1.4 *e*).

A real space visualization of the highest occupied molecular band (HOMO) is shown in Fig. 9c, where the orbital is found to be distributed over a group of atoms. Locally, the shape of the HOMO is similar to that of *c*-Er₂O₃ (Fig. S4); however, some deviations occur caused

Table 4 Average atomic charges and volumes calculated using the Bader method.

System	Er		O	
	Q_{eff} (<i>e</i>)	V_{at} (Å ³)	Q_{eff} (<i>e</i>)	V_{at} (Å ³)
<i>c</i> -Er ₂ O ₃	+2.03	13.77	−1.35	15.22
<i>l</i> -Er ₂ O ₃	+1.96	15.25	−1.31	16.25

by the aforementioned distorted tetracluster network in *l*-Er₂O₃. Figure 9d shows a real space visualization of the lowest unoccupied molecular band (LUMO), where most of the orbital is distributed over nonbonding regions in-between the ErO_{*n*} polyhedra. The orbital projections for each of the bands reveal that the HOMO band shows mainly an O-2*p* character, while the LUMO band consists mainly of Er-5*d* states and some Er-5*p* character, in agreement with the DOS and IPR in Fig. 9a.

The DF-MD simulations above the melting point at 2650 °C show that the atoms move rapidly, breaking old and forming new Er-O bonds on a picosecond time scale.

The MSD analysis (Fig. S2) shows a consistent linear behavior as a function of time, the evaluated self-diffusion constants are 2.40×10^{-5} and 5.84×10^{-5} cm²/s for Er and O, respectively, and the average self-diffusion constant is 4.64×10^{-5} cm²/s. By using the average value and assuming spherical particles in the Stoke-Einstein relation, one can estimate the viscosity, and the obtained value is $\sim 3 \times 10^{-3}$ Pa s⁻¹ for *l*-Er₂O₃ in comparison to the previously reported value for *l*-ZrO₂, i.e., $\sim 2 \times 10^{-3}$ Pa s⁻¹ at 2800 °C¹⁸. Since these values are an order of magnitude smaller than that for *l*-Al₂O₃ (fragile liquid) and 9–10 orders of magnitude smaller than that for *l*-SiO₂ (strong liquid), we characterize *l*-Er₂O₃ as an “extremely fragile” liquid¹⁸.

We combined an aerodynamic levitation technique and a synchrotron high-energy X-ray diffraction and density measurement at the ISS for *l*-Er₂O₃ to reveal the structure of A₂X₃-type non-GFLs. As the main finding, we observed a very sharp PP in the diffraction data. The Er-O coordination number was estimated to be 6.1 from a combined MD-RMC simulation, which is comparable to that of another nonglass-forming liquid, *l*-ZrO₂, and to that of crystalline Er₂O₃. The formation of distorted OEr₄ tetraclusters in the liquid is confirmed, while OZr₃ triclusters are dominant in *l*-ZrO₂ and OAl₃ triclusters dominate in another A₂X₃ non-GFL, *l*-Al₂O₃. Apparently, the formation of a distorted tetracluster network in *l*-Er₂O₃ gives rise to a long periodicity, yielding the sharp principal peak. This long-range periodicity originates from the significantly increased weight at $\sim 180^\circ$ in the Er-O-Er bond angle distribution, suggesting that the arrangement of distorted OEr₄ tetraclusters involves nearly linear connections, which are not observed in other oxide liquids. Furthermore, persistent homology suggests that *l*-Er₂O₃ is homologically similar to the crystalline phase and that both phases are very densely packed, in contrast to a typical GFL such as *l*-SiO₂. This similarity is presumed to be the signature of the liquid, and a considerable difference between two A₂X₃-type oxide liquids, *l*-Al₂O₃ and *l*-Er₂O₃, is uncovered. The additional DF-MD simulations demonstrate that *l*-Er₂O₃ has an electronic band gap of 0.6 eV, which is considerably lower than that of *c*-Er₂O₃ due to angular distortions and nearly linear connections within the polyhedral network. The dynamics of atoms show pronounced mobility, as evidenced by the MSDs, resulting in a very low viscosity, and thus place *l*-Er₂O₃ within the regime of extremely fragile liquids.

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Author contributions

S.K. and C.K. designed this research. The high-energy X-ray diffraction measurements were performed by S.K., C.K., Y.O., At.M., Ak.M., Y.W., K.O., H.T., and J.T.O. The density measurements were conducted by C.K., T.I., Y.W., Y.N., H. T., and H.O. The classic molecular dynamics simulations were performed by S.T. The density functional – molecular dynamics simulations were conducted by D.R.S., S.M.S., and J.A.; S.K., D.R.S., S.M.S., J.A., I.O., Y.H., and O.S. analyzed the data, and S.K., C.K., and J.A. wrote the article.

Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Conflict of interest

The authors declare that they have no conflict of interest.

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